Development of an inverted stabilised bubble fluidised bed reactor for adsorptive processes

This item was submitted to Loughborough University's Institutional Repository by the/an author.

Additional Information:

- A Doctoral Thesis. Submitted in partial fulfillment of the requirements for the award of Doctor of Philosophy of Loughborough University.

Metadata Record: https://dspace.lboro.ac.uk/2134/7508

Publisher: © Paul Collings

Please cite the published version.
This item is held in Loughborough University’s Institutional Repository (https://dspace.lboro.ac.uk/) and was harvested from the British Library’s EThOS service (http://www.ethos.bl.uk/). It is made available under the following Creative Commons Licence conditions.

For the full text of this licence, please go to: http://creativecommons.org/licenses/by-nc-nd/2.5/
Development of an Inverted Stabilised Bubble Fluidised Bed Reactor for Adsorptive Processes

by

Paul Collings

A doctoral thesis submitted in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy of Loughborough University

October 1997
# Table of Contents

**Abstract** vii  
**Acknowledgements** viii  
**Notation** ix  
**List of Figures** xiv  
**List of Tables** xviii  

**Introduction**  
1  

**Chapter 1 - Literature Survey**  
1.1 Introduction 5  
1.2 The formation of bubbles using plunging jets  
1.2.1 Mechanisms of gas entrainment 10  
1.2.2 Jet diameter and velocity 10  
1.2.3 Minimum entrainment velocity 12  
1.2.4 Volumetric gas entrainment rate 13  
1.2.5 Bubble size distribution 16  
1.2.6 Maximum depth of bubble penetration 23  
1.2.7 Summary 24  
1.3 Particle-bubble attachment and Aphrons 25  
1.3.1 Mineral flotation 26  
1.3.2 Forces between particles and bubbles 28  
1.3.3 The contact angle and bubble-particle hydrodynamics 34  
1.3.4 The use of Aphrons in process engineering 38  
1.3.5 Summary 40  
1.4 The hydrodynamic behaviour of Inverse Fluidised Beds 41  
1.4.1 Conventional liquid-solid fluidised beds 41  
1.4.2 Inverse fluidised beds and applications 43  
1.4.3 Hydrodynamics of inverse fluidised beds 45  
1.4.4 Summary 48
3.1.2 Stabilised air bubbles 136
3.2 Experimental Method 139
  3.2.1 Experimental apparatus and materials 139
  3.2.2 Experimental method 140
3.3 Results 141
3.4 Evaluation of the expansion data for inverted fluidised beds 153

Chapter 4 - Batch Adsorption Trials

4.1 Introduction 165
4.2 Liquid-solid adsorption theory for dilute systems 165
4.3 Experimental method 169
  4.3.1 Materials 169
  4.3.2 Method 169
4.4 Results 171
4.5 Discussion 177

Chapter 5 - Column Adsorption Trials

5.1 Introduction 181
5.2 Shell adsorption theory 182
5.3 Materials and experimental method 191
  5.3.1 Materials 191
  5.3.2 Experimental method 192
    5.3.2.1 The 50 mm diameter column procedure 192
    5.3.2.2 The 100 mm diameter column procedure 194
    5.3.2.3 Sample analysis 196
5.4 Results 199
5.5 Discussion 208
  5.5.1 Analysis of the results 208
  5.5.2 Activated carbon loading 211
  5.5.3 The role of oleyl alcohol 213
  5.5.4 The counter-current process 214
  5.5.5 Summary 216
Chapter 6 - Conclusion and Recommendations

6.1 Conclusion

6.2 Recommendations

References

Appendix 1 - Raw Data

A) Data for Figs. 5.1 - 5.11
B) Data for Figs. 4.2 - 4.4
C) Data for Figs. 5.8 - 5.15

Appendix 2 - Sample calculations

A) Calculating the Richardson-Zaki model for an inverted fluidised bed
B) Changing the experimental data into a useful form for comparison with the Richardson-Zaki model
C) Batch trials - how to calculate the Freundlich isotherm
D) Calculating the diffusion data for Fig. 5.1
ABSTRACT

Granular Activated Carbon (GAC) is used in packed beds to treat trace quantities of micropollutants. Many years of research and industrial use has ensured that it is highly effective as a water treatment process. However, GAC is expensive and economic considerations mean it has to be recovered and re-used. Powdered Activated Carbon (PAC) is a cheaper alternative but the particle size range means it is unsuitable for packed bed applications.

This thesis describes a novel method for utilising PAC to treat micropollutants. By contacting carbon particles with air bubbles, under conditions of rotational shear and a binding agent, oleyl alcohol, carbon-coated air bubbles form which remain stable while agitated by flowing water. A stabilised air bubble can be visualised as a sphere with an impervious core (the air bubble), surrounded by a thin layer of porous material (PAC). Theory dictates that if these stabilised air bubbles can be moved counter-currently to a contaminated stream, higher throughputs than conventional packed beds are possible.

Several aspects of this process are investigated. Bubble generation is critical and so the literature was reviewed to explain the mechanisms involved. Practical use was made of this knowledge in designing a larger bubble generator. Transferring the coated-bubbles to a contacting column was difficult. Problems associated with the various methods employed are described and recommendations are made for improvement. The contacting column was used to assess the stability and adsorptive capacity of the bubbles. The possibility of counter-current flow using stabilised air bubbles was also evaluated and found to be incompatible with the current column design.

The stabilised bubbles collected in the column resembled an inverted fluidised bed. Experiments were performed to test if Richardson and Zaki's hydrodynamic laws for conventional fluidised beds were applicable to inverted beds. The adsorptive capacity of the bubbles was assessed by dosing the water with trace levels of phenol and p-chlorophenol. Samples taken from before and after the fluidised bed were analysed and compared. The results were inconclusive, although the concentration profile produced indicated that flow through the bubble bed was piston-flow.
ACKNOWLEDGEMENTS

There are many people to whom I am grateful for their guidance, input and support :-

I would like to thank my supervisor, Prof. Michael Streat, for all his expertise and guidance over the years, particularly during the last year of writing up. He has an uncanny ability to motivate me - an asset that proved invaluable at times of duress. For that, I forgive him being a Man. Utd. supporter.

The workshop boys, Tony, Barry, Pip and Leo, all deserve great credit for manufacturing the relevant pieces of equipment. I apologise for all the times I changed my mind as to what I wanted. Good luck to you all.

A big thank you to my partner in experimental crime, Graham Moody. Not only was he invaluable in helping out but I shall always remember those conversations we had. His genius knew no bounds - culminating in the ground-breaking design of the ARFAW (Air Removal From Aerated Water) device. I salute you! (Promise I won't mention marshmallows)

Many other technicians helped out during my time. These include Hugh Peters, Dave Smith, Martin Kerry, Andy Milne and Pravin Jethwa. Other “assistants” have included Dr. Guan Zhang, Danish Malik and Dan Horner. I thank you all.

Prof. Buffham and Drs. Akers, Cumming, Holdich and Tarleton deserve thanks for their academic input. It was, as always, invaluable.

I would like to thank Steve Graver and (the late) Geoff Boyden for producing the videos and photographs associated with the project and thesis.

The ladies of the department also deserve much praise. Gwen, Eileen, Janey, Anne, Anna, Yasmin and Jean. Thanks for everything.

I would like to thank Paul Izzard for all his help and troubleshooting regarding the computers

There are many other people inside and outside the department I wish to thank. First and foremost, my family, who were a tower of strength. I love you all very much and I hope I have made you proud.

There are many friends who have all helped and have had some great times with. I want to thank everyone who has been involved in CheERS, my friends at Elvyn, Franz, Richard and Abi and others including Sarah, Rachel, Sam and Declan.

Last, but not least, I would like to thank my “wing-men”, Gareth Butt and Steve Middleton. Recently, they have been my writing-up buddies, but before that they were my best friends and confidantes. Long may it continue! (And on that bombshell.....)

“One day, I am going to grow wings.....”

- Thom Yorke

viii
Notation

Chapters 1 and 2

a  particle radius (m)
b  core radius (m)
c  equilibrium concentration of solution (mg l⁻¹)
C_D  drag coefficient
D  diffusion coefficient of the solute
d_j  jet diameter (m)
d_m  maximum bubble diameter (m)
d_o  nozzle diameter (m)
d_r  jet diameter at reference point (m)
d_e  jet diameter at impact (m)
E  energy dissipation rate per unit volume (kg m⁻¹ s⁻³)
E_k  kinetic energy of a particle (kg m⁻² s⁻²)
e  bed voidage
Fr  Froude number = V_j²/gd_o
g  acceleration due to gravity (ms⁻²)
H_C  critical distance below which a particle-bubble collision will occur
H_p  depth of bubble penetration (m)
h  distance between nozzle exit and pool surface (m)
k  constant measuring the extent of adsorption (mg g⁻¹)(l mg⁻¹)⁰ᵐ
L_B  jet break-up length (m)
L_j  jet length (m)
L_MZ  length of mixing zone below plunge point (m)
l  nozzle length (m)
l_m  mean jet length (m)
Oh  Ohnesorge number = μ/√ρσ_o
P  probability of particle flotation
P_A  probability of adhesion
P_c: probability of particle-bubble collision
P_D: probability of particle detachment
Q_A: volumetric air flow rate (m^3 s^-1)
Q_L: volumetric liquid flow rate (m^3 s^-1)
q: equilibrium concentration of pollutant on carbon (mg g^-1)
R_b: radius of bubble (m)
R_o: minimum approach radius (m)
R_p: radius of particle (m)
R_e: jet Reynolds number = V_j \rho_l / \mu_l
Re_i: Reynolds number for a particle falling/rising at a maximum velocity = U_i d_p \rho_l / \mu_l
r: jet radius at any point on the jet (m)
t: time (s)
U: observed fluidisation velocity (ms^-1)
U_i: superficial velocity at e = 1 (ms^-1)
U_t: terminal particle velocity (ms^-1)
V_e: critical jet velocity at which air entrainment occurs (ms^-1)
V_j: jet velocity (ms^-1)
V_o: jet velocity at nozzle outlet (ms^-1)
V_r: jet centre line velocity (ms^-1)
W_SL: work of adhesion between a solid and liquid interface (Nm^-1)
We_c: critical Weber number
We_j: jet Weber number = V_e^2 d_p \rho_l / \sigma
w: pore width (nm)

Greek Letters

\alpha: angle of inclination (°)
\alpha_c: critical angle at which entrainment occurs (°)
\varepsilon: measurement of extent of jet disturbances (m)
\mu: viscosity (kg m^-1 s^-1)
\nu: kinematic viscosity (m^2 s^-1)
\rho: density (kg m^-3)
\[ \sigma \quad \text{surface tension (Nm}^{-1}\text{)} \]
\[ \tau_i \quad \text{induction time (s)} \]

**Subscripts**

g \quad \text{gas}
L \quad \text{liquid}
p \quad \text{particle}
W \quad \text{water}
LG \quad \text{liquid-gas}
SG \quad \text{solid-gas}
SL \quad \text{solid-liquid}

**Chapter 3**

A \quad \text{cross-sectional area of the column (m}^2\text{)}
Ar \quad \text{Archimedes number} = \rho_l[(\rho_l - \rho_p)/\mu^2]gd^3
C_D \quad \text{drag coefficient}
D \quad \text{column diameter (m)}
d \quad \text{particle/bubble diameter (m)}
e \quad \text{voidage}
e_0, e_1 \quad \text{bed voidage at heights } h_0, h_1 \text{ respectively}
Ga \quad \text{Galileo number}
g \quad \text{acceleration due to gravity (ms}^{-2}\text{)}
h_0, h_1 \quad \text{initial and current bed height (m)}
N_D \quad \text{Best number} = 4/3 \text{ Ar (when } \rho_p < \rho_l) \text{ }
n \quad \text{fluidisation index}
Re_{mf} \quad \text{Reynolds number at minimum fluidising velocity} = d U_{mf} \rho_l/ \mu_l
Re_i \quad \text{particle Reynolds number} = d U_i \rho_l/ \mu_l
U \quad \text{observed superficial velocity (ms}^{-1}\text{)}
U_i \quad \text{superficial fluidising velocity at } e = 1 \text{ (ms}^{-1}\text{)}
U_t \quad \text{particle terminal velocity (ms}^{-1}\text{)}
Greek Letters

μ viscosity (kg m⁻¹ s⁻¹)
ρ density (kg m⁻³)

Subscripts

l liquid
p particle

Chapter 4

a constant that is a measure of energy of adsorption (J g⁻¹)

Cₑ equilibrium concentration (mg l⁻¹)

K Freundlich constant, a measure of the capacity of an adsorbent (mg g⁻¹)(l mg⁻¹)ⁿ

n constant, a function of the strength of the adsorption bond

qₑ mass of sorbate adsorbed per unit mass of sorbent (mg g⁻¹)

qₑ₋ₑₙₓ the maximum value qₑ can achieve at monolayer coverage (mg g⁻¹)

Chapter 5

a external radius of a particle/shell (m)
b radius of impervious core (m)
C solute concentration (mg l⁻¹)

Cₒ concentration at sphere surface (mg l⁻¹)

C₁ initial concentration of solute in particle (mg l⁻¹)
c average concentration of the sorbate in the shell (mol m⁻³)
D solute diffusion coefficient
L length of column (m)
N number of particles per unit volume (m⁻³)
r radius of a sphere (m)
S cross-sectional area of column (m²)
t  contact time (s)

\( t_o \)  contact time for a completely porous particle (s)

\( V \)  volume of one shell adsorbent (m³)

\( Q \)  amount of adsorbate retained by unit amount of adsorbent (mg g⁻¹)

\( Q_{\infty} \)  amount adsorbed after infinite time (mg g⁻¹)

\( q \)  dimensionless radius, based on impervious core = \((a-b)/b\)

\( q' \)  dimensionless radius, based on external radius = \((a-b)/a\)

\( W \)  number of moles passing through the column per unit time (mole s⁻¹)

\( W_R \)  ratio of \( W \) for shell adsorbents to \( W \) for completely porous particles

\( x,y,z \) co-ordinates

**Greek Letters**

\( \beta_n \) roots of equation \( \beta \cot \beta + q = 0 \) (where \( n = 1,2,\ldots \))

\( \theta \) dimensionless time = \( Dt/(a-b)^2 \)
List of Figures

Fig. 1.1 - A simple bubble column 6
Fig. 1.2 - Various types of bubble column 6
Fig. 1.3 - Different bubble diffusers 6
Fig. 1.4 - The twin-jet bubble disperser 6
Fig. 1.5 - Plunging liquid jet bubble column 8
Fig. 1.6 - Mechanism of air entrainment for low viscosity liquid jets 11
Fig. 1.7 - Regions of air entrainment 13
Fig. 1.8 - Air volume entrained as a function of jet velocity and nozzle diameter 17
Fig. 1.9 - Extent of boundary layer and air entrainment 19
Fig. 1.10 - A confined plunging jet system 21
Fig. 1.11 - Dispersed air flotation as used for processing minerals 27
Fig. 1.12 - The electric double layer surrounding a charged particle 29
Fig. 1.13 - van der Waals ($\psi_A$), electrical ($\psi_R$) and total ($\psi_{TOTAL}$) interaction energies as a function of separation distance 30
Fig. 1.14 - Hydrocarbon chains adsorbed on particle surface inserting into bubble 32
Fig. 1.15 - Representation of the forces and contact angle in a 3-phase system 34
Fig. 1.16 - Contact angle during flotation 35
Fig. 1.17 - Trajectories of a particle approaching a bubble with (dashed) and without (solid line) the influence of the resistance due to viscous film thinning 36
Fig. 1.18 - A colloidal gas aphron 38
Fig. 1.19 - The various stages of fluidisation, illustrated by the pressure gradient across the bed due to the fluid velocity 41
Fig. 1.20 - Relationship between fluid velocity (U) and bed voidage (e) for fluidisation of steel spheres in water 43
Fig. 1.21 - An inverse fluidised bed biofilm reactor 44
Fig. 1.22 - Comparison of the standard drag curve with the curve for 'light' spheres 46
Fig. 1.23 - Prediction of bed expansion data using Richardson-Zaki and Karamanev's modified version 47
Fig. 1.24 - Structure of graphite 51
Fig. 1.25 - Pore shapes 53
Fig. 1.26 - Evolution of surface areas by CO$_2$ activation at 800 °C 59
Fig. 1.27 - Some acidic surface groups found on activated carbon 61
Fig. 1.28 - Protonation of the pyrone-like structure 62
Fig. 1.29 - Isotherm classification according to Giles et al (1960) 63
Fig. 1.30 - A continuous fractional adsorption column where the adsorbent floats counter-currently against a descending adsorbate solution 70
Fig. 1.31 - The effect of modification of activated carbon on the adsorption of 5-aminoacridine hydrochloride 71
Fig. 1.32 - A pulse-flow semi-fluidising column for counter-current contacting 74
Fig. 1.33 - Time $Dt/a^2$ to reach a required equilibrium as a function of dimensionless shell adsorbent thickness (a-b)/a 75
Fig. 1.34 - Flow sheet of a counter-current adsorption process as envisaged by Weiss and colleagues 77
Fig. 3.7 - Comparison of experimental data and Richardson-Zaki correlation for an inverted fluidised bed (initial depth = 13.5 cm) in the 2-D contactor (D = 67 mm)

Fig. 3.8 - Comparison of experimental data and Richardson-Zaki correlation for an inverted fluidised bed (initial depth = 9.5 cm) in the 2-D contactor (D = 67 mm)

Fig. 3.9 - Predicted inverted bed expansion for monosized spheres in a column of diameter (D) 50 mm using Richardson-Zaki

Fig. 3.10 - Comparison of experimental data and Richardson-Zaki correlation for an inverted fluidised bed (initial depth = 13.0 cm) in a column of diameter (D) 50 mm

Fig. 3.11 - Comparison of experimental data and Richardson-Zaki correlation for several inverted fluidised beds in a column of diameter (D) 50 mm

Fig. 3.12 - Predicted inverted bed expansion for monosized spheres in a column of diameter (D) 100 mm using Richardson-Zaki

Fig. 3.13 - Comparison of experimental data and Richardson-Zaki correlation for an inverted fluidised bed (initial depth = 14.6 cm) in a column of diameter (D) 100 mm

Fig. 3.14 - Comparison of experimental data and Richardson-Zaki correlation for an inverted fluidised bed (initial depth = 12.9 cm) in a column of diameter (D) 100 mm

Fig. 3.15 - Comparison of experimental data and Richardson-Zaki correlation for an inverted fluidised bed (initial depth = 4.7 cm) in a column of diameter (D) 100 mm

Fig. 3.16 - A comparison of expansion data of beds of similar depth (12.9 - 14.6 cm) in columns of various diameters (50, 67 and 100 mm)

Fig. 3.17 - A comparison of the expansion of beds of different bed depths

Fig. 3.18 - Segregation of the bubbles allows the bed to be visualised as a series of mono-sized fluidised beds

Fig. 3.19 - Richardson-Zaki predictions for various mono-sized beds, assuming a column of infinite width

Fig. 3.20 - Comparison of experimental data for a bed of initial depth 13.0 cm and Richardson-Zaki

Fig. 3.21 - Experimental data points fitted by Richardson-Zaki

Fig. 3.22 - The data for a 13.0 cm fluidised bed can be fitted by the correlation of Hartman et al (1992)

Fig. 3.23 - All data for beds 13.0 - 14.6 cm fitted by the Hartman correlation

Fig. 4.1 - The L2 (Langmuirian) isotherm

Fig. 4.2 - Freundlich isotherms for phenol batch adsorption. Effect of adding surfactants

Fig. 4.3 - Freundlich isotherms for para-chlorophenol batch adsorption. Effect of adding surfactants

Fig. 4.4 - Modified Langmuir isotherms for phenol batch adsorption. Effect of surfactants

Fig. 4.5 - Modified Langmuir isotherms for para-chlorophenol batch adsorption. Effect of surfactants

Fig. 5.1 - Comparison of rates of adsorption for porous shells of varying
Fig. 5.1 - Comparison of rates of adsorption for porous shells of varying thickness with a homogeneous porous sphere

Fig. 5.2 - The time (Dt/a^2 in dimensionless form) to reach a given level of adsorption as a function of the dimensionless shell thickness (a-b)/a

Fig. 5.3 - Relative increase in throughput W_R (using shell adsorbents) plotted against b/a

Fig. 5.4 - The process used in the trials involving the 50 mm diameter column, including the feed tank and sample points

Fig. 5.5 - Adsorption process apparatus for the 100 mm diameter column

Fig. 5.6 - phenol calibration curve

Fig. 5.7 - p-chlorophenol calibration curve

Fig. 5.8 - Stable fluidised bubble bed adsorption trial No. 1 - 50 mm diameter column

Fig. 5.9 - Stable fluidised bubble bed adsorption trial No. 2 - 50 mm diameter column

Fig. 5.10 - Stable fluidised bubble bed adsorption trial No. 3 - 100 mm diameter column

Fig. 5.11 - Stable fluidised bubble bed adsorption trial No. 4 - 100 mm diameter column

Fig. 5.12 - Stable fluidised bubble bed adsorption trial No. 5 - 100 mm diameter column

Fig. 5.13 - Dispersion of p-chlorophenol through column in the absence of bubbles - 100 mm diameter column

Fig. 5.14 - Stable fluidised bubble bed adsorption trial No. 6 - 100 mm diameter column. Comparison of p-chlorophenol dispersion in presence of stabilised bubbles

Fig. 5.15 - Stable fluidised bubble bed trial No. 7 - 100 mm diameter column. Bubble bed between points sp5 and sp6

Fig. 5.16 - The shaded area represents the mass of pollutant passing through the bed

Fig. 5.17 - Inlet and outlet traces from Fig. 5.11, plotted as C against V. This is used to calculate the mass of p-chlorophenol passing through the fluidised bed

Fig. 5.18 - Traces seen at inlet and outlet with no bubbles present. Both curves were extrapolated to calculate the mass of p-chlorophenol passing through

Fig. A2.1 - Predictive data for the expansion of an inverted fluidised bed of stabilised bubbles, of size 1.0 mm in diameter, in a column of 50 mm diameter

Fig. A2.2 - The converted data is plotted onto a log-log graph of e vs. U and compared to the model prediction

Fig. A2.3 - A log-log plot of the data for phenol in the absence of any surfactant
## List of Tables

Table 1.1 - Materials that have been studied for the production of activated carbon
Table 1.2 - Classification of pores by pore width, w
Table 2.1 - Physical properties and particle size range (activated carbon)
Table 2.2 - Properties of oleyl alcohol
Table 2.3 - Bubble generation requirements
Table 2.4 - Observations during coated bubble generation
Table 4.1 - Freundlich constants for phenol and p-chlorophenol
Table 4.2 - Langmuir constants for phenol and p-chlorophenol
Table 5.1 - phenol
Table 5.2 - p-chlorophenol
Table 5.3 - Carbon loading on various fluidised beds of coated bubbles
Table A1 - Data for Fig. 3.5
Table A2 - Data for Fig. 3.6
Table A3 - Data for Fig. 3.7
Table A4 - Data for Fig. 3.8
Table A5 - Data for Fig. 3.9
Table A6 - Data for Fig. 3.10
Table A7 - Data for Fig. 3.11
Table A8 - Data for Fig. 3.12
Table A9 - Data for Fig. 3.13
Table A10 - Data for Fig. 3.14
Table A11 - Data for Fig. 3.15
Table B1 - Data for Fig. 4.2
Table B2 - Data for Fig. 4.3
Table B3 - Data for Fig. 4.4
Table B4 - Data for Fig. 4.5
Table C1 - Data for Fig. 5.8
Table C2 - Data for Fig. 5.9
Table C3 - Data for Fig. 5.10
Table C4 - Data for Fig. 5.11
Table C5 - Data for Fig. 5.12
Table C6 - Data for Fig. 5.13
Table C7 - Data for Fig. 5.14
Table C8 - Data for Fig. 5.15
Introduction

Removal of pollutants and toxic substances is an essential focus of water management. Governmental legislation and “watchdog” groups, such as the National Rivers Authority (NRA), Drinking Water Inspectorate (DWI) and H.M. Inspectorate of Pollution (HMIP), carefully ensure that required levels are met. It is the purpose of the water companies to ensure treatment methods comply with legislation and water quality is met with minimal charge to customers. For this reason companies are always searching to improve services, efficiency and reduce operating and capital costs. Efficiency enhancements enable companies to deliver improved services at affordable levels, in comparison with conventional techniques. Such cost-reducing technical innovation provides an incentive for companies to perform better and fulfils customer expectation in the resulting lowering of bills (Booker, 1994).

The craft of water treatment is based upon a series of unit processes. The choice of which process is used is dependant upon several factors, including supply source quality, desired finished water quality, process equipment reliability, available space for construction of treatment facilities, waste disposal constraints and capital and operating costs (Hamann et al, 1990). The many unit operations available to the treatment works manager comprise aeration, flocculation, flotation, filtration, ion exchange, chemical oxidation and adsorption, amongst many others.

For the removal of dissolved organics, colour and taste-causing compounds, adsorption by powdered or granular activated carbon (PAC or GAC) is generally used. Although being the most expensive form of activated carbon, GAC is often used in preference to PAC as it is more effective at removing a wide range of organics, for example total organic carbon (TOC), volatile organic compounds (VOC) and synthetic organic compounds (SOC). Application of GAC in beds or columns permits higher adsorptive capacities and easier process control than is possible using PAC in conventional techniques. The higher cost is offset by better efficiency, especially when decontamination is necessary on a continuous basis (Snoeyink, 1990). Capital and
Introduction

Operating costs are controlled by contactor size and activated carbon usage rate, which are influenced by the contact time and application rate. As the contact time increases, contactor size and capital costs increase but activated carbon usage rate and operating costs decrease. A compromise between contactor size and activated carbon usage rate will keep capital and operating costs at a minimum, although legislative targets must still be met. Thermal reactivation of the spent activated carbon may be necessary to make the process cost-effective.

The finely divided nature of PAC means it is not applicable to continuous unit processes. Packed beds of PAC are not feasible due to the very small throughputs possible. There are batch applications where the PAC is mixed with a volume of contaminated liquid and this method is very effective. However, the PAC must be removed and this means the suspension requires filtering, thus incurring added expense. PAC does have an advantage over GAC in that the rates of adsorption are much quicker, due to the small particle size (NORIT). Nevertheless, the problem of utilising PAC effectively nullifies this advantage.

Adsorption processes in general are packed bed or column operations. In water purification systems, the stream to be treated is slowly percolated through the packed bed of GAC. Eventually, this bed becomes saturated with the pollutant and the bed has to be replaced and the adsorbent recovered. Often, the beds are replaced when the effluent concentration reaches a critical value. This can mean that a significant proportion of the bed is unused. This is inefficient and costly.

In Australia, in the late 1950's, Dr. Don Weiss and colleagues advocated the process of continuous counter-current adsorption. They believed that moving the adsorbate against a contaminated stream would increase the rate of adsorption, improve adsorbent efficiency and hence reduce the inventory required. However, they found the process of moving granular particles cumbersome and extremely difficult to achieve. As an alternative, Weiss proposed that if adsorbents could be developed where the porosity of a spherical particle could be restricted to an outer shell, the adsorbent would attain equilibrium faster. Simultaneously, if the impervious core could be made from a
material less dense than the liquid stream, then the particle could be floated against the stream, enabling counter-current flow. Weiss envisaged the ideal shell adsorbent being an air bubble (the impervious core) surrounded by a coating of a finely divided adsorbent material.

The project was abandoned, but Weiss returned to it in the late 1980's, this time using PAC as the adsorbent material. Weiss believed his idea could intensify water treatment processes, leading to reduced costs, more efficient adsorption and less capital costs. If the carbon inventory is significantly reduced then regeneration is not required. Early work succeeded in producing carbon-coated air bubbles but applications of the stabilised bubbles were not investigated due to a lack of funding. A system of plunging jets was devised to entrain air bubbles, which were stabilised by attaching carbon particles to the bubble surface with the aid of a spreading agent, oleyl alcohol. Once generated, they were collected in a column containing a flowing stream of clean water. The natural buoyancy of the air bubbles meant they had to be retained by a distributor plate. This fact meant that a collection of these bubbles resembled an inverted fluidised bed.

The project came to Loughborough University where funding was acquired from Severn Trent Water Ltd., who were interested in assessing the process, and EPSRC who provided the finance for a doctoral thesis. This thesis describes the effort and results of that project. Following on from the work of Weiss, the aims of the project were:

- Reproduce the findings of Weiss, i.e. recreate the conditions to generate sufficient quantities of activated carbon-coated bubbles.
- Investigate the hydrodynamic properties of the inverted fluidised bed, i.e. do conventional fluidised bed models apply to an inverted system? If not, what changes need to be made?
- Transfer the stabilised bubbles to a suitable vessel where they can then be assessed for adsorption potential and as a counter-current process.

This thesis addresses the findings of the investigations. The inverted fluidised bed stable bubble process is a novel idea and hence, Chapter 1 is a literature survey which discusses
Introduction

aspects of other areas of chemical engineering which use similar phenomena. The aim of the survey is to make conclusions about some of the unexplained phenomena in the process and draw on areas of expertise to facilitate the design of the equipment.

Chapter 2 describes the development of the process. This includes designs of the various apparatus used, the rationale behind the designs and how the stable bubbles were generated. Chapter 3 details the investigations into the fluidised bed hydrodynamics. The theory behind the investigation is examined and methods for predicting the behaviour are described. Chapter 4 begins to look at adsorption aspects of the process. The adsorption capacity of the fluidised bed is predicted based on the results of batch adsorption test in the presence of spreading agents. Mechanisms of adsorption are also discussed with reference to the results.

Chapter 5 describes the adsorption trials using the stabilised air bubbles. The advantages of shell adsorbents are discussed using mathematical theory. The discussion attempts to justify the results based on the experimental conditions, current adsorption theory and physical properties of the coated bubbles themselves. Chapter 6 summarises the findings of the thesis and makes recommendations for improvement and future work.
Chapter 1 - Literature Survey

1.1 Introduction

The stabilised bubble process, as it is referred to here, is novel in its potential as an effluent treatment process. The theoretical advantages of this process have been mentioned and will be discussed later in this thesis. The technique can be divided into two main stages: the first being the actual generation of stabilised air bubbles by coating the outer surface with a thin layer of activated carbon, the second being the utilisation of these bubbles in some form of contacting vessel where the bubble assembly behaves, according to observation, as an inverted fluidised bed. This literature review will attempt to identify the underlying principles concerned in both of these stages. Fortunately, it is possible to begin to understand the physical processes involved, as elements of the process are analogous or very similar to other related processes.

The most novel element of the process is the use of coated bubbles as "pseudo-particulates". However, bubbles are used in many other chemical and physical processes. Bubbles are ideal for use when a small quantity of gas is required to be absorbed in a liquid phase. The equipment developed for this purpose is referred to as a "bubble column" (Penney, 1988). A simple bubble column consists of a tower in which bubbles of gas flow co-currently with a liquid phase, either up or down depending on the residence time required. A simple bubble column is shown in Fig. 1.1 (Deckwer, 1992). The higher density of the liquid flow means the liquid can operate at a low flow rate and therefore the gas flow rate is usually the important parameter. At low gas rates, the bubble size is sharply defined and the bubbles rise uniformly across the cross-section of the reactor. At higher rates, the bubbles aggregate and larger bubbles are formed which rise rapidly. The advantages of the bubble column are that it is simple to construct, has no mechanically operated parts, delivers high heat transfer coefficients which ensure a uniform temperature throughout and the bubbles entrain air as they rise, forming a distinctive flow pattern which causes high radial intermixing.
Chapter 1 - Literature Survey

Figure 1.1 - A simple bubble column (Source - Deckwer, 1992)

Figure 1.2 - Various types of bubble column (Source - Deckwer, 1992)

Figure 1.3 - Different bubble diffusers (Deckwer, 1992)

Figure 1.4 - The twin-jet bubble disperser (Deckwer, 1992)
Bubble columns come in many varieties and have a large number of applications. A simple, but effective modification to the column in Fig. 1.1, is to introduce perforated plates as in Fig. 1.2. The plates redistribute the gas, intensifying mass transfer and reducing the fraction of larger bubbles. This effect can also be reproduced using columns containing dumped or structured packing. Other modifications can include deliberate internal circulation of the liquid phase using internal loops or liquid jets.

The bubbles are produced by gas distributors. The most common types are static gas distributors through which the gas is dispersed by holes or pores (see Fig. 1.3). Sintered plates manufactured from glass or bronze produce small bubbles of uniform size distribution. Perforated plates with holes 1 - 5mm in diameter are also effective. They are normally made from metal and consist of a free area of 0.5 - 5%. Bubbles can be directly injected via a tube, the bubbles being dispersed relatively uniformly as the gas jet breaks up. Twin jets, in which the gas and liquid phases are injected simultaneously, are highly effective for producing a large gas-liquid interfacial area. The jets create a high energy dissipation zone in which the gas is broken into small primary bubbles. The bubbles coalesce as they rise until an equilibrium bubble diameter is established (see Fig. 1.4).

There are many applications for bubble columns; two of the most common involve absorbing ozone or oxygen. Ozone is an oxidant and will react with certain natural constituents in water, making it invaluable in water treatment (Naas, 1990). For example, the colour properties of water are caused by the presence of organic and inorganic substances which absorb visible light. Ozone can attack the bonds or complexes that cause the colour, therefore removing them by reaction. The ozone is contacted with the water using a bubble column, more specifically, a counter-current sparged tank with diffuser. In this reactor, the ozone-containing gas forms small bubbles as it passes through a porous stone at the bottom of the tank. As the bubbles rise, ozone is transferred from the gas phase into the water.

Oxygenation (sometimes referred to as diffused aeration) also uses bubbles to transfer oxygen to the liquid phase, particularly in biological applications. A common reactor is
very similar to that used in ozonation, except the air is compressed before release at the bottom of the column (Cornwell, 1990). Another method involves using a plunging vertical liquid jet. In this design, both the liquid and gas phases enter at the top of the column as shown in Fig. 1.5 (Evans and Jameson, 1995). The liquid is introduced as a high velocity jet that entrains gas from the headspace at the top of the column, into the liquid below. The entrained gas is broken into very fine bubbles by the forces generated inside the column, carried downstream and discharged through an outlet at the base of the column. Plunging jets are becoming ever more common because they produce a large gas-liquid interface, are simple in construction and operation and low in capital and running costs (Moppett et al., 1995).

As well as bubble column technology, where gases are absorbed into a liquid phase, there are other techniques called "adsorptive-bubble separation techniques". These are based on selective adsorption or attachment of material on the surfaces of bubbles as they pass through a solution or suspension. In most methods, the bubbles rise to form a foam or froth which is collected and carries the desired (or undesired) material with it. The important aspect of this work is that the materials involved must be surface-active, i.e. allow adsorption of polar substances at a surface or interface (Shaw, 1994). If the material to be removed is not surface-active, then a suitable surfactant (known as a "collector") must be added to attach it to the bubble surface.

There are several different types of bubble separation techniques, including solvent sublation, bubble fractionation and foam fractionation. But, by far and away the most
common is flotation. This exists in many forms, but the most widely used is ore (or mineral) flotation. In this process, an ore is selectively removed from other minerals by attaching the ore to the surface of bubbles which pass through the pulp. The surface of the mineral ore is altered using the aforementioned collector, which renders the ore sufficiently hydrophobic to attach it to the bubble surface. The bubbles rise to the top where they form a stable froth on reaching the air-water interface overhead. The concentrate is then removed and washed, retrieving the required ore.

Another novel bubble process is that of the gas aphron. An aphron is defined as a phase (gas or liquid) which is encapsulated by a thin aqueous soapy film (Sebba, 1986). A soap bubble can be described as a giant gas aphron. However it is possible to make bubbles which are 25 - 50μm in diameter. These are known as colloidal gas aphrons (CGA). A consequence of their size is that they rise slowly, so they have a long enough life-time to be generated at one place and pumped to another for utilisation. The soap film acts as a strong barrier to coalescence, which never occurs as long as the bubbles are immersed in water.

The aphrons can be used for solvent extraction, with the CGA carrying the liquid solvent aphrons in a piggy-back fashion. They rise to the surface where they collapse to form a solvent layer. Aphrons are still relatively novel and many applications are being discovered including liquid-liquid extraction, mineral separation, clarification and fermentation.

Considering the different aspects of bubble technology referred to here, it is clear there are several similarities between these processes and that using stabilised air bubbles. For example, the bubbles are generated using plunging jets, the activated carbon is attached to the bubble surface using a spreading agent as in flotation and the bubbles have a stability which is similar to colloidal gas aphrons. This survey will attempt to review the relevant literature, in order to derive an understanding of the processes involved. As well as analogous bubble technology, it will consider relevant work in the fields of liquid-phase fluidised beds and adsorption using activated carbon. Finally, there will be a summary of the initial work of Dr. D.E. Weiss, whose early work inspired this process.
1.2 The formation of bubbles using plunging liquid jets

1.2.1 Mechanisms of gas entrainment

An understanding of the mechanisms involved in generating bubbles via plunging jets is important as a number of small scale plunging jets are used in the generation of stabilised air bubbles. There is an abundance of literature available and one would be led to believe that the knowledge available is comprehensive. Fortunately, the vast majority of these papers have already been reviewed extensively by Bin (1993). The review covers data and findings from every conceivable published experiment. It is quickly established that there are many factors governing the entrainment of gases, such as nozzle geometry, jet diameter, jet velocity, liquid viscosity, surface tension, angle of inclination and jet surface roughness. Bin has shown that while many authors have attempted to correlate their data, both theoretically and empirically, there is considerable variety in the experimental conditions, which makes it difficult to compare one set of data with another. This highlights the fact that there are still many areas to investigate.

This section will be based on the review by Bin, with some updated work since the review was written. To simplify matters, only work relevant to the process will be considered, i.e. low velocity and low viscosity (water) jets are considered. The pertinent effects of jet and nozzle parameters will also be considered.

A liquid jet produced from a cylindrical nozzle will, put simplistically, have a definitive diameter and jet length, which many authors state is dependent upon the jet velocity (Burgess et al, 1972; Cumming, 1975; Kusabiraki et al, 1990a; McKeogh and Ervine, 1981; van de Sande and Smith, 1973). Sufficiently low velocity jets can break up before they hit the plunge pool surface, while high velocity jets can appear conical shaped in long-time exposure photographs.

Low viscosity jets have disturbances on their surfaces and it is the interaction between these surfaces and the surface of the plunge pool that forms the mechanism of gas
entrainment. Fig. 1.6 illustrates this mechanism. As the jet falls through the gas space above the pool, an associated boundary layer of gas flows with it.

![Diagram of air entrainment for low viscosity liquid jets](image)

**Figure 1.6 - Mechanism of air entrainment for low viscosity liquid jets**

The jet and surrounding gas impact on the surface and induce a small depression, resembling an inverted meniscus. As the disturbances on the jet surface hit the liquid, there is a simultaneous movement of the pool surface and a transverse bulk liquid movement. The resulting deformation and closure of the surface leads to gas entrainment at the plunging point. The liquid surface is not quick enough to follow the jet as it moves past, resulting in the capture of bubbles. The effect of longer jets is to produce greater surface entrainment, caused by bigger surface irregularities. Larger (in diameter) and swifter jets lead to entrainment of large amounts of gas and at high velocities, entrainment becomes more regular and finer bubbles are produced. Inclined jets entrain greater amounts of air due to the increased number of surface irregularities.

Another suggested mechanism is that most of the entrained air enters via the layer of foam forming on the surface of the receiving liquid. The jet impinging upon the surface induces a wave action and air enters the interstices of the foam. The air is then entrained into the main body of the flow along with the recirculating foam. Thomas *et al* (1984) showed that the dominant factor in entrainment by foam is the impact angle of the jet. At low angles, the recirculating flow has a higher velocity than at steep angles, allowing large quantities of air to be entrained with the foam.
Chapter 1 - Literature Survey

The effectiveness of a jet can be measured by how much air it can entrain, the minimum velocity at which the entrainment occurs and the size distribution of the bubbles. These factors are dependent upon the experimental conditions associated with the jet. The next sections review the findings of some principal investigators with regard to these effects.

1.2.2 Jet diameter and velocity

The jet diameter and velocity are considered the most important parameters in air entrainment and many authors have discovered that the problem is how to calculate these at the plunging point. Theoretical considerations are difficult due to complicated hydrodynamics, for example, contraction of the jet at the nozzle outlet.

One equation considered by Lin (1963) for representing the jet diameter at the plunging point, was deduced by considering an energy balance on the jet:

\[ \frac{d_j}{d_r} = \left( \frac{\pi^2 g L_j d_r^2}{8 Q_L^2} + 1 \right)^{-1/4} \]  

where \( d_j \) = jet diameter (m), \( d_r \) = jet diameter at a reference point (m), \( L_j \) = jet length (m), and \( Q_L \) = liquid flow rate (m\(^3\)s\(^{-1}\)). Lin found that at a reference point, \( L_j = 0.03 \)m, the variation of \( d_j \) obeyed Eq. 1.1.

For turbulent jets just above the minimum entrainment velocity and inclined jets Ciborowski and Bin calculated, the jet velocity simply using Benoulli’s equation:

\[ V_j = \left( V_o^2 + 2g L_j \right)^{1/2} \]  

where \( V_j \) = jet velocity (ms\(^{-1}\)), and \( V_o \) = jet velocity at nozzle outlet, (ms\(^{-1}\)). This value of the jet velocity may, of course, be over simplified as the velocity may differ due to energy losses caused by jet turbulence. McKeogh and Ervine (1981) showed how turbulence levels can affect the velocity profile within a jet. They also correlated a relationship for the jet centre line velocity, \( V_r \), decay with vertical distance from the plunging point.

The findings given here are merely a summary of the extensive literature available. However, due to the experimental conditions concerned, they are the most relevant ideas.
It is obvious though that jet fluid hydrodynamics is very complex, and correlations can only be produced for different velocity regimes. However, due to the large variation in nozzle sizes and liquids used, there is still no rationalised expression to quantify all the data available.

1.2.3 Minimum entrainment velocity

The mechanism of entrainment has already been briefly explained, however, for coherent liquid jets, air will only be entrained if the jet velocity exceeds a critical value, $V_e$. To further complicate matters, the jet length is also crucial. If, for example, the length of the jet is less than that of the distance between the nozzle and liquid surface, the jet will be disrupted as it loses energy and it will break up into droplets. This is referred to as the break-up length, $L_b$. The droplets from the jet can also entrain air. As summarised by Bin (1993), Lara established in 1979 that this causes two regions at which $V_e$ occurs: (i) where the jet breaks into droplets; (ii) where the jet is continuous. These regions are illustrated in Fig. 1.7.

![Figure 1.7 - Regions of air entrainment](image)

In the droplet region of entrainment, as the jet velocity is increased, the distance to break-up, $L_b$, increases until it becomes equal to the distance between the nozzle and the pool surface. At this point, entrainment ceases. As the jet velocity increases further,
entrainment does not occur until the impact pressure of the jet and gas film layer are sufficient to penetrate the surface. The jet transfers its momentum to the pool giving rise to shear and normal stresses which pulls the liquid surface deeper into the pool. For low viscosity liquids the length of the gas film is quite short. The gas film is unstable and breaks up into bubbles, which can be also broken up into finer bubbles by the shear forces present.

The literature available on minimum entrainment velocity tends to concentrate on well defined jets, i.e. those that are coherent, viscous and laminar. Theoretical predictions for \( V_e \) have proved unsuccessful and most correlations are based on experimental data. Turbulent jets are more difficult to predict as the threshold value of \( V_e \) is dependent upon the turbulence level. Most authors prefer to correlate data in dimensionless form, and \( V_e \) is usually predicted in the form of the Jet Weber number, \( W_e_j \), which is defined as the ratio of the jet friction forces to surface tension forces:

\[
W_e_j = \frac{V_e^2 d_j \rho_L}{\sigma}
\]

where \( \sigma = \) surface tension (Nm\(^{-1}\)). Most authors relate this to the dimensionless jet length, \( L_j/d_w \), or for the droplet region of entrainment, the dimensionless break-up length, \( L_B/d_w \).

The data for water jets is restricted to Londong, van de Sande and Smith (1976), McKeogh and Elsawy (1980), Ervine et al (1980) and McKeogh and Ervine (1981), Bin (1988) and Moppett et al (1995). Londong (1973) performed experiments on very short, vertical water jets with diameters 1-80 mm (\( L_j/d_w \leq 2 \)) and for circular jets, he established that entrainment occurs if the Froude number, \( Fr = V_e^2/(gd_w) > 10 \) and \( Re_j > 7000 \). McKeogh and Ervine (1981) demonstrated that \( V_e \) is a function of the turbulence intensity; the minimum velocity reducing with increased turbulence. This agrees with the observation that surface disturbances on the jet are crucial to air entrainment. Their results were for one particular nozzle diameter only.
Bin (1988) performed a series of experiments on water jets for various nozzle sizes and velocities. For short cylindrical nozzles ($l = 10-24$ mm), his data showed the two regions of entrainment as claimed by Lara (as shown in Fig. 1.7), but Bin also found that the region of no entrainment diminishes for increasing nozzle diameter. For long cylindrical nozzles, there was a larger scatter of data, owing to the greater surface instability of the jets produced from these nozzles.

In the droplet region of entrainment, Bin recommended the following correlation:

$$L_j/d_o = 1.4 \times 10^{-5} d_o^{-1.79} W_e^{0.937}$$  \hspace{1cm} (1.3)

for jets produced from nozzle diameters in the range 2-10 mm. He found an accuracy to within ±10%. By comparing the correlation with data for viscous jets, he found that the greater the viscosity, the greater the deviation from this equation. He suggested that a liquid viscosity term should be added to compensate for this effect.

A simple correlation was recommended by Bin for the continuous jet region, for large nozzle diameters ($d_o \geq 7$ mm) with short cylindrical lengths, $l (l/d_o \leq 3)$ within the range $L_j/d_o = 1-100$:

$$V_e = 1.4 (L_j/d_o)^{1.4}$$  \hspace{1cm} (1.4)

Bin compared this correlation with the data of Ervine et al (1980), McKeogh and Elsawy (1980) and McKeogh and Ervine (1981), amongst other authors. The data shows a large scatter which Bin attributes to the turbulence induced by long cylindrical nozzles. This only serves to highlight that providing an empirical correlation is extremely difficult for all experimental data, and despite Bin’s attempt, this is only applicable for very short nozzle lengths.

More recently, Moppett and co-authors (1995) investigated the effects of jet length, nozzle diameter and nozzle design upon the minimum entrainment velocity. They found that $V_e$ increased with $L_j$ and $d_o$ (range of nozzle diameters 4.9-13.5 mm). They
attributed this effect to the fact that although the turbulence intensity increases, the momentum is spread over a greater area, i.e. the scale of surface instabilities decreases relative to the nozzle diameter increasing, requiring a larger jet velocity to initialize gas entrainment. Introducing a turbulence promoter into the nozzle design reduced $V_c$, although again, this value rose as the jet length increased. These findings agree with the results of the previous authors.

There has also been some work upon the effect of impact angle upon bubble entrainment. Detsch and Sharma (1990) studied the critical angle that would result in bubble appearance at a given jet velocity. They studied nozzle diameters in the range 1-4.6 mm and various liquids including water. They obtained a dimensional relationship between the critical angle, $\alpha_c$ and the parameters, jet velocity, $V_j$, liquid viscosity, $\mu_L$, liquid density, $\rho_L$ and surface tension, $\sigma$.

$$\alpha_c = -242.13 \log_{10} \left[ \frac{\sigma V_j}{(\mu_L \rho_L)} \right] - 79.1 \quad 1.5$$

The range of validity is established by the term $[\sigma V_j/(\mu_L \rho_L)]$ for values between 0.01 - 0.5 m$^3$kg$^{-1}$s$^{-2}$. However, as this is the only work that has undertaken such a study, there is no data to compare the validity of this equation and it should be noted that this equation was derived for one particular system geometry.

1.2.4 Volumetric Gas Entrainment Rate

A measure of the efficiency of a plunging jet is the amount of gas it will entrain into a plunge pool. This is normally given as the volumetric flow rate, $Q_A$, although many authors prefer to give this in dimensionless form as the ratio of the gas entrainment rate to the volumetric liquid flow rate, $Q_A/Q_L$ (or $Q_W$ for water). The gas or air flow rate is measured by one of two methods: (i) catching the gas after it has been entrained or (ii) measuring the rate of air removal from the space above the liquid surface at the plunge point. In the second case, the jets are usually inclined at an angle as the parabolic flow stream followed by the entrained bubbles means it is easier to catch them in an air hood. The data is often then extrapolated for vertical jets.
Generally, the rate of air entrainment increases with increasing jet velocity and nozzle size, as shown in Fig. 1.8, taken from van de Sande and Smith (1973). These authors and others (Kumagai and Endoh, 1982, 1983; Kusabiraki et al, 1990; Evans et al, 1996) established that the rate of gas entrainment shows at least three distinct regions: (i) low jet velocity region, (ii) transition region and (iii) high jet velocity region.

![Figure 1.8 - Air volume entrained as a function of jet velocity and nozzle diameter (Source - van de Sande and Smith 1976)](image)

This review considers papers which deal with the low velocity region only, which van de Sande and Smith (1976) stated was valid up to a jet velocity of 5 m s$^{-1}$. They tried to correlate the entrainment rate in terms of the jet’s kinetic energy, length and impact angle. This resulted in a correlation as follows:-

$$Q_A = 0.018 \left( \frac{d_n^2 V_j^3 L_j^{1/2}}{\sin^{1.5} \alpha} \right)^{3/4}$$  \hspace{1cm} (1.6)

This equation is valid for nozzles with $d_n = 2.85-10$ mm, $l/d_n = 50$, to ensure turbulent flow from the nozzle, $2 < V_j < 5$ m s$^{-1}$, $L_j < 0.5$ m and $\alpha = 20-60^\circ$. Bin compared this equation with data from other authors (Cumming, 1975; Ervine et al, 1980 amongst others) and found a decent agreement with the data. The correlation, it appeared, gave the upper limit of entrainment for nozzles with significantly long cylindrical sections. Comparing the equation with data for short nozzles, there is a marked difference, although the data for Ohkawa and Kusabiraki correlates to a similar equation:-
The inversely proportional nature of the impact angle, $\alpha$, shows that inclined jets entrain more air than vertical ones. The fact that $Q_A$ is a function of $(d_o^2V_j^3)$ and the length term, $L_j$, indicates these parameters are important for any system geometry or conditions. Afify and Urroz (1993) confirmed this dependence on the kinetic energy and angle of inclination, by relating $Q_A$ to the jet energy parameter, $E_p$, for low velocity jets, where:

$$E_p = \rho_w Q_w V_j^2$$

Their data also implied that air entrainment increases with jet energy, and for the same jet energy, it increases with nozzle diameter. Their correlation was in the form:

$$Q_A = 2.558 \times 10^{-4} \left( E_p \right)^{0.658} (\sin\beta)^{0.828}$$

where $V_j = \left[ V_o^2 + 2gh \right]^{1/2}$ and $\beta = \left( V_o \cos \alpha / V_j \right)$. This equation is similar to that of van de Sande and Smith (Eq. 1.6), but the power terms differ, as might be expected if the experimental conditions are different. Unfortunately, no mention is made of the aspect ratio of the nozzles and this is reflected in the lack of a $L_j$ term in the correlation.

Note that Eq. 1.9 includes the density of water, $\rho_w$. Other authors have also looked into the effects of liquid physical properties on air entrainment, i.e. viscosity and surface tension as well as density. Kumagai and Endoh (1983) and Yamagiwa et al. (1993) compared the gas entrainment rate for water with that of other more viscous liquids. Kumagai and Endoh found that for the low velocity region, the rate of entrainment decreased with the kinematic viscosity, $\nu$, which is represented in Eq. 1.10:

$$Q_A = 1 \times 10^{-5} \left( 100 V_j \right)^{1.650} l_{10}^{0.17} d_o^{5.85} L_j^{2.15} (\sin\alpha)^{-0.27} \nu^{-0.95}$$

As is evident in this correlation and from the data, the effect of surface tension was seen to be negligible over all the jet velocities. In order to try and retain some comparison with other data, Kumagai and Endoh used a long cylindrical nozzle ($l/d_o = 50$) as adopted by van de Sande and Smith (1973, 1976). Yamagiwa et al. (1993) followed a similar route as Kumagai but tried to relate directly the ratio $Q_g/Q_l$ to the parameter $\mu/\sqrt{\rho \sigma l}$? Their correlation was more complex:

$$Q_g/Q_l = \frac{l (Fr, L_j/d_o, l/d_o, Oh, \sin\alpha)}{Oh = Ohnesorge number = \frac{\mu}{\sqrt{\rho \sigma l}}}$$

18
and \( Fr = \text{Froude number} = \frac{V_o}{\sqrt{gd_o}} \)

Their paper details the many coefficients and powers required for each region of entrainment and they found the data agreed with the correlation to within an error of \( \pm 20\% \).

Another factor that has been investigated by several authors is the actual shape of the jet and how it affects entrainment. Jets are usually described as laminar or turbulent and often the level of turbulence is noted if it has been measured. The relationship between turbulence and the minimum entrainment velocity was discussed earlier and the entrainment mechanism at the plunge pool surface has been described. The turbulence within the jet is crucial to this mechanism as many authors believe that the jet also entrains air as it passes through a gaseous atmosphere (Burgess et al., 1972; Ervine et al., 1980; McKeogh and Ervine, 1981; Kusabiraki et al., 1992; Bonetto et al., 1994). As described by Ervine et al. (1980), a liquid jet will become unstable as it leaves the nozzle and develop a sinusoidal surface shape. This shape becomes more sinuous or wavy as the turbulence develops, i.e. as it passes through the atmosphere (see Fig. 1.9).

![Figure 1.9 - Extent of boundary layer and air entrainment](image)

As well as the boundary layer surrounding the jet, the air can be encompassed within the jet disturbances. The extent of these jet disturbances is characterised by the parameter, \( \varepsilon \). While Burgess et al. (1972) attempted to characterise the rate of entrainment by relating the jet diameter at impact to that at the nozzle, as seen in the expression:-
Ervine and colleagues used photographic methods to measure the surface roughness \((\varepsilon/r)\), where \(r\) is the jet radius at any point along the jet. Using a simple analysis technique, they were able to relate the jet roughness to the ratio of air entrainment to liquid flow in the correlation:

\[
\frac{Q_{\gamma}}{Q_{w}} = \left( \frac{d_{e}}{d_{o}} \right)^{2} - 1
\]

They concluded that at lower values of \((\varepsilon/r)\), the majority of the air is being entrained at the plunge point, but a proportion of the air comes from the boundary layer. This occurs up to values of \((\varepsilon/r) = 0.6-0.7\), at which point the jet becomes too intensely sinuous. Above this value, the rate of entrainment does not increase so sharply as the disturbances are seen to break away from the main body of the jet leading to the lower entrainment rate.

More recently, Kusabiraki et al (1992), related the shape of the jet in terms of the mean length, \(l_{m}\). They measured the lengths of the left and right hand sides of the jet using an opisometer and took the average of these values to be \(l_{m}\). The shape of the jet was then characterised by the term \((l_{m} - h)/h\), where \(h\) is the distance between the nozzle exit and the surface of the pool. The larger this number, the greater the distortion in the jet. While, Ervine and colleagues had used \((\varepsilon/r)\) to define the roughness of the jet, Kusabiraki et al, stated that two types of jet are possible. At a nozzle geometry, \(l/d_{o} < 20\), the roughness of the jet is due to jet disturbances. At \(l/d_{o} > 20\), the jet is disturbed by the sinusoidal motion of the jet. The authors revealed how the jet shape is related to the entrainment ratio \(Q_{g}/Q_{l}\) by plotting these individually against the Froude no., Fr. Both graphs had the same shape, showing that changing \(l_{m}\) altered the gas entrainment rate. The authors indicated that \(l_{m}\) and \(Q_{g}\) also follow the Ohnesorge no. similarly, but there is no increase in \((l_{m} - h)/h\) with nozzle diameter, \(d_{o}\). From the author’s previous results, it could be supposed that \(Q_{g}\) does not vary with \(d_{o}\), but other authors (van de Sande and Smith 1973, 1976; Ervine et al, 1980; McKeogh and Ervine, 1981; Kumagai and Endoh, 1982; Kumagai and Imai, 1982) have shown that it does increase with \(d_{o}\). As long as the nozzle geometry \(l/d_{o}\) does not exceed 15, the \(Q_{g}/Q_{l}\) ratio increases. Beyond this, the ratio
is constant indicating an upper region for entrainment. Kumagai and Imai (1982), ascribed the increase in $Q_g$ with $d_e$ to the increased contact perimeter of the jet flow.

Some of the most recent papers consider the gas entrainment rate, but rather than consider phenomenological based correlations, they have tried to model the entrainment mechanism theoretically. Bonetto et al (1994), attempted to model $Q_g$ by basing their hydrodynamic manipulations on the fact that air is entrained by the instability of the jet and pool depression surface, i.e. at some point the wave amplitude causes the two surfaces to meet, thus entraining the air in the form of a bubble. They tested their model against the results of McKeogh and Ervine (1981) and they claim remarkable agreement.

![Figure 1.10 - A confined plunging jet system](image)

Evans et al (1996) attempted to model the gas entrainment rate for a plunging jet in a confined system, chosen because the industrial applications using plunging jets are contained within a vertical column. Jets within confined columns produce very fine bubbles, of the order 100-500 μm, and a large interfacial area. This is caused by the intense recirculation of the flow and high energy dissipation rates. In Evans’ plunging column, they identified certain characteristic flow rates as shown in Fig. 1.10. As well as the metered gas flow rate, $Q_g$ and the liquid flow rate, $Q_l$, the amount of air entrained is
Chapter 1 - Literature Survey

denoted, $Q_E$, the bulk recirculation rate, $Q_b$, and the flow rate of gas recirculated back into the headspace, $Q_R$. As well as taking into effect the diameter of the column, the authors also assume that $Q_E$ is the sum of the boundary layer of gas and the quantity of gas that is trapped within the jet itself.

The effect of increasing the ratio $Q_g/Q_l$ is to increase the interfacial area. At low gas rates, the level of the gas-liquid mixture is just below the nozzle outlet. This indicates that the jet can effectively entrain all of the gas supplied to the headspace. If the gas rate is increased, a point is reached where the jet can no longer entrain all the gas and the froth level starts to drop. As the jet length increases, the rate of air entrainment increases and a new equilibrium height is reached where the jet can entrain all the air. At very high gas rates, large slugs of gas form in the liquid, restricting the downward flow of gas. The pressure in the headspace increases causing a drop in the froth level, ultimately leading to system collapse.

The aim of Evans' paper is to model the free jet length. They claim that their correlation is superior in that it includes the column diameter and gas recirculation rate, which have a profound effect on the gas entrainment rate, as well as the usual parameters. Their model is based upon the extent that the boundary layer and encompassed gas contribute to $Q_E$. For example, at a free jet length 3-5 $d_0$, it is assumed that all the entrained gas comes from the boundary layer. For longer jets, both mechanisms contribute and at long lengths, the contribution is limited to the trapped air. A model is given for each condition and the authors compare the calculated values of $Q_g/Q_l$ to the experimental ones. They found the model to be within ±20% accuracy and the amount of recirculated air is significant; values of $Q_b/Q_l$ in the region 0.6-0.9. The model predicts that this value increases with the column diameter, up to a ratio of 0.93 for a 95 mm dia. column. As the ratio of $Q_E/Q_l$ varies from 0.6-1.5, it is clear that the recirculated gas significantly reduces the amount of fresh gas feed required. The only down-side of this paper, is that some of the model's constants have to be predicted experimentally, but the authors claim that they are currently undertaking a study to predict them from first principles.
1.2.5 Bubble Size Distribution

Despite the amount of literature available on plunging jets, there is relatively little on the size of bubbles, particularly on modelling the average bubble size. There is general agreement that there are two distinct regions of bubble sizes after the shear forces created by the jets momentum have broken the film of entrained air into bubbles (Ervine et al., 1980; McKeogh and Ervine, 1981; Bin, 1988, 1993; Evans and Jameson, 1995). The first consists of a conical region containing fine bubbles (known as primary bubbles) of diameter less than 1mm. These bubbles penetrate the pool to a considerable depth due to the submerged jet momentum. Eventually, buoyancy forces compensate and the bubbles begin to rise and coalesce. These bigger, rising bubbles (known as secondary bubbles) comprise the second region.

Bubble sizes are often measured using photographic techniques and graticules, although this means that only secondary bubbles can be measured. Van de Sande and Smith used a photo-electric technique by sampling the dispersion through a capillary tube. More recently, Randall et al. (1989) measured bubble size by passing the bubbles up a capillary tube and measuring their dimensions and velocities using two photo-transistors. The total volume of gas is measured and the bubble volumes are determined as a fraction of this total. For a 2-phase system, they found the mean bubble size to be 2.8 mm and for a 3-phase system (containing 10% quartz in water), the mean size was 3.0 mm. Barigou and Greaves (1991) also used a capillary suction technique and found mean bubble sizes of 2.5 mm. Randall et al. and Barigou and Greaves did not use plunging jets to produce bubbles for their measurement system. Randall used a sparged air system and Barigou used a stirred vessel.

In plunging jet systems, the secondary bubbles have a Sauter mean diameter of 3-4 mm, independent of nozzle diameter and jet velocity and the size distribution is normal. Evans et al. (1992) attempted to predict the maximum possible bubble size generated within the mixing zone below the plunge point. With a knowledge of the length of the mixing zone, \(L_{MZ}\), found by measuring the pressure profile of the column, and the critical Weber no., \(We_c\), the max. bubble diameter, \(d_m\), is found from:-
where $E$ is the energy dissipation rate per unit volume (kgm$^{-1}$s$^{-3}$), which can be calculated from liquid-jet gas ejector theory. By using a value of $We_e=1.2$, they found the predicted values compared to the measured values to within ±20%. They also found the bubble size distribution was bimodal, consisting of (i) the initial distribution of fine bubbles generated by the plunging jet and (ii) the distribution caused by the break-up of larger bubbles in the recirculating zone. Their Sauter mean diameter bubble sizes were much smaller than other authors, 0.12-0.42 mm, which is symptomatic of the shear forces generated in confined plunging jet systems.

### 1.2.6 Maximum depth of bubble penetration

The depth to which an entrained bubble will penetrate will fluctuate as the entrainment process is not regular. However, several authors have tried to predict the maximum depth to which a swarm will penetrate by measuring the depth and correlating the results (Ciborowski and Bin, 1972; Cumming, 1975; Kusabiraki et al., 1990; McKeogh and Ervine, 1981; van de Sande and Smith, 1973). McKeogh and Ervine suggested a simple correlation, relating the depth of penetration, $H_p$, to the nozzle velocity and diameter: 

$$H_p = 2.6(V_o d_o)^{0.7}$$

which related well for their own data, but on comparison with other authors data, it did not correlate satisfactorily. Bin (1993) attributed this to the differences in pool vessel geometry, which agrees with Evans et al (1996) who believed that the confining column is important and should be considered in entrainment correlations.

More recently, Moppett et al (1995), extended this work by manipulating Eq. 1.14 to show that $H_p$ is merely a function of the Froude no.: 

$$\frac{H_p}{d_o} \approx 5.14 Fr^{0.66}$$

His data compared reasonably well with this correlation. The effect of increasing the jet velocity was to increase the depth of penetration, as expected. Higher velocity jets have larger dissipation rates, resulting in the generation of smaller bubbles. Smaller bubbles
have lower buoyancy forces and so are carried to greater depths. The effect of increasing \( L_j \) was noted as initially causing a reduction in \( H_p \), but after \( L_j/d_o > 20 \) there was no further change. Longer jets lose more of their energy as they pass through the air-space and so shorter jets are better for large penetration depths.

Kumagai et al (1993) first attempted to expand on these correlations to include \( L_j, d_o \), and the jet angle, \( \alpha \). For an inclined system, the bubble swarm region has a different shape as the bubbles penetrating follow the jet trajectory to some distance, and then rise so that the entrainment shape is that of a bowl. In these experiments, the depth of penetration was measured as the maximum vertical distance. They correlated their data in terms of jet momentum, \( (V_o d_o) \), jet length, \( (L_j/d_o) \) and angle of inclination:

\[
H_p = 50 (V_o d_o)^{A} (L_j/d_o)^{0.55} \sin^{1.5} \alpha
\]

The authors compared their data with others (Suciu and Smigelschi, 1976; McKeogh and Ervine, 1981) and found good agreement with their simpler correlations over the conditions they were used. It appears that the Kumagai et al correlation works over a wider range of operating conditions by incorporating these extra parameters.

1.2.7 Summary

It is evident from this review that the volume of published work available is enormous. The literature available on high velocity, large diameter jets has been specifically avoided as it is deemed inappropriate to the present bubble generation process. Modeling the hydrodynamics of water jets is extremely complex and so far there is little success in this area. Attempts at modeling the rate of air entrainment have also proved difficult as the number of parameters affecting this process is large. Correlations have been based on empirical data, which has led to many different correlations dependent upon the experimental conditions used. As yet no empirical or theoretical model is available to account for the different jet geometry or liquid physical properties. There is little theoretical work on bubble size distribution, although from observation, many authors agree on the expectant size of bubbles produced in open and confined spaces. However, the wealth of literature does allow speculation on how the bubble generator
works; at least phenomenologically if not theoretically. The relevant aspects will be discussed later in the thesis.

1.3 Particle-bubble attachment and Aphrons.

1.3.1 Mineral flotation

An important aspect of the stabilised bubble process is the coating of an air bubble with a layer of activated carbon. It has not been an objective of this project to investigate thoroughly the ideal conditions and mechanisms for coating the air bubbles, however an elementary understanding of particle-bubble attachment, in conjunction with a knowledge of plunging jet effects, should indicate how the coated bubble generator works. This section will review the literature pertaining to investigation of the mechanism of particle-bubble attachment.

The vast majority of research into particle-bubble interactions is related to the field of froth flotation. More specifically, dispersed-air flotation, as used in mineral technology and dissolved-air flotation (DAF), which is used for effluent treatment (Kitchener, 1982). These are the two common types of flotation. Mineral flotation uses air bubbles of the order 0.5-4 mm in diameter to float particles and aggregates, while dissolved-air flotation bubbles are 20-100 μm in diameter and float smaller and less dense particles (Gregory and Zabel, 1990). As the stabilised bubble process resembles mineral flotation more closely in terms of particle and bubble size, the review will therefore concentrate on this topic, but will refer to DAF literature when necessary.

Mineral flotation is used to selectively separate and concentrate a particular ore from a pulp containing other minerals. This is achieved by allowing air bubbles to rise up and attach to the mineral particles in an air sparged suspension. To do this, a bubble must displace water from the particle surface, which can only occur if the mineral is sufficiently hydrophobic. The bubbles and attached particles rise to an air-water interface where a froth is formed and collected. The froth must be stable in order to
retain the particles. If the bubbles burst, the particles will fall back into suspension. A typical flotation rig is shown in Fig. 1.11.

![Flotation Rig Diagram](image)

**Figure 1.11 - Dispersed air flotation as used for processing minerals**

The nature of a mineral surface is usually insufficiently hydrophobic to allow attachment of an air bubble. Hence, chemical reagents are added to compensate. There are a variety of different reagents, their use depending on the action required:-

a) **Collectors** - these render the mineral surface hydrophobic
b) **Activators/Depressants** - these heighten/suppress the hydrophobic nature of a mineral
c) **Frothers** - these ensure the froth is stable. Some frothers are also collectors.

Collectors form a thin, water-repellent layer on the surface of the mineral. Collectors are classified as oily, anionic or cationic. Their use is dependent upon the surface chemistry of the mineral involved. Oily collectors usually consist of a long hydrocarbon back-bone which is hydrophobic. The collector attaches itself to the surface of the mineral with the hydrocarbon “tails” facing out into the bulk suspension. Anionic and cationic collectors ionise in solution, the resulting ion adsorbing onto the mineral surface, rendering it hydrophobic.

Activators alter the chemical nature of a mineral so that it will react more favourably with the collector. For example, copper sulphate is added to flotation suspensions to
promote reaction between sphalerite, a zinc sulphide ore body, and a xanthate collector. The mechanism is thought to be due to the formation of copper sulphide molecules on the mineral surface, which readily reacts with xanthate. Depressants hinder the interaction between mineral and collector and are used to suppress unwanted minerals attaching to a bubble.

The reagent used in a particular flotation process is dependent upon the chemical nature of the mineral; more specifically, the functional groups that exist at the surface. Some groups will ionise in aqueous solution, leading to a surface charge and others are polar, attracting ions or other polar groups by a variety of electrostatic forces. This section will now consider the theory behind the electrostatic interplay that causes collector adsorption and bubble attachment.

1.3.2 Forces between particles and bubbles

Separation processes such as sedimentation, filtration and flotation rely on short-range interaction to promote attachment of particles to each other or to surfaces. The removal efficiencies of such processes are dependent upon particle size and so can be enhanced by coagulation. The forces that cause particle aggregates to form are only significant for particles in the colloidal size range, i.e. less than a few μm. These forces vary with particle size such that gravitational and drag forces predominate over colloidal forces for large particles. In the stabilised bubble process, the particle size varies from 0-50 μm in diameter. Some particles are therefore colloidal and so these forces should be taken into account.

The theory of colloidal interaction was developed independently by Derjaguin and Landau (1941), and Verwey and Overbeek (1948), and is known as the DLVO theory. This theory, as reviewed recently by, Amirtharajah and O’ Melia (1990) and Gregory (1993), defines colloidal interaction as the result of two forces:

1) van der Waals attractive forces
2) electrostatic repulsion between electrical double layers of identical charge
van der Waals forces arise from interactions of dipoles in the atoms of the colloidal particles and water. The attractive forces between two particles decrease as the separation distance increases. A potential energy of attraction, $\psi_A$, results from these forces which also decreases with separation.

Most particles in aqueous suspensions possess an electrically charged surface due to ionisation of a surface functional group or specific adsorption of ions. This charge is negative for most particles. Ions of opposite charge are attracted to the surface. DLVO theory states that these counter-ions together with the surface charge form the electrical double-layer as shown in Fig. 1.12. At low ionic strength, the counter-ions extend into the bulk suspension to form a diffuse layer of some considerable distance, and means that particles approaching each other experience repulsive forces. At high ionic concentrations, the diffuse layer is smaller and so particles have to approach quite close before repulsion is felt.

![Figure 1.12 - The electric double layer surrounding a charged particle (Source - Amirtharajah, 1990)](image)

If an electrical potential is applied across a suspension of charged particles, they move towards the appropriate electrode. The potential at the plane of shear, between the layer of ions moving with the particles and the bulk fluid, is referred to as the zeta potential.
Chapter 1 - Literature Survey

Activators increase the potential for attraction between the mineral surface and the collector molecules by amplifying the magnitude of the zeta potential.

The DLVO theory combines the van der Waals attraction and electrical double layer repulsion and assumes that the attractive and repulsive energies, $\psi_A$ and $\psi_R$, are additive to produce a total energy of interaction which is a function of separation distance. These combined energies are shown in Fig. 1.13. When the zeta potential of the particles and ionic strength are such that repulsion outweighs attraction, then there is a potential energy barrier which hinders aggregation of the particles. If ionic strength is increased or zeta potential reduced, the energy barrier is lowered and contact can occur readily.

![Interaction energies](image)

Figure 1.13 - van der Waals ($\psi_A$), electrical ($\psi_R$) and total ($\psi_{TOTAL}$) interaction energies as a function of separation distance (Source - Gregory, 1993)

This theory of interaction is important in flotation of minerals as it explains why certain combinations of minerals and reagents are preferable. Mineral flotation requires aggregation of particles and if the collector or activator can reduce electrostatic repulsion levels, aggregation is promoted. Commonly, bubbles carry a negative charge over a wide range of pH values. In a solution of anionic surfactant, the gas-liquid interface will become more negative due to anion adsorption (Lu, 1991). If the mineral also carries a negative charge, then electrostatic interaction is likely to be repulsive and particle-bubble
adhesion is hindered. Modification of surface charge, by adsorption of ions from the collector or activator, would help the mineral to interact attractively with the bubble.

However, this particle-bubble interaction cannot be explained totally by colloidal forces. It is true that electrostatic forces must play a role as adsorption of ions on the surface can reduce the charge allowing particle-bubble interaction. However, a strict definition of a hydrophobic surface is one that carries no polar, ionic or hydrogen-bonding groups and hence no affinity for water (Gregory, 1993). Negatively charged particles can be modified to produce a hydrophobic surface by adsorption of cations from a surfactant. While the ions are neutralised by the ionic “head” of the molecule, the hydrophobic “tails” will align perpendicularly with the surface and face into the bulk solution. This hydrophobic surface prevents hydration of the mineral by water molecules and eliminates repulsion between particles. The attractive force that now exists between the mineral and bubble was defined by Kitchener (1984) and Laskowski (1986) as hydrophobic interaction, and it exists over a longer range than colloidal forces.

Lu (1991) attempted to quantify the role of hydrophobic interaction in comparison with van der Waals and double layer forces. He believed that electrostatic forces could not predominate as there would be a strong repulsive interaction between the negatively charged bubble and the mineral. This meant that hydrophobic forces must dominate and the hydrocarbon chains of the adsorbed surfactant penetrate into the bubble, as in Fig. 1.14.

Lu calculated the potential energies involved in the flotation of rhodochrosite, a manganese carbonate mineral, using oleic acid as the surfactant. His calculations showed that the potential energy of hydrophobic interaction was of two orders greater than double layer or van der Waals interaction. Consequently, hydrophobic interaction must be the governing factor in particle-bubble attachment. Lu’s results seem conclusive, but it must be remembered that the calculations are based on theory. However, the role of hydrophobic interaction is obviously important.
Despite the agreement amongst authors when considering particle-bubble interaction, there is still no completely satisfactory mechanism to explain it. A recent paper by Paulson and Pugh (1996) attempts to reconcile double layer repulsion with hydrophobic interaction. They floated inherently hydrophobic graphite particles using solutions of inorganic electrolytes. As expected, the divalent and trivalent cations present in the electrolyte reduced the negative charge and so reduced the double layer thickness, aiding flotation. At 100% mineral recovery, the double-layer thickness is so small that electrostatic repulsion is virtually zero. However, for monovalent electrolytes, the flotation performance was poor, irrespective of electrolyte concentration and double layer thickness. The authors concluded that electrostatic repulsion must play an important role but cannot be solely responsible for flotation.

The mechanism of hydrophobic interaction is not fully understood, and has included arguments based on cavitation (Christenson and Claesson, 1988) and/or electrical forces (Tsao et al, 1991). The reasoning behind these mechanisms is now being challenged by recent observations of long range attraction between hydrophilic and hydrophobic surfaces (Tsao and Evans, 1993). Ducker et al (1994) also found long range attraction between an untreated glass particle and an air bubble. Fielden et al (1996) attempted to reproduce these findings for air bubbles and silica particles, before and after hydrophobising. They found the interaction between an air bubble and a hydrophilic
silica particle to be monotonically repulsive on approach, in agreement with theory, and with no long range hydrophobic force as observed by Ducker. On removal of the particle from the bubble, a small adhesion force was measured, indicating an attractive force. The authors presume this to be due to charge reversal, which is predicted in DLVO theory for an asymmetric system. When the silica was partially hydrophobised, a hydrophobic attraction was observed. For attachment to occur, the aqueous film between the particle and bubble must be drained. For partial hydrophobic character, a balance between the hydrophobic attraction and van der Waals repulsion determines whether a film is present or not. For fully hydrophobic silica particles, the magnitude of adhesion was stronger, leading to rapid film drainage and attachment.

The mechanisms involved are obviously very complex and theory does not extend for all cases, as with Ducker’s findings. Often, authors will investigate a particular particle and find the best conditions at which flotation occurs. Zouboulis et al (1994) studied the separation of powdered activated carbon (PAC) from water by flotation. A cationic surfactant, cetyltrimethyl-ammonium bromide (CTMA-Br), and anionic surfactant, sodium dodecyl-sulphate (SDS), were used to modify the PAC surface. HCl and NaOH was added to adjust the suspension pH accordingly.

CTMA-Br proved to be more effective than SDS at low concentrations, and at higher concentrations the separation efficiency was reduced. As would be expected, SDS worked better in acidic pH values, while CTMA-Br worked better in alkaline pH. At ideal conditions, 100% of PAC was removed by the cationic CTMA-Br, while at ideal acidic conditions the SDS removed about 85%. These results highlighted several points. The authors believed that the reduction in performance at higher surfactant concentrations was due to hydrated micelle formation at the carbon surface or a stable, hydrated envelope of surfactant on the bubble surface. They also noted that as most carbon surfaces are negatively charged, the better performance of CTMA-Br is logical. Also, the hydrocarbon chain length is longer (\(C_{16}\) compared to \(C_{12}\)). However, it was observed that PAC can float both types of surfactant reasonably well, meaning that the PAC surface can adsorb both positive and negative charges. Zouboulis believed that the
main factors affecting flotation was the extent of adsorption on the surface and the orientation of the surfactant.

This duality offered by PAC was noted previously by Plaksin (1960). He found that collector molecules do not form a monolayer on the surface. He thought this was caused by the heterogeneous nature of the carbon surface, caused by imperfections in the crystal lattice. Hence only certain regions are reactive, leading to non-uniform distribution of collector, localised patches of oxidation and therefore, both anodic and cathodic regions.

The literature reviewed here indicates that the majority of flotation behaviour can be explained by electrostatic and hydrophobic forces but exceptions are always found and the mechanisms are not completely understood. Current literature is looking to explain the inconsistencies, however, poor reproduction of results and unusual observations are making this difficult. To further complicate matters, there are other factors that can affect flotation efficiency.

1.3.3 The contact angle and bubble-particle hydrodynamics.

Before the introduction of theories on electrostatics and hydrophobic interaction, the classic method for indicating the extent of the hydrophobic nature of a solid surface was by the contact angle (Jowett, 1974; Edzwald, 1995). If we consider a three-phase system, as in Fig. 1.15, the contact angle is measured between the tangent at the liquid and gas interface and the particle surface.

![Figure 1.15 - Representation of the forces and contact angle in a 3-phase system](image-url)
The significance of the contact angle becomes clear if a force balance is taken over the system:

$$\sigma_{sg} = \sigma_{sl} + \sigma_{lg}\cos\theta$$  \hspace{1cm} (1.16)

where $\sigma_{sg}$ is the surface tension at the solid-gas interface ($\text{Nm}^{-1}$), $\sigma_{sl}$ is the surface tension at the solid-liquid interface, $\sigma_{lg}$ is the surface tension at the liquid-gas interface and $\theta$ is the contact angle. For a surface to be hydrophobic, the work of adhesion between the liquid and particle must be less than the energy of cohesion of the liquid:

$$W_{sl} = \sigma_{sg} - \sigma_{sl} = \sigma_{lg}\cos\theta$$  \hspace{1cm} (1.17)

where $W_{sl}$ is the work of adhesion between the solid-liquid interface ($\text{Nm}^{-1}$). The larger the contact angle, $\theta$, the lower the value of $W_{sl}$, which means the liquid can be easily displaced from the solid surface by the gas bubble. Hence, hydrophobic materials are characterised by a large contact angle.

In mineral flotation, the idealised system shown in Fig. 1.15 is not true. In reality, the bubble is much larger than the particle. Fig 1.16 shows how the contact angle is represented in this system. The bubble will peel away if an attached particle is subjected to external forces, such as turbulence or weight effects. The bubble will remain attached to the particle as long as the angle, $\theta$, does not exceed the contact angle. Hence, the analogy still holds for hydrophobic materials with a large contact angle, since the bubble-particle can withstand larger forces before detachment.

![Diagram](image.png)

Figure 1.16 - Contact angle during flotation

The conditions for attachment between bubbles and particles are largely based on modifying the surface chemistry of a mineral. However, there is also a hydrodynamic factor, i.e. a particle must pass close enough to a bubble for attachment to occur. One of
the earliest publications on this matter is attributed to Sutherland (1948). He saw flotation as a stochastic process, where the chance of a particle being floated was the product of three probability terms:

\[ P = P_C P_A (1 - P_D) \]

where \( P_C \) = probability of particle-bubble collision

\( P_A \) = probability of adhesion

\( P_D \) = probability of detachment

A quick analysis of this equation shows how flotation is affected by particle size. \( P_D \) should increase with particle size, while \( P_C \) should decrease. According to Luttrell and Yoon (1992), flotation is usually effective over a narrow range of particle sizes, typically 10-100 µm.

As reviewed by Kitchener (1982), the theory of collision between bubbles and particles was developed by Derjaguin and Dukhin (1981), Flint and Howarth (1971) and Reay and Ratcliff (1973). The concept of hydrodynamic theory is that the particles in suspension follow streamlines around the front of the bubble, as in Fig. 1.17.

![Figure 1.17 - Trajectories of a particle approaching a bubble with (dashed) and without (solid line) the influence of the resistance due to viscous film thinning (Source - Luttrell and Yoon, 1992)](source.png)
A particle flowing along these stream lines will avoid the bubble unless it is within a critical distance, $H_C$. It is usual that adhesion occurs between the particle and bubble when they are in contact for long enough to rupture the thin water film between them. Some particles will not be retained for a sufficient time, and so will skate around the surface of the bubble before being detached. Those that do will be swept to the front of the bubble before adhesion. The minimum time required for thinning and rupturing the film is referred to as the induction time, $\tau_i$ (Sutherland, 1948; Trahar and Warren, 1976; Luttrell and Yoon, 1992; Bloom and Heindel, 1997). Sutherland stated that the induction time was independent of particle size, but this disagrees with the findings of Klassen and Mokrousov (1963). Trahar noted that they found larger particles needed a longer time to establish contact. The induction time is related to $P_A$, where $P_A$ is the fraction of particles whose contact times are longer than $\tau_i$. In general, the more hydrophobic a particle, the shorter the induction time. $\tau_i$ is also a function of the force with which a particle strikes a bubble, although this has not been accounted for in models predicting $P_A$.

Luttrell and Yoon (1992) attempted to update the hydrodynamic theory by using an alternative method to describe $P_A$. They used the notion that particle-bubble adhesion occurs when the kinetic energy of the particle, $E_k$ is greater than the energy barrier, $E$, which is determined by the surface forces involved. The distance at which this occurs is the critical rupture thickness, $H_C$. Thus, they defined the criteria for bubble-particle adhesion as $E_k \geq E$ when $H < H_C$. The authors state that for hydrophobic particles, $H_C$ is in the range 100-150 nm and decreases with decreasing hydrophobicity. Defining the probability of particle collection, $P$, as the fraction of particles in the path of a bubble that are collected, the authors calculated $P$ using $R_o$, $R_b$, $R_p$ and $H_C$ as defined in Fig. 1.17:-

$$P = \left[ \frac{R_o}{R_b + R_p + H_C} \right]^2$$ \hspace{1cm} 1.19

Eq. 1.19 shows that $P$ is a function of both physical parameters (bubble and particle size) and surface chemistry ($H_C$). Although $H_C$ is small compared to $R_b$ and $R_p$, $P$ is sensitive to changes in $H_C$. The reason is that a change in $H_C$ requires a large change in $R_o$ for the particle to still be collected by the bubble. Luttrell and Yoon plotted the values of $P$
against $H_c$ for various particle sizes and saw that $P$ decreases with particle size, but increases with $H_c$. This is in agreement with industrial findings which recognise that floating fine particles is difficult. However, this can be corrected by increasing the particle hydrophobicity. The authors concluded that the model predictions suggest that problems of flotation can be overcome by using smaller air bubbles or increasing $H_c$ (increasing the hydrophobicity).

The model was then validated using hydrophobic coal over a wide range of bubble and particle sizes. The results show general agreement if $H_c$ is set at a value of 150 nm. The authors claim this value is reasonable as Blake and Kitchener (1972) had observed a similar value for highly hydrophobic methylated silica.

1.3.4 The use of Aphrons in process engineering

A novel technique that has some similarities to coated air bubbles is the aphron. First recognised by Sebba (1972), aphrons are similar to foams and can exist in two particular forms. A foam is simply an aggregate of bubbles, held together by the surface forces in the thin soapy film between them. Sebba (1986) compared foams to aphrons, and considered an individual soap bubble as a giant gas aphron. Sebba was able to make similar bubbles which were only 25-50 μm in diameter, which he termed colloidal gas aphrons (CGA).

![Figure 1.18 - A Colloidal Gas Aphron](image-url)
Sebba described a CGA as a soap bubble consisting of a sphere of gas surrounded by a shell of aqueous soapy film (see Fig. 1.18). CGA’s are similar to stabilised air bubbles in the sense that the soapy film is a strong barrier to coalescence as long as the aphrons are completely immersed in water. The aphrons rise to the surface very slowly. Once they reach the surface, the upper layer of aphrons exposed to the air forms a conventional foam. Drainage occurs between the gas bubbles and the lamella film becomes so thin that the bubbles coalesce.

The exact mechanism of generation of aphrons is not fully understood, but the apparatus consists of a vessel incorporating a spinning disc, which entrains air into the surfactant solution which forms the robust, outer shell. The life time of the CGA is such that they can be pumped from this vessel to another site for utilisation. A typical dispersion contains up to 65% gas in water. A full description of the generation process is given in Sebba (1985).

CGA’s are used in conjunction with smaller, sub-micron liquid versions of gas aphrons, called colloidal liquid aphrons (CLA). In CLA’s the gas interior is replaced by a liquid that is immiscible in water, for example an oil-based liquid. The problem with the CLA is that the rise velocity is so small that they receive a “piggy-back” on the surface of the CGA. This is possible because the oil droplets adhere to the surface of the bubble. The difference in size is such that several hundred liquid aphrons can be carried.

Sebba envisaged that aphrons could be used for solvent extraction. The advantage he proposed is that only the solvent phase is comminuted into aphrons, dispensing with the need for a conventional mixer-settler arrangement and reducing energy requirements. By adding a chelating agent to the solvent phase, aphrons can be used to extract metals, which Sebba confirmed using copper, uranyl and chromate ions.

The reason why the stability of aphrons is so impressive is not fully understood and there is little literature available on this subject. Caballero et al (1989) reported that the concentration of surfactant used in the production of CGA’s is important to their stability. When the surfactant concentration reaches a critical value, the hydrophobic
tails of the surfactant will cluster together inside the structure with the hydrophilic heads exposed to form a micelle. The surfactant concentration at which micelles form is the critical micelle concentration (CMC). Caballero discovered that aphrons are less stable below the surfactant CMC.

Since their introduction, researchers have been investigating further applications of aphrons. Roy and colleagues (Roy et al, 1992; Zhang et al, 1996[a],[b]) have investigated the use of aphrons in organic dye removal. Roy et al (1992) used CGA’s to remove organic dyes. They found that gas aphrons are effective for removing the dyes by using a suitable choice of ionic surfactant. This result, they inferred, meant that the mechanism of removal was ion flotation. In a later paper, Zhang et al (1996 [a],[b]) used solvent CLA’s floated on CGA’s to extract a hydrophobic dye. They found kerosene, in conjunction with an anionic surfactant, to be a capable solvent in the removal of the dye. The mechanism of interaction they claim is coulombic forces.

The level of research into aphrons is increasing. Applications are being investigated in microbiological areas (Save and Pangarkar, 1994; Hashim et al, 1995, Lye et al, 1996), flotation of minerals (Cilliers and Bradshaw, 1996) and liquid-liquid extraction (Save et al, 1994).

1.3.5 Summary

The mechanisms involved in the formation and generation of stabilised air bubbles can be inferred from the literature available on particle-bubble attachment. The mechanisms are not completely understood, but are thought to be a combination of electrostatic, hydrophobic and hydrodynamic forces. For many minerals, flotation is not possible without the addition of surface-active agents which modify the hydrophobic nature of the mineral surface.

Gas aphrons are an interesting phenomenon in relation to stabilised air bubbles as they also show remarkable stability whilst submerged. The mechanism of formation is
unknown, but again, surface active agents are critical and the stability of the aphron is related to the surfactant concentration.

1.4 The Hydrodynamic Behaviour of Inverse Fluidised Beds

1.4.1 Conventional liquid-solid fluidised beds

A bed of solid particles packed into a vessel will retain its shape if a fluid is passed downwards through it. No movement of the particles occurs unless the initial orientation is unstable. The pressure drop across the bed is proportional to the flow rate. If a fluid passes up through the bed, the pressure drop will be the same as for downward fluid flow until the frictional drag on the particles becomes equal to their apparent weight (actual weight minus buoyancy) and the particles rearrange themselves so they offer less resistance to the fluid flow. At this point, the bed starts to expand. This process continues until the bed assumes the loosest form of packing. If the flow rate is increased further, the particles separate from one another and the bed is said to be fluidised. The fluidising medium can be either liquid or gas, but only liquid-solid systems will be considered here. The various stages of fluidisation, from fluid flow through the fixed bed to the point of incipient fluidisation to transport of particles, is shown in Fig. 1.19 along with the pressure gradient in the bed as a function of fluid velocity.
Chapter 1 - Literature Survey

The common use of fluidised beds is in highly exothermic reactions where close
temperature control is important. The fluidised bed behaves as a fluid of the same
density as that of the solids and fluid combined. Intimate mixing takes place and heat
transfer within the bed is very rapid, allowing uniform temperatures to be attained
quickly. The particles act as heat-transferring elements and bring the fluid at a certain
temperature into close contact with the particle surface. For a liquid-solid system, the
heat transfer coefficient may increase by a factor of 2 or 3 (Coulson et al, 1978).

Liquid-solid fluidised systems show regular expansion of the bed as the velocity
increases between the minimum fluidising velocity and the terminal falling velocity of
the particles. Richardson and Zaki (1954) showed that a fluidised bed system and a
sedimentation system are hydrodynamically similar. The particles in a fluidised bed
undergo no net movement and are maintained in suspension by the upward flow of the
liquid, whereas in sedimentation the particles move downwards and the upward liquid
flow is a result of liquid displacement by the settling particles. Richardson and Zaki
related the liquid velocity to the voidage of the bed for sedimentation and fluidised
systems by the following Eq., 1.19:-

$$\frac{U}{U_i} = e^n$$

where

- $U =$ observed fluidisation velocity (ms$^{-1}$)
- $U_i =$ superficial velocity at e=1 (ms$^{-1}$)
- $e =$ bed voidage
- $n =$ index of the system.

A typical relation between the fluid velocity, $U$, and the bed voidage, $e$, is shown in Fig.
1.20, for the fluidisation of stainless steel spheres in water.

At low velocities the voidage remains constant, corresponding to a fixed bed. During
fluidisation, there is a linear relationship between log($U$) and log($e$).
Chapter 1 - Literature Survey

1.4.2 Inverse fluidised beds and applications

While classical fluidised beds have been the subject of intensive research for many years, more recently an alternative form of fluidisation has become a point of interest. This fluidisation, known as "inverse fluidisation", differs from conventional fluidisation in that the solid particle density is less than the continuous fluid. This means that the bed of particles are fluidised by a down-flowing fluid. The stabilised bubble reactor is characterised by the buoyancy of the stable bubbles, which can be considered a thin shelled particle. Hence, a review of the literature available on inverse fluidisation is important. The initial research into the behaviour and applications of an inverse system were conducted independently by Nikolov et al (1981) and Fan et al (1982). Fan and colleagues were the first to explore the hydrodynamic behaviour of liquid-solid and gas-liquid-solid inverse fluidised beds, whereas Nikolov and colleagues were working on a more efficient form of biofilm reactor.

The only crucial development of an inverse fluidised bed is known as the inverse fluidised bed biofilm reactor (IFBBR), or as the inverse fluidisation airlift bioreactor (IFAB), of which many applications are being investigated (Nikolov et al, 1982; Garnier

Figure 1.20 - Relationship between fluid velocity (U) and bed voidage (e) for fluidisation of steel spheres in water (Source - Richardson and Zaki, 1954)

43
et al, 1990; Nikolov and Karamanev, 1990; Choi et al, 1995; Karamanev and Nikolov, 1996). A typical IFBBR system is shown in Fig. 1.21.

The reactor essentially consists of two concentric tubes, the inner tube containing sparged air and the outer containing "light" particles, i.e. a solid with a density less than the continuous liquid phase, such as expanded polystyrene. The sparged air results in an air-lift effect which entrains liquid which flows into the outer tube. The downward liquid flow in this section expands the bed of particles towards the bottom of the vessel, creating an inverse fluidised bed.

Figure 1.21 - An inverse fluidised bed biofilm reactor (Source - Karamanev and Nikolov, 1996)

Almost all micro-organisms will attach themselves to an inert solid surface, using exopolysaccharide bridges to attach themselves (Karamanev and Nikolov, 1996). This structure of micro-organisms and exopolysaccharides is known as a biofilm. This film has a larger density than that of the particle and so increases the overall density leading to enhanced bed expansion. At certain operating conditions, the bed will be fully expanded and begin to recirculate in the inner tube.

In a conventional biofilm reactor, there is a problem in that the thickness of the biofilm increases to an extent where diffusion of oxygen is restricted and so the micro-organisms at the base of the film begin to starve. This causes pieces of the biofilm to detach, leading to ineffective operation. In the inverse fluidised system, the recirculated particles experience shear forces created by the two-phase flow. These forces erode the
biofilm, maintaining a constant thickness at which no diffusional limitation is observed. The particles exit the inner tube and the process is repeated.

Recently, Karamanev and Nikolov (1996) reported that this research has progressed from laboratory scale, pilot-plant scale (Choi et al, 1995), through to a full-scale waste-water treatment plant. At a Bulgarian waste-water treatment plant, eight vessels were connected in series with a total working volume of 64 m$^3$. The bioreactor was dosed with activated sludge for a two-week period during which a stable biofilm was formed. The waste-water to be treated was tested with various residence times. At a residence time of 1.8 hours, the Biological Oxygen Demand (BOD) removal rate improved significantly and only three sections were required to completely treat the water. The authors claim that this result, along with the high volume efficiency and long term biofilm efficiency, means that there is an application in the treatment of low concentration pollutants, such as phenol, nitrobenzene and pentachlorophenol.

The design of the IFBBR relied on a knowledge of the hydrodynamics of the inverse fluidised bed. The most important research into this area was undertaken by the same authors and is reviewed next.

1.4.3 Hydrodynamics of inverse fluidised beds

The literature available compares the hydrodynamic behaviour of an inverse fluidised bed to a conventional one. Classic fluidising theory is attributed to Richardson and Zaki (1954) and most authors have attempted to relate inverse fluidisation to this work. Fan et al (1982) produced the first significant attempt to model bed hydrodynamics for an inverse bed, which consisted of polyethylene and polypropylene balls of various sizes. Fan states that correlations of fluidised beds are divided into three particular types. Type 1 models are those based on Eq. 1.19, i.e. Richardson-Zaki. Type 2 models develop the correlation of bed expansion by modifying the drag coefficient for a single particle. Type 3 models relate the expanded bed height to the systems operating parameters, e.g. particle diameter and liquid velocity. In terms of popularity, type 1 models are favoured the most.
Fan developed the type 1 and 2 models for bed expansion in the inverse fluidised bed. For the Richardson-Zaki model, he found that this model only predicted the bed expansion for the range $\text{Re}_i < 500$ (Re$_i$ is the Reynolds number of a particle falling/rising at the maximum velocity). Fan developed an empirical correlation for the index $n$ (see Eq. 1.19) for the ranges $350 < \text{Re}_i < 1250$ and $\text{Re}_i > 1250$, the coefficient of variation being 8%.

More recently, Karamanev and colleagues (Karamanev and Nikolov, 1992 [a],[b]; Karamanev, 1994; Karamanev et al, 1996) examined the behaviour of inverse beds with reference to the Richardson-Zaki correlation. For free settling particles, the drag coefficient, $C_D$, is well known and obeys the standard drag curve for various spherical particles and fluids, except at very high Reynolds numbers and certain density ratios, $\rho_p/\rho_L$. At these extreme conditions, the particles show a secondary motion, i.e. a spiral trajectory, which results in a higher drag coefficient.

Karamanev identified that for inverse fluidisation, it has always been presumed that particles in the bed obey the standard drag curve. However, observation of light particles rising through a denser medium showed that certain particles rose with a spiral motion, hence the drag coefficient must be different. Karamanev and Nikolov (1992 [a]) investigated the drag coefficient for spheres whose density was lighter than water. Their results are shown in Fig. 1.22.

![Figure 1.22 - Comparison of the standard drag curve with the curve for 'light' spheres (Source - Karamanev and Nikolov, 1992[a])](image-url)
For $\text{Re}_t < 130$ and/or $\rho_p > 900 \text{ kg m}^{-3}$, the light particles obey the standard drag curve. However, for $130 < \text{Re}_t < 9 \times 10^4$ and $\rho_p < 300 \text{ kg m}^{-3}$, the particles deviate from this curve. Karamanev predicted that the new drag coefficient value was constant at 0.95 (compared with $C_D = 0.5$, for the standard drag curve). To test the validity of this result, the new value of $C_D$ was incorporated into the Richardson and Zaki equation ($C_D$ is used indirectly to calculate the value of $U_i$ - see Chapter 3).

The bed voidage was calculated from the bed expansion data at various liquid velocities. Karamanev compared this data with the correlations of Richardson-Zaki, Fan et al (1982), and his predictions using the modified drag coefficient. The index $n$, was found to be in good agreement with Richardson-Zaki as is evident in Fig. 1.23, where the calculated curve is parallel to the experimental data. The exponent calculated using Fan’s correlation was found to differ by up to 27%.

![Figure 1.23 - Prediction of bed expansion data using Richardson-Zaki and Karamanev’s modified version (Source - Karamanev and Nikolov, 1996)](image)

However, the predicted value of $U_i$, obtained from the intercept at $e=1$, deviated by up to 54%. Karamanev attributed this variation to the break down of the standard drag curve at densities below 300 $\text{kg m}^{-3}$. By incorporating the new value of $C_D$ at $\text{Re}_t > 130$, the predicted curves were in good agreement with the experimental data (see Fig. 1.23).

Since Karamanev’s work on inverse fluidised bed hydrodynamics, the only other paper to attempt to model the behaviour is by Ulaganathan and Krishnaiah (1996). They have chosen to ignore the current theory and relate the bed expansion behaviour to the
measured bed pressure drop and friction factor. They divided the bed expansion into three regimes; fixed-bed, semi-fluidised and fluidised. They empirically calculated the minimum fluidisation velocities, \( U_{mf} \), for various beds and then used the correlations to predict the pressure drop variation with velocity. Their results showed a varying degree of success depending on the experimental conditions. The authors credit this variation to channelling in the bed which would reduce the pressure drop.

1.4.4 Summary

Inverse fluidised beds differ from conventional beds in that the solid particles which comprise the bed are less dense than the fluidising liquid medium. The hydrodynamic characteristics of such beds means they have potential applications in biofilm reactors, where the thickness of the film is critical to operation. Karamanev and colleagues have shown successful application of this system in a waste-water treatment plant.

The design of the reactor is based on the hydrodynamic behaviour of the inverse fluidised bed. Karamanev based the calculations upon the correlations of Richardson and Zaki for conventional fluidised beds. The bed expansion behaviour of these beds cannot be satisfactorily predicted by Richardson and Zaki as the inertial forces operating on a rising sphere are different than those for a free settling sphere. However, Karamanev found that the drag coefficient for a rising sphere differed considerably. Using this value, the Richardson and Zaki model agreed well with the experimental data.

1.5 Activated carbon - Porosity Development and Liquid-phase Adsorption Properties

1.5.1 Introduction to activated carbon and adsorption

Activated carbon has been used for many centuries as a purifier of gases and liquids (Hassler [a], 1967). As long ago as 1550 B.C., the Egyptians used carbon for medicinal purposes. The ability of a solid to remove gaseous or liquid substances from the bulk
surroundings relies on the ability to retain them at the interface between the two phases (i.e. gas-solid or liquid-solid). The gas or liquid substances, known as adsorbates, are retained by physical forces associated with the internal surface of the porous solid. The extent of accumulation of the adsorbate on the solid, known as the adsorbent, depends on the internal surface area available (Snoeyink, 1990). Good adsorbents will have a large internal surface area, hence the wide use of activated carbon as an adsorbent. The discovery of the phenomenon of adsorption is generally attributed to Scheele who, in 1773, described experiments on gases exposed to carbon (Deitz, 1944). The earliest known documentation in liquid adsorption dates back to 1785 when Lowitz observed that charcoal would decolourise many liquids. By 1808, wood char was being used to clarify sugar beet in France.

The success of carbon was variable depending on the application and extent of purification required. During the nineteenth century, a number of attempts were made at developing decolourising carbons from materials which would have greater adsorption powers. Amongst the many attempts, Lee, in 1863, prepared a carbon by using superheated steam and air on peat.

Following the success of activated carbon in gas masks during World War I, the enthusiasm generated for the substance permeated through to liquid-phase applications. Initially, consideration was given to improving decolourising solutions. This led to carbon being used in removing unwanted flavours and odours in the food industry. This ability to purify led inevitably to the use of activated carbon in water supplies. The industries first credited with using activated carbon for water supplies were meat packing companies in Chicago, in 1928. Activated carbon is now widely used in water treatment plants all over the world to adsorb those organic molecules that affect taste, odour, colour and toxicity (Snoeyink, 1990).

Activated carbon is a porous material; a by-product of pyrolysis and activation of various organic substances of mainly biological origin. Activated carbon can be manufactured from numerous source materials (see Table 1.1).
Recent literature is still concerned with developing an understanding of the properties of activated carbons made from more traditional precursor materials such as peat (Dubinin et al, 1993), coal (Dubinin, 1983; Dubinin et al, 1993; Kuhl et al, 1992; Alvarez et al, 1994) and fruit stones (Gergova, et al, 1992 and 1994). Third world economics means that there is also parallel research into alternative materials, such as straw and used tyres (Merchant and Petrich, 1992 and 1993; Streat et al, 1995; Teng et al, 1995).

Table 1.1: Materials that have been studied for the production of activated carbon. (Source - Hassler /bf/, 1967)

<table>
<thead>
<tr>
<th>Bagasse</th>
<th>Kelp and Seaweed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beet-sugar sludges</td>
<td>Lampblack</td>
</tr>
<tr>
<td>Blood</td>
<td>Leather waste</td>
</tr>
<tr>
<td>Bones</td>
<td>Lignite</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>Lignite</td>
</tr>
<tr>
<td>Cereals</td>
<td>Melasses</td>
</tr>
<tr>
<td>Coal</td>
<td>Nut shells</td>
</tr>
<tr>
<td>Coconut shells</td>
<td>Oil shale</td>
</tr>
<tr>
<td>Coffee beans</td>
<td>Peat</td>
</tr>
<tr>
<td>Corn cobs and corn stalks</td>
<td>Petroleum acid sludge</td>
</tr>
<tr>
<td>Cottonseed hulls</td>
<td>Petroleum coke</td>
</tr>
<tr>
<td>Distillery waste</td>
<td>Potassium ferrocyanide residue</td>
</tr>
<tr>
<td>Fish</td>
<td>Pulp-mill waste</td>
</tr>
<tr>
<td>Fluor dust</td>
<td>Rice hulls</td>
</tr>
<tr>
<td>Fruit pits</td>
<td>Rubber waste</td>
</tr>
<tr>
<td>Graphite</td>
<td>Sawdust</td>
</tr>
<tr>
<td>Pyrolysis of the starting material with the exclusion of air (or other gaseous oxidisers) or chemical agents, produces an inactive material with a specific surface area of only several m²/g (Smisek, 1967). Only by activation of this material does it develop the highly porous structure which gives activated carbon its most important property - a large adsorptive capacity.</td>
<td></td>
</tr>
</tbody>
</table>

In this section of the literature review, the development of the internal surface area of activated carbon is examined because of its importance in adsorption processes plus a brief summary of the important aspects of adsorption theory and a review of pertinent literature investigating the mechanisms of adsorption of simple molecules, particularly phenols, which have been used in this study.
1.5.2 The Structure of Activated Carbon

Pure carbon is available in two crystalline forms - graphite and diamond. The basic unit of a diamond crystal consists of a carbon atom bonded covalently to four adjacent carbon atoms, to form a regular tetrahedron around the central atom. In graphite crystals, each carbon is covalently bonded to three other carbon atoms, to form planes of regular hexagons, similar to rings of aromatic organic compounds (see Fig. 1.24).

This arrangement is made possible by $sp^2$ hybridisation of the 2s and 2p electron orbitals, which form three equivalent hybrid orbitals (Fitzer and Huttner, 1981). Each plane of carbon is stacked one above the other. Two or more of these planes contribute to a basic crystal of submicroscopic dimensions, known as a crystallite. The distance between each plane is 3.35 Å (Cerny, 1967; Fitzer and Huttner, 1981). Any carbons which consist of an elementary crystallite structure similar to that of graphite are known as amorphous carbons (Hassler, 1967). Coke, chars and activated carbons are all termed amorphous carbons.

However, the crystallites for activated carbon do have structural differences to those for graphite. Based upon the interpretation of X-ray diffraction patterns by Riley, Warren and Biscoe, and others, it is generally agreed that while activated carbon consists of carbon atoms arranged in a hexagonal lattice, the parallel planes are not perfectly oriented with respect to a common perpendicular lattice (Hassler, 1967). The displacement of one layer with respect to another is completely random. This random structure is called turbostratic (Cerny, 1967). As well as differences in stacking, activated carbon crystallites also vary in size. In graphite, the planes are stacked closer
together, while for activated carbon the random orientation means this is not possible. The crystallite dimensions are dependent on temperature, the width varying from 20 to 23 Å up to 700 °C, while the height does not vary much until after 1300 °C, i.e. the number of graphitic layers changes insignificantly.

A considerable amount of non-organised carbon exists between the layers of the hexagonal carbon plates, i.e. atoms not bound as part of the structure. The activation process removes this non-organised carbon to form voids throughout the material. The ratio of the volume of voids to the total volume of the material is called the porosity, and the voids are known as pores. The walls of the pores provide the large internal surface area that gives activated carbon its high adsorption capacity. To complicate the study of activated carbon, pores come in various shapes and sizes. According to the International Union of Pure and Applied Chemistry (I.U.P.A.C.), pores are classified as macropores, mesopores and micropores, which correspond to various sizes of pore widths, $w$, as shown in Table 1.2.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Size Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macropore</td>
<td>$w &gt; 50$ nm</td>
</tr>
<tr>
<td>Mesopore</td>
<td>$2$ nm &lt; $w &lt; 50$ nm</td>
</tr>
<tr>
<td>Micropore</td>
<td>$w &lt; 2$ nm</td>
</tr>
<tr>
<td>Supermicropore</td>
<td>$0.7$ nm &lt; $w &lt; 2$ nm</td>
</tr>
<tr>
<td>Ultramicropore</td>
<td>$w &lt; 0.7$ nm</td>
</tr>
</tbody>
</table>

While classifying the structures and adsorption properties of various carbons, Dubinin used a slightly different size classification. Instead of dividing micropores into supramicropores and ultramicropores, he defined supermicropores as pores whose width was 1.3 - 1.4 nm < $w < 3$ -3.2 nm, compared to micropores of the size, $w < 1.3$ - 1.4 nm, i.e. they are larger than micropores (Dubinin, 1983). For clarity, the I.U.P.A.C. classifications will be adopted here.

The adsorption properties of activated carbon also depend on the shape of the pores as this affects the mechanism and extent of adsorption. The shape of the pores is based on the structure of the precursor material. Fig. 1.25 shows different possible pore shapes (Kaneko, 1994). In general, activated carbons have two-dimensional slit-shaped pores,
but cylindrical and ink bottle pores have been found in activated carbons made from apricot stones (Gergova et al, 1992).

![Figure 1.25 - Pore shapes (Source - Kaneko, 1994)](image)

The three groups of pores contribute to the specific surface area (and volume of voids) to different extents and all have different roles to play in adsorption. Micropores, having the smallest pore width, comprise the largest proportion of the surface area - in some cases this can be as much as 95% of the total, or an equivalent of more than 1000 m²/g (Dubinin, 1983; Gergova et al, 1992) and approximately 92% of the total pore volume, or around 0.5 ml/g (Gergova et al, 1994; Alvarez et al, 1994). It is obvious from this that micropores are the most important feature amongst the different characteristics of activated carbon. Mesopores, also known as transitional pores, serve to pass the sorbate molecules from the macropores to the micropores. They are not predominantly used for adsorption, unless adsorbing vapours at high pressures, as the pore walls only contribute 5% to the total surface area. Macropores account for only 0.5 to 2 m²/g, an almost negligible amount. The significance of macropores is that they allow sorbate molecules to pass rapidly from the external surface to the smaller pores situated deep within the particle.

For a particle of activated carbon to be used efficiently, the size of the sorbate molecule must be small enough to penetrate into all the smallest pores. The shape of the pores is therefore very important. The volume of a particular pore may be large enough to adsorb
a molecule or two, but access may be restricted by the pore opening. This is specifically
the case with slit-shaped and ink bottle pores. This means that activated carbon can have
molecular-sieve properties, i.e. it can adsorb molecules of a certain size. This can be
controlled to some extent by activating the carbon under specific conditions for specific
lengths of time.

1.5.3 Mechanisms of Activation and Porosity Development

The production of activated carbon is usually a two-step process; pyrolysis of the raw
material (see Table 1.1) to produce the carbonised material which is then activated by
various methods at high temperatures. It is widely believed (Smisek, 1967; Hassler, 1967;
Kuhl et al., 1992) that during pyrolysis, the volatile non-carbon elements, hydrogen, oxygen, etc., are removed and the freed carbon atoms regroup into organised
crystallites. The irregular arrangement of the crystallites means that there are many free
interstices between them. As stated earlier, the surface area available for adsorption is
very small and this is as a result of the thermal decomposition of tarry substances
blocking such interstices. Simple removal of this disorganised carbon is possible by
heating the carbon in an inert gas or extracting it with a suitable solvent. However, to
develop the microporosity necessary for activated carbons, the actual carbonised material
must be activated. It has been shown (Alvarez et al., 1994) that pre-oxidation at 200 °C
of low volatile bituminous coal before pyrolysis at 600-850 °C produces chars that show
a significant level of microporosity which makes them excellent preursors for activated
carbon production.

Activated carbon can be prepared by two methods :-
I. *Chemical activation* - usually limited to woody precursors, the raw material is
carbonised in the presence of chemical activating agents which restrict the formation
of void-clogging tars.
II. *Physical activation* - the inactive carbonised material is reacted with various gases to
develop the pore structure.
Chapter 1 - Literature Survey

Chemical activation will not be considered in any great detail here as the activated carbon used in this research is prepared by physical activation using steam. Briefly, the activation agent prevents the formation of tar so that the yield of carbon is increased. Compared with physical activation, the process requires only one-step and in some cases the temperature of activation is lower, i.e. the temperature range is generally 400 - 800°C. Widely used activation agents include potassium sulphide, potassium thiocyanate, sulphuric acid, phosphoric acid and zinc chloride.

Physical activation uses oxidising gases at 700 - 1100°C to develop the porosity. The most common gases used for physical activation are steam, carbon dioxide and oxygen (air). The action of these gases is to first remove the disorganised carbon, exposing the surfaces of the crystallites to activation. The gases do not randomly erode layers of carbon. Structural defects and strain energy differences within the carbon atom networks mean that not all the carbon atoms have the same reactivity to the oxidising gas molecule. Instead, they react selectively with the carbon to increase the number of micropores in each particle. As the process continues, adjacent micropore walls are burnt out, causing formation of larger pores - the meso- and macropores. As the volume of mesopores increases, there is a simultaneous decrease in the volume of micropores. To measure the degree of activation, the term "selective burn-off" is used. This is the percentage weight decrease of material with respect to the weight of the original carbonised material. The burn-off value can be related to the development of the porous system within a particle. This should not be confused with "external" burn off which is simply the removal of carbon without any increase in porosity. Most authors quote a burn-off range of 25-50% when producing an activated carbon with an extensive microporous structure (Kuhl et al, 1992 ; Ahmadpour and Do, 1995), and between 50 and 75% for a meso- and macroporous structure (Gergova et al, 1992 and 1994).

In order to develop the porous structure, carbons must be removed from the lattice by gasification. This activation process is usually performed with oxidising gases such as steam, CO2 and O2. Due to the variety of reactivity of the gases, each gas develops the pore structure at different temperatures. For example, steam activation is quoted in the range 750 - 1000°C, while oxygen activation is not performed above 600°C because of
its aggressive action. At higher temperatures, oxygen would erode the particle surface as well as the internal pores. The mechanisms of activation are not fully understood and will not be covered here but several authors have made estimates of the mechanism, based on the reaction products evolved (Blackwood, 1954; Smith, 1959; Culver and Watts, 1960; Ergun and Mentser, 1965; Hassler [b], 1967; Smisek, 1967; Byrne and Marsh, 1995).

Perusing the recent literature on the development of the internal surface area during activation, it is easy to become engulfed in the quagmire of reaction conditions. It is clear that there is no clear “optimum method” for developing an ideal active carbon. The porosity of a particle is a function of the nature of the precursor material, the activating agent, the temperature and retention time, the burn-off percentage and even the nature of the gases evolved during activation. For example, it would be unfair to compare the ideal conditions for making activated carbons using olive stones (Gonzalez et al, 1994) with those made from anthracite (Kovacik et al, 1995). Both substances produce good microporous carbons using steam and produce the best results over similar burn-off ranges (50 - 65 %), but the reactivities are much different and so while olive stones produce the better carbons at 650°C for 2 hours, anthracite works best at 900°C for 1 hour. This evidence, amongst many others, points to the fact that the nature of the raw material defines the conditions required for activation.

Gergova and co-workers (Gergova et al, 1994) compared activated carbons produced from different agricultural by-products. By analysing the elemental components of the raw materials, such as carbon, sulphur, oxygen, nitrogen and hydrogen, they showed that the porosity achieved in activated carbons is not only dependant upon the relative amounts of these elements but also upon the macromolecular structure. This was highlighted using the highly microporous activated carbons produced from apricot stones. The raw stones had levels of carbon and oxygen comparable to the other starting materials but the activated stones had a higher carbon content and lower oxygen content, suggesting that the activation process is sensitive to the differences in the starting materials. Being woody materials, the levels of cellulose and lignin were compared in the raw materials. Those materials which produced the better microporous carbons
showed higher levels of cellulose while the more mesoporous carbons showed higher levels of lignin.

Other authors have compared different starting materials and the carbons produced by them. Kuhl and co-authors (Kuhl et al., 1992) compared the activated carbons produced by coal coke, pitch coke and a low-temperature oxidised coke. As expected, they produced differing levels of surface area, the oxidised coke providing the best results. Kovacik (Kovacik et al., 1995) compared carbons produced from anthracite and semi-anthracite coals. The semi-anthracite coals produced carbons with a larger proportion of mesopores. This was attributed to the larger proportion of volatiles present in the raw coal, hence a greater reactivity and burning of the pore walls. The message prevalent in the literature is that in order to develop the desired activated carbon, an understanding of the structure and chemical composition of the precursor is required. The activating conditions suitable for one material may not, therefore, be good enough for another.

Rodriguez-Reinoso and co-workers compared carbons developed by different gases, i.e. steam and carbon dioxide, using olive stones as the starting material (Rodriguez-Reinoso et al., 1995; Molina-Sabio et al., 1996). Steam is more reactive as an activating agent, requiring lower temperatures and is smaller in molecular size, leading to faster diffusion rates and greater penetration into the particle. In theory, therefore, steam-activated carbons should develop a more microporous structure. The authors realised that comparing carbons made from activating agents of different reactivities is inconsistent. In order to compare data, they reduced the reactivity of steam by making carbons at a lower temperature and diluting the steam flow with an inert gas.

They found that, for similar gasification rates, carbons produced by CO$_2$ have a larger micropore volume than steam based carbons. This behaviour was attributed to the different attacking styles of the gases - the steam molecules were perceived to widen the existing micropores (resulting in a greater proportion of mesopores), while the carbon dioxide reacted more selectively producing new openings, followed by widening of the pores. The reason for the difference in mechanisms was associated with the shape of the molecules, the CO$_2$ being linear while the H$_2$O is angular. Lowering the temperature
meant that the effect of the inhibiting products increased, particularly to the interior of the particle which meant reaction at the external surface was favoured, destroying the porosity.

The authors also related the oxygen surface groups present in the carbons to the activation method (Molina-Sabio et al, 1996). By treating the samples with an inert gas at different temperatures, the oxygen groups are evolved as CO and CO$_2$. They found that steam activated carbons evolved lower amounts of CO, indicating some connection to the microporous development. They also saw that carbon dioxide activated carbons evolved these gases at higher temperatures, indicating the surface groups are more thermally stable.

The results of these papers contradict popular belief and the results of other authors and yet the reasons offered seem plausible. Kuhl and co-workers compared the effects of steam and carbon dioxide on an oxidised char, a pitch coke and coal coke (Kuhl et al, 1992). They found that the oxidised char produced a larger surface area, agreeing with the results of Rodriguez-Reinoso, but the two cokes produced better results by steam activation. The authors offer no explanation, but comparing these results with those of Rodriguez-Reinoso, the striking similarity is the better performance of CO$_2$ activation in the presence of oxygen surface groups. The authors do offer the explanation that the surface groups might be blocking the entrance to pores reducing the pore width to microporous dimensions, but it is clear that surface chemistry does have some part to play, and it is likely that future work will follow this path.

The role of carbon dioxide in the development of porosity has also varied from author to author. Rodriguez-Reinoso and colleagues stated that CO$_2$ produced new openings and then widened these pores. A typical diagram showing pore volume with burn-off would depict a large micropore surface area or volume, followed by an increase in meso- and macropore development. This development was also seen by Ahmadpour and Do (1995). Fig. 1.26 shows the trend in micropore surface area development with activation, passing through a maximum at about 27% burn-off and then decreasing with further activation.
According to Ahmadpour and Do, the trend in micropore development is due to two effects. The first effect is the pore volume increase which occurs by enlargement (causing an increase in the pore width) and drilling of existing holes. This agrees with Rodriguez-Reinoso, but no mention is made here of the development of new micropores as described by the other authors. The second effect, the decrease in micropore surface area, is attributed to a shrinkage in size of the carbon particles which causes a narrowing of the pore entrances. This idea has not been postulated by other authors as they have attributed the decrease in micropore numbers to the widening of the walls.

Figure 1.26 - Evolution of surface areas by CO$_2$ activation at 800 °C (Source - Ahmadpour and Do, 1995)

Another interesting parameter is the development of porosity with increasing particle depth. Buczek (1993) used steam to make carbons from various different precursors, including peat. He found that the nearer the centre of the particle, there was an overall decrease in micropore volume, but the volume accessible to the larger micropores remained the same. The outer layers which had achieved a significant level of burn-off, produced a better quality of porous structure. The inner layers had a significantly lower level of burn-off caused by mass transfer resistance, resulting in poor pore development.
This work highlights the importance of particle size and accessibility of the oxidising molecules to the interior in the manufacture of good microporous carbons.

Most authors use temperature and activation time as parameters. In general, it has been shown that the surface area of activated carbons increases with temperature and the best activation times are between 1 and 2 hours, depending on the raw precursor (Gergova et al., 1992 and 1994; Kuhl et al., 1992; Gonzalez et al., 1994; Kovacik et al., 1995). However, it should be noted that the surface area does not increase continuously with temperature. As the temperature increases, the pore walls are burnt out due to the high reactivity of the gases, and predominantly meso- and macroporous carbons are made.

1.5.4 Surface chemistry of activated carbon

The phenomenon of adsorption is generally concerned with retaining molecules of a substance at an interface between two surfaces. There are five types of interface possible at which adsorption can occur, however, for the purposes of this study, only adsorption at a liquid-solid interface is considered. The importance of surface area in adsorption has already been discussed. An extensive microporous network will provide an activated carbon particle with a large surface area available for adsorption, depending upon the size and orientation of the adsorbed molecules. In his review of adsorption using activated carbon, Hassler (1967[c]) showed how the affinity of activated carbon for Aniline Blue increased as the extent of activation, and hence surface area, increased. However, it is not enough to rely on a knowledge of the carbon internal surface area to predict how a particular molecule will adsorb. Adsorption occurs by two possible methods. One is termed physical adsorption and is regarded as a consequence of attractive forces operating between the solute molecules and the surface. These forces, typically van der Waals or hydrogen bonds, are weak and reversible. The other method of adsorption is called chemical adsorption or chemisorption. In this mechanism, the adsorbed molecule will actually form a bond with the solid surface. Evidence of this is seen with the adsorption of oxygen at 0°C. If an attempt is made to liberate the oxygen by elevating the temperature, the oxygen is liberated in the form of CO or CO\textsubscript{2}, indicating a bond must have formed. If in a particular system, it is recognised that
attractive or chemical forces are contributing to adsorption, then one must consider the surface chemistry of activated carbon.

During activation of the carbon precursor, the carbon atoms become bonded with atoms of oxygen and hydrogen, from the oxidising gases, to form surface oxygen complexes (Cookson Jr., 1975; Boehm, 1994). These surface oxides are classified as acidic or basic, depending on their pH in aqueous solutions. A large oxygen content at the carbon surface indicates strong acidity values. Acidic surface oxides are formed when the carbon is exposed to oxygen at temperatures between 200 - 500°C. The acidic oxides show behaviour similar to that of functional groups at the end of hydrocarbon chains on organic chemicals. Typical surface groups are shown in Fig. 1.27.

![Some acidic surface groups found on activated carbon](image)

The surface oxides shown in Fig. 1.27 are all weakly acidic and hence show cation exchange properties. An example of how acidic properties can affect adsorption was demonstrated recently by Polyakov and colleagues (Dubinin et al, 1993). Despite the hydrophobic nature of activated carbon, there was a significant proportion of the micropore surface coated with adsorbed water molecules. Comparing these carbons with those where the oxygen complexes were removed by heat treatment, a much lower surface area is available for adsorption. The authors attributed this behaviour to the surface oxide groups acting as primary adsorption sites for water molecules. However, this evidence is only seen for adsorption of gases at a relative humidity of 60% or above. The effect of surface oxygen complexes on liquid-phase adsorption of simple molecules is discussed in the next section.

Basic surface oxides exhibit anion exchange properties and are formed by removing all the surface oxides by heating the carbon to approximately 1000°C in a vacuum or inert
gas and then contacting the carbon with oxygen after cooling to low temperatures (below 200°C). In the 1950’s, Garten and Weiss (1957) ascribed the basic properties to chromene-like structures, but it is now believed that \( \gamma \)-pyrone-like structures are more plausible (Voll and Boehm, 1971; Leon Y Leon et al, 1992). The basic nature of these structures is due to the aromatic \( \pi \) electrons (Boehm, 1994). This allows hydrochloric acid to be adsorbed at the carbon basal planes, causing protonation of the carbon, as shown in Fig. 1.28.

![Figure 1.28 - Protonation of the pyrone-like structure](image)

A typical activated carbon will contain both acidic and basic sites, but the activation process favours a larger proportion of acidic sites. Evidence for the dual nature of activated carbon was produced by Kazmierczak and colleagues (1991). They took a commercial granulated activated carbon and modified the surface groups as required. One carbon was heated to 975°C in hydrogen while the others were first oxidised in nitric acid and then heated in hydrogen at various temperatures in the range 175 - 425°C. The carbon exposed to the high temperature showed a large number of basic groups present, while the proportion of acidic groups was small by comparison. The other carbons showed a large proportion of acidic groups, but with an increase in the temperature, the proportion of basic sites increased to 20% of the total number of sites at 425°C.

### 1.5.5 Adsorption of phenols on activated carbon

A potential application of the stabilised bubble process is in water treatment of simple pollutants. As the bubbles are coated by a layer of activated carbon, which has extensive
use in the removal of organics from waste-water, it seems logical to pursue this avenue of investigation. The pollutants chosen in this study are simple organic aromatics - phenol and para-chlorophenol. The phenolics have been well investigated in the literature and a review provides an insight into the expected behaviour and adsorption mechanisms using activated carbon.

In their review of the classification of adsorption isotherms, Giles et al (1960) identified that the adsorption mechanism of phenol depended upon the substrate used. If phenol is adsorbed onto a polar substrate, e.g. alumina, the interaction with the molecules is via the polar O-H bond. Hence the phenol is adsorbed end on with the molecule oriented perpendicularly to the sorbate surface. The adsorption isotherm for such a system is termed an "s-curve" (see Fig. 1.29).

![The S2 isotherm](equil. conc. of solution, C (mg/l)
equil. conc. of solute on substrate, q (mg/g))

![The L2 (Langmuirian) isotherm](equil. conc. of solution, C (mg/l)
equil. conc. of solute on substrate, q (mg/g))

**Figure 1.29 - Isotherm classification according to Giles et al (1960)**

The initial part of an s-curve indicates that the more solute there is already adsorbed, the easier it is for additional adsorption to occur. This implies a side-by-side association between adsorbed molecules, helping to hold them to the surface.

For adsorption of phenol onto carbon, the adsorption isotherm is classified by Giles as a Langmuirian or L2 isotherm (Fig. 1.29). In this situation, and in the latter part of the S-curve, the rate of adsorption decreases with sorbate loading. Giles and co-workers (1960) suggest that the attraction between the phenol molecule and non-polar surface is via the benzene ring, i.e. the molecule is oriented parallel to the surface, covering a larger area and more adsorption sites.
From the research of Garten and Weiss (1957) and Boehm in the 50’s and 60’s, the presence of surface oxides on the surface of activated carbon was well established. Although many authors had investigated the adsorption properties of phenols on carbon, there was little interpretation of the results in terms of the oxygen complexes. Coughlin and Ezra (1968) investigated the effect of oxidation on the adsorption of low concentrations of phenol and nitrobenzene using activated carbon. They prepared various samples of carbon - one which was unaltered, another which had been oxidised and another which had been reduced following oxidation. For each pollutant, the effect of the surface oxides was to decrease the adsorption capacity of the carbon. Reduction of the oxidised carbon improved the capacity but not to the original extent. Coughlin and Ezra speculated that the acidic surface groups must interact with the weakly acidic nature of phenol, reducing the adsorption capacity. The authors cite surface carboxylic groups as those responsible. However, some adsorption is possible and Coughlin attributed this to surface carbonyl groups at the edge of the basal plane. Initially, it was thought that hydrogen bonding of the phenol was the cause of the adsorption mechanism. However, this does not explain the adsorption of nitrobenzene which does not have the same substituent group. Instead, they theorised that the surface groups served to withdraw the electron density from the π-system of the basal planes, allowing interaction between the carbon and the phenol nucleus.

It is also worth noting that Coughlin and Ezra (1968) reported that other authors had seen no effect of oxidation on phenol adsorption. This was because the other researchers used higher concentrations of phenol, causing layer upon layer of phenol molecules to be adsorbed, presumably by interaction of the polar O-H bonds. Coughlin and Ezra proved this by performing adsorption tests over a wide range. The isotherms showed several plateau’s, corresponding to each layer of phenol adsorption.

The reduction in adsorption capacity due to surface oxides was also reported by Mattson et al (1969). As well as for phenol, the reduction in adsorption was also seen with m- and p-nitrophenol, although to a lesser extent. Mattson and colleagues did not accept the mechanism offered by Coughlin and Ezra, as they thought the electron withdrawal capability of the carbonyl group would not extend over the large distances of the basal
plane. The improved adsorption of the nitrophenols over phenol lead the authors to believe that the NO₂ group is a stronger contributor to adsorptive interaction than the OH group. If the nitro group was responsible for the adsorption mechanism, then the level of phenol adsorption would not be so high. Congruently, infra-red internal reflection spectroscopy of the carbon surface showed some hydrogen bonding with the surface groups, but this interaction is small and not the primary cause of adsorption. These findings led Mattson and co-workers to conclude that the adsorption interaction must be between the π-systems of the aromatic ring and the basal plane. The phenol and carbon form a donor-acceptor complex, i.e. the carbonyl oxygens act as the electron donor to the aromatic ring acting as the acceptor. The interaction of the respective π-electrons means that phenol molecules would be adsorbed parallel to the surface, as in the L₂ isotherm. During the adsorption of nitrophenol, the electron withdrawing NO₂ group reduces the electron density of the π-system and so forms stronger donor-acceptor complexes in comparison with phenol. Mattson also suggests that the reason that surface carboxyl groups do not adsorb phenol so well is that the dipole moment is not as strong as that in a carbonyl group and so cannot form strong donor-acceptor complexes.

This effect of surface oxygen groups has also been reported by other authors including Drago et al (1964), Cookson Jr. (1975) and Koganovskii et al (1987). However, more recently, several authors have found that surface oxygen groups can actually improve the adsorption of phenols (Vidic et al, 1993; Abuzald and Nakhla, 1994; de Jonge et al., 1996). These authors acknowledge the findings of Coughlin and Ezra, but they do not offer any explanations as to the discrepancy. The accepted theory, proposed by Vidic et al (1993) is that molecular oxygen promotes the formation of adsorbate polymers on the surface of the carbon. The surface oxygen reacts with the phenolic compound to form a phenoxy radical which can form dimers or trimers with other phenol molecules. Activated carbons containing large amounts of surface oxygen were referred to as oxic and those with little or no oxygen as anoxic. Vidic showed that the adsorption capacity of some phenolic compounds, such as various isomers of methylphenol, can be improved by up to 200%. However, nitrophenols showed no dependence on the oxic state of the carbon, nor a reduction in adsorption capacity. This behaviour was credited to the effect of the substituent groups on the O-H bond.
Abuzald and Nakhla (1994) continued this work by preparing carbons that had varying degrees of surface oxygen. As expected, they discovered that the adsorption capacity of phenol and o-methylphenol improved with increasing levels of oxygen. The adsorption isotherms were based on the Freundlich model (Eq. 1.20), which is an empirical formula that covers a wide concentration range of single-solute adsorption systems:

$$q = k c^{1/n}$$  \hspace{1cm} 1.20

where $q =$ amount of pollutant adsorbed per gram of carbon (mg g$^{-1}$)  
$c =$ equilibrium concentration of the solution (mg l$^{-1}$)  
$k =$ a constant measuring the extent of adsorption (mg g$^{-1}$)(l mg$^{-1}$)$^{1/n}$  
$n =$ a constant measuring the strength of the adsorption intensity

With an increase in the adsorption capacity, the value of $k$ increased as expected. However, with an increase in the oxic conditions, the value of $1/n$ decreased. This indicated to the authors that the mechanism of adsorption must be governed by surface polymerisation reactions, rather than physical adsorption.

Vidic et al (1993) and Abuzald and Nakhla (1994) reported how increased levels of surface oxygen also enhanced the extent of irreversible adsorption; a situation that is avoided in waste-treatment plants as activated carbon is expensive and must be regenerated to make the process economically viable. de Jonge et al (1996) investigated the extent of irreversible adsorption on two types of activated carbon - Norit SA4 (a thermally activated peat-based carbon) and CA1 (a chemically activated wood-based carbon). The CA1 carbon had a larger internal surface area than the SA4, however the adsorption capacity for o-methylphenol and m-chlorobenzoic acid was larger for SA4 than for CA1. Also, a substantial amount of irreversible adsorption was seen using both carbons for o-methylphenol, but only for SA4 involving m-chlorobenzoic acid. From these results, de Jonge concluded that adsorption and reversible adsorption is dependent upon the surface properties of the carbon (influenced by the activation method) rather than the pore structure of the carbon. The surface chemistry of the carbon also influences how a particular sorbate molecule will adsorb.
To explain the different results in the literature, de Jonge’s conclusions must be considered. In all the papers considered here, different activated carbons have been used, with the exception of Vidic and Abuzald, who produced similar results. It has been shown in this review that the activation method can seriously affect the pore and surface chemistry characteristics. This would explain the variation in phenol adsorption. de Jonge et al (1996) also postulated that the functional group affects the adsorption mechanism. An unsaturated group on the sorbate molecule, e.g. a carboxyl or nitro group, is resistant to oxidative coupling and so might adsorb under the donor-acceptor mechanism, while a saturated functional group, e.g. a methyl group, would increase the probability of sorbate polymerisation by oxidative coupling. This theory does not extend to the discrepancy in results for phenol, and so one can only speculate that the specific surface chemistry of the carbon and some other mechanism must be responsible.

1.5.6 Summary

Activated carbon is widely used in treatment plants to remove simple micropollutants from waste water. A major property of activated carbon is the large internal surface area which is developed by the activation process. A large surface area means less material is required to adsorb the pollutant - an important economic consideration. However, the cost of the activation process is such that the carbon must be regenerated to make the process viable.

Carbon activation is achieved by chemical or physical means. During physical activation, oxidising gases, such as oxygen, steam or carbon dioxide, burn the tar and ash substances to reveal an extensive porous network. The pores are classified according to size. In ascending size, the pores are called micropores, mesopores and macropores. Micropores can contribute to 95% of the surface area and so are a requirement of good adsorbents.

The oxidising gases also serve to alter the surface chemistry of the carbon. The oxygen and hydrogen molecules bond with the carbon to form surface functional groups which are generally acidic in nature, although basic groups do exist simultaneously. Recent
literature points to the surface oxygen groups as the major contributor to the adsorption mechanisms of simple aromatic molecules, such as phenol. Some authors report that oxygen groups have a detrimental effect on the adsorption of phenol. In this case, the aromatic ring is thought to interact with the electrons existing on the carbon basal plane.

Other authors believe that oxygen groups can improve the adsorption properties of carbon with certain aromatic compounds. They believe that the aromatic functional groups interact with certain oxygen groups to form polymers of the adsorbate at the carbon surface. However, under these conditions, it is difficult to regenerate the carbon - a situation economically unsuitable.

1.6 Modified activated carbon, counter-current adsorption processes and stabilised bubbles - the work of Dr. Donald Weiss

1.6.1 Introduction

The literature review has so far concentrated on areas of chemistry and chemical engineering which have some bearing upon stabilised bubbles research. To complete this review, one must consider the work of Dr. Donald Weiss at CSIRO, Melbourne, Australia. Weiss is the originator of this project. Since the 1940's, Weiss has been concerned with adsorptive processes and particularly methods of improvement and/or intensification. Traditionally, liquid-phase industrial adsorption has been confined to batch-wise column-adsorption and vat-adsorption techniques (Weiss, 1950). In column adsorption, the liquid stream to be treated is slowly percolated through the adsorbent in a packed bed. The adsorbent particles are usually granular for ease of liquid flow and to minimise pressure drop. Granular activated carbon (GAC) is more expensive to produce than powdered activated carbon (PAC), however, the finely divided nature of PAC means it is unsuitable for column adsorption as the liquid flow rate through the bed is too low (Snoeyink, 1990). PAC is used in particular instances where vat-adsorption techniques are required - the adsorbent is mixed with an adsorbate in a vessel and later
recovered by filtration, prior to desorption. Economic considerations necessitate efficient use of activated carbon, hence, the carbon is regenerated and reactivated.

Weiss, however, identified that if industrial adsorption processes were continuous, large scale treatment of liquid streams would be possible. Complex mixtures could be fractionated into separate components by selective adsorption. To render this possible, Weiss recognised that a continuous process must incorporate the following features:-

- efficient use of adsorbents by using truly counter-current flow between the adsorbent and adsorbate
- the ability to fractionally adsorb from aqueous solutions
- simple regeneration of the adsorbent

Weiss envisaged that the first feature was possible if the adsorbent had an appreciably different density to the adsorbate solution. One such technique was the "floating" method, based on froth flotation, which was the precursor to stabilised bubbles. In this technique the adsorbent particles are attached to a froth of air bubbles. The density difference between the froth and the liquid stream to be treated allows the adsorbent to float counter-currently. In theory, Weiss devised the process as illustrated schematically in Fig. 1.30 (Weiss, 1950). A pH gradient is maintained in the fractionating column which allows rectification of the required product and desorption of the used adsorbent which is then recycled into the base of the column.

Weiss believed the other characteristic features of a continuous adsorption column, listed above, were possible by modification of the adsorbent to increase selectivity. Addition of a particular modifying agent would alter the adsorptive properties and condition the adsorbent for froth flotation.
Figure 1.30 - A continuous fractional adsorption column where the adsorbent floats counter-currently against a descending adsorbate solution (Weiss, 1950)

### 1.6.2 Modified activated carbon adsorbents

In 1949, Weiss published a paper which reviewed his work on modifying activated carbons for continuous fractional adsorption (Weiss, 1949). Surface chemists, at that time, were aware of the existence of acidic and basic oxides on the carbon surface. According to Steenberg (1944), activated carbons are categorised into two particular types:

1. **L carbons** - possess the ability to adsorb NaOH (anions), i.e. they are acidic
2. **H carbons** - could not adsorb NaOH, i.e. have basic properties

H carbons can adsorb anions at certain pH’s by short-range forces, e.g. van der Waals. However, the L carbon has a heterogeneous surface that contains H- parts and surface acidic oxides. This meant that L carbons can adsorb by short-range and electrostatic forces. This ability is observed at different pH values - at a low pH (acidic), L carbons
can adsorb anions by short-range forces, at a high pH (alkaline) they can adsorb cations by ionisation of the surface oxide groups.

Despite the large adsorption capacity of activated carbon, its use is uneconomic without the ability to regenerate. Unfortunately, the binding affinities of certain adsorbates on activated carbon means that regeneration is only possible via a separate process. Weiss, however, thought that if carbon could be modified such that desorption and regeneration was possible by a change in pH, then the process could operate continuously. Hence, a modified L carbon would be ideal for this purpose.

Weiss illustrated this potential by modifying an L carbon using a non-electrolyte, decyl alcohol. The adsorption ability of this modified activated carbon for an organic cation, 5-aminoacridine, was tested at various pH’s and compared with an unmodified activated carbon. The results are shown in Fig. 1.31.

![Figure 1.31 - The effect of modification of activated carbon on the adsorption of 5-aminoacridine hydrochloride (Weiss, 1949). The graph shows the extent of adsorption achieved, as a percentage of the maximum achievable adsorption, with pH](image)

The results show a reduction in the level of adsorption of the cation with the addition of decyl alcohol. Further addition of the alcohol continues to reduce the level of
adsorption. While this may seem a disadvantage, Weiss demonstrated that desorption of the cation was possible by a change in pH, making the adsorbent ideal for a continuous adsorption process. Weiss described the effect of the decyl alcohol as follows:

I. It competes with the cation for adsorption by short-range forces
II. It acts as a solvent for the cation
III. It reduces the dielectric constant in the immediate vicinity of the surface, reducing sorption affinity

Point II is not strictly true because if the cation was completely soluble in the alcohol, the adsorption capacity would increase with the level of alcohol addition. Nor is it completely immiscible as zero adsorption would occur if the alcohol was more strongly adsorbed. Hence the adsorbate is partially miscible in the alcohol.

Adsorption of the cation was a minimum at pH 2.8. Weiss believed that at this point the carbon behaved as an H carbon. Above 2.8, the acidic surface oxides are ionised and the electronegative charge increased. Additional cations are attracted to the surface, with some adsorbed by short-range forces and others by electrovalent forces to form an ionic atmosphere near the ionised groups. Hence the adsorption capacity increases with pH to a maximum, at which point complete ionisation of the surface oxides has taken place. Below pH 2.8, the carbon behaves as an H carbon, with addition of HCl increasing the adsorption of the aminoacridine ion.

In a continuous process, pH adjustment enables the L carbon to behave selectively. At high pH, adsorption takes advantage of short- and long-range forces to separate cations from anions or non-electrolytes. At low pH, a modified adsorbate would utilise the more selective short-range forces. Weiss postulated that the adsorption capacity of the modified activated carbons was comparable to that of synthetic ion-exchange resins and no swelling took place with pH adjustment as compared with the resins. Combining these advantages with the ability to desorb readily, Weiss was convinced of their potential for use in a continuous process.
A colleague of Weiss' also investigated the effect of modifying agents on adsorption using activated carbon (Harrap, 1951). Harrap investigated the effect of competitive adsorption between the adsorbate ion and the modifying agent. If such an agent were used for flotation, displacement by the adsorbate would impair flotation of the carbon and the system would collapse. Harrap used an H carbon treated with oleyl alcohol (the flotation agent used in this study) to adsorb quantities of aniline (a benzene derivative with a substituted NH₂ group) from aqueous solution.

Harrap discovered that adsorption of oleyl alcohol was independent of pH, as expected with adsorption of non-electrolytes. He found that 0.1g of carbon could adsorb 0.0535-0.0545g of oleyl alcohol. He then investigated the adsorption of aniline in the presence of oleyl alcohol. As also shown by Weiss (1949), the extent of adsorption decreased with oleyl alcohol loading. At low pH values, adsorption was a minimum, indicating that the charged aniline ions in the adsorbate were repulsed by dissociated surface groups. The level of adsorption increased with pH. Above pH 6, the amount of aniline adsorbed does not increase, denoting that the carbon is saturated.

Harrap also discovered that the amount of oleyl alcohol adsorbed in the absence of aniline and the amount of aniline adsorbed in the absence of oleyl alcohol was similar. This suggested to Harrap that the same adsorption sites were available to both molecules. Harrap examined his data and calculated that oleyl alcohol can replace aniline molecules on a 1/1 basis. He postulated that this displacement of 1 molecule of aniline by 1 molecule of oleyl alcohol continues until an equilibrium is reached, dictated by the binding affinities of each molecule. Harrap calculated that the affinity of oleyl alcohol for adsorption is five and a half times greater than that of aniline.

1.6.3 Counter-current adsorption processes

Weiss and co-workers later produced a series of papers, detailing their investigations into the feasibility of a counter-current adsorption process (Swinton and Weiss, 1953; Weiss, 1953; Minty et al, 1953; Minty, McNeil et al, 1953; Moir et al, 1953). The authors recognised the potential for the process, but identified certain technical difficulties which
had prevented the development of the continuous adsorption process. Amongst these problems, the most important was that an adsorbent had not yet been found that had a high and reversible adsorptive capacity. For a counter-current process to work effectively, the adsorbent must reach equilibrium quickly, be resistant to abrasion and be transported simply.

Part I of the series (Swinton and Weiss, 1953) reviewed types of equipment that could move large adsorbent particles (diameter exceeding 0.3 mm) counter-currently to a solution. In most of the techniques devised, the adsorbent particles descended against a rising adsorbate solution. Several patents used rotary scrapers and rollers to remove the particles from the base of the column. However, the considerable height of the column produced a pressure at the base of the adsorbent bed that caused serious crushing of the particles, making withdrawal difficult.

A technique favoured by Weiss was the pulsating semi-fluidised bed, as shown in Fig. 1.32.

![Figure 1.32 - A pulse-flow semi-fluidising column for counter-current contacting (Source - Swinton and Weiss, 1953)](image-url)
Chapter 1 - Literature Survey

A column is divided into a series of compartments by means of sieve plates interconnected with downcomers. A diaphragm at the base of the column pulsates the feed solution which is evenly distributed by a bed of large particles. The adsorbent is fed into the top tray and semi-fluidised by the liquid pulse. This results in an expanded bed which possesses the properties of a fluid and the particles flow across the plate and discharge over a weir to the plate below. The advantage of this technique is that there is little turbulence within the bed and so each particle has the same residence time on each tray. Each particle is therefore uniformly equilibrated.

\[ \frac{q}{q_{\text{max}}} = 0.98 \]

\[ (a-b)/a \]

\[ \frac{Dt}{a^2} \]

Dimensionless time

Dimensionless shell thickness

Figure 1.33 - Time $Dt/a^2$ to reach a required equilibrium as a function of dimensionless shell adsorbent thickness $(a-b)/a$ (Source - Weiss, 1953)

In all of the techniques reviewed in Part I (Swinton and Weiss, 1953), the limiting factor was the size of the particles which must exceed 0.3 mm for counter-current movement to be applicable. In an adsorption process utilising completely porous particles, the principal diffusional resistance is from the internal pores, therefore, the equilibrium time is long. The rate of mass transfer can be increased by using finely divided adsorbents, but counter-current movement would be impractical. In Part II of the papers, Weiss
(1953) proposed that large particles, suitable for counter-current handling, could attain high rates of mass transfer if the pores of the particle were limited to a thin outer shell. Weiss named these particles *shell adsorbents*.

Weiss showed how, in theory, shell adsorbents are ideal for counter-current adsorption processes. Weiss took the equation for diffusion into a spherical particle and manipulated it to produce a corresponding equation for a spherical shell of external radius $a$, having an impervious core of radius $b$. Fig. 1.33 shows how the time to reach equilibrium, in dimensionless form $(Dt / a^2)$, (where $D$ is the diffusion coefficient and $t$ is the time) is a function of the shell thickness, in dimensionless form $(a-b)/a$. This shows that the time to reach equilibrium is much more rapid for thin shells than thick shells or completely porous particles. In Fig. 1.33 $Q/Q_\infty$ is a measure of the degree of saturation of the adsorbent. $Q/Q_\infty = 1$ means the adsorbent is completely saturated.

Part II also shows how the throughput of the adsorbate increases, the rate of movement of the adsorbent must increase and the height of an adsorption column is reduced using thin shell adsorbents. In conventional adsorption systems, the rate of diffusion into the pores is much slower than that through the liquid phase. However, for thin shells the diffusional resistance in the liquid phase is comparable to the pore resistance. This, however, is overcome by increasing the relative velocities of the liquid and adsorbent phases.

In Part III, Weiss and colleagues prove the stability of a shell adsorbent, using particles of diatomaceous earth that adhere to the surface of rough quartz particles by a film of water saturated with an immiscible solvent (Minty *et al*, 1953). The stability of the adsorbent particles is a function of the amount of solvent-saturated water added. At the correct dosage the particles are very stable, the earth still adhering to the quartz despite vigorous shaking. Further addition of water re-disperses the earth into the solution. Weiss believed that the particles adhere due to the interfacial area between the adhering particles being much less than the interfacial area of the separate particles. To remain stable, the work of adhesion must be greater than the disruptive forces.
Part IV examined a batch method of fractionation involving the shell adsorbents (Minty, McNeil et al, 1953). The authors attempted to remove penicillin from a solution, but found the process too difficult as the adsorbent (the quartz particles from Part III) became sticky under certain conditions and would not flow freely.

In Part V, Weiss and co-workers introduced the concept of the stabilised air bubble (Moir et al, 1953). In this technique, an air bubble is coated with a layer of finely divided adsorbent, such as activated carbon, which is rendered hydrophobic by addition of a flotation agent. This aggregate functions hydrodynamically as a large particle. A bed of stabilised bubbles can rise, due to buoyancy, against a descending liquid stream. The rise velocity is a function of the bubble diameter.

This paper describes a method for producing the stabilised air bubbles and utilising them for a fractional adsorption process. Fig. 1.34 shows a simple flow sheet of the process.

![Flow sheet of a counter-current adsorption process](image)

**Figure 1.34 - Flow sheet of a counter-current adsorption process as envisaged by Weiss and colleagues (Source - Moir et al, 1953)**
Weiss produced the stabilised air bubbles by mixing the activated carbon, water and flotation agent in a vessel. The slurry was agitated by the rotating impeller, creating a vortex by which the slurry was aerated. The various circulating streams within the slurry retained and agitated the bubbles around the vessel, enabling the hydrophobic activated carbon to adhere to the bubble surface. A diaphragm pumped the stabilised bubbles into the column which was held under a vacuum to aid in the filling of the column by adsorbent. Baffles within the column imparted a rotational movement to the bubbles to remove any wall effects. At various intervals, the column expanded into wider sections. Weiss envisaged these points as liquid feed and removal points, where the pH could be altered to affect the adsorption conditions as in a fractionating column.

Despite the success of Weiss and co-authors in devising this process, no evidence exists for successful application of the counter-current adsorption process. Weiss, himself, recognised the limitations of activated carbon utilised in this manner from previous work (Weiss, 1949; Harrap, 1951). The final recommendation of Weiss is to find a suitable adsorbent where the adsorption properties are not hindered by the flotation agent.

1.6.4 Recent work (1988-91)

After the published work of the 1950's, research into the stabilised bubble column was halted while Weiss' collaborators continued working on penicillin removal via the quartz/diatomaceous earth technique. Weiss continued his work on adsorbents and ion-exchange and produced some literature on the surface chemistry of activated carbon (Garten and Weiss, 1957). However, the potential of the stabilised bubble technique was never fully realised and this prompted Weiss to return to the subject in 1988. His latest work has led to no published literature except for a patent application (Weiss, 1990/91). However, a series of internal reports of his work at the Royal Melbourne Institute of Technology were produced and access to these reports provided the basis for this project.

Weiss was particularly interested in the aphron work of Sebba (1985 and 1986) and found certain similarities between the two techniques - namely the stability of the aphrons and bubbles. Weiss believed that his bubble technique was simpler as the
stabilising agent did not have to be soluble in water as is the case for the aphron technique. The success of Sebba enthused Weiss to continue his work.

Weiss began by reviewing his work from the 50's (Weiss, 1989 [a]). The first major change Weiss made was in the production of stabilised bubbles. Despite numerous attempts, he could not recreate stabilised bubble production as previously. Coupling this with the realisation that scale-up of the process would be difficult as the impeller power requirement would be excessive, this method of generation was abandoned. Weiss adopted the method of air entrainment by plunging jets (Weiss, 1990 [b]). In this technique, the carbon/oil/water slurry is pumped to a vessel containing a distributor plate which divides the flow into a series of jets. The vessel is divided into a series of compartments by crossed louvre plates and the vessel is filled with slurry except for a small air gap. The plunging jets entrain air from this space into the slurry. The air pressure in this gap is regulated so further entrainment of air is possible. The crossed louvre plates provide the hydrodynamic shear, similar to that encountered in the stirred vessel, by which the modified activated carbon can adhere to the surface of the air bubble. A more complete description of the generator is provided in Chapter 2 of this thesis.

The development of air entrainment by plunging jets was a variation of another technique Weiss had tried. In this method, air was injected at right angles to a rapidly moving carbon/oil slurry in a short length of tubing (Weiss, 1989 [a]). Flow differentials between the slurry at the walls and in the centre of the tube allowed the bubbles to roll along the wall of the tube, completely coating the bubble with carbon. This technique of air sparging is used in some flotation devices (Finch, 1995). Weiss claims he was not aware at the time of the use of plunging jets in the Jameson cell and developed this idea independently. The principle of using crossed louvres to create hydrodynamic shear evolved from the use of in-line static mixers. Weiss tried using some commercial versions but the expense led to the development of the crossed louvres - a cheaper alternative. Various in-line mixers are now commercially available which create bubbles by shear (Finch, 1995).
Weiss also developed some thoughts on the mechanism of adsorption using stabilised bubbles. In the quartz/diatomaceous system, these materials were completely wetted by the solvent-saturated water (Minty et al., 1953). If adsorption of a pollutant in the presence of a flotation agent is possible, as Weiss' and Harrap’s studies showed, then in the carbon/oil system, the carbon must be only partially wetted by the oleyl alcohol. Weiss attributed the stability of the bubble to the configuration that had the minimum oil/water interfacial energy (Weiss, 1989).

The mechanism for adsorption Weiss termed *oil agglomeration.* Harrap had showed how simple adsorbents can displace oil from the adsorption sites on activated carbon. Weiss believed that as the oil in the pores met the air interface, the oil forms a monolayer which expands on the air/water interface and continues until the voids between the adhering particles are filled. In this manner, the extent of the interface between the bulk water and the spreading agent is kept to a minimum. This frees some carbon surface area for adsorption. If an adsorbate enters the pores of the carbon, the oil is displaced into the bulk oil phase in the voids. It should be noted that no experimental evidence was offered for this mechanism, except the adsorption work of Weiss and Harrap. An alternative mechanism would be that the oil displaces into the bulk water, reducing the stability of the air bubble (Harrap, 1951).

Weiss offered no evidence of successful treatment of micropollutants by stabilised bubbles, and it was at this stage that the project moved to Loughborough University. As well as treatment using activated carbon, Weiss believed that other materials could be used, e.g. iron hydroxide (Fe(OH)₃) can recover trace metals due to its ability to exchange cations or anions, depending on the system pH (Weiss, 1991). Weiss also believed an application existed in mineral recovery (Weiss, 1989). The advantage of using this technique was that the entire surface of a bubble is coated, therefore requiring less air. As with the Jameson cell, the wash water requirements are minimal, i.e. enough to displace pulp from the interstices of the floating layer.
1.7 Literature Review Summary

After reviewing the research of Weiss, it is now possible to see how all the particular sections of this review fit into place. A key aspect of this project is the successful generation of stabilised bubbles. The equipment used to do this combines air entrainment by plunging liquid jets and particle attachment using hydrodynamic shear and the hydrophobic properties of activated carbon. Hence, it was necessary to review key work on gas entrainment (Section 1.2) and particle-bubble attachment (Section 1.3). With this knowledge, an attempt to identify the principal mechanisms involved in stable bubble generation is possible.

Once generated, the bubbles are transferred to a column for contacting with a contaminated water stream. The collected bed of bubbles resemble an inverted fluidised bed. The literature reviewed in Section 1.4 discusses the hydrodynamic properties of an inverted bed and presents current theory on correlating bed expansion behaviour. The results of bed expansion will be compared with current theory.

The potential of the stabilised bubbles for pollution treatment is to be examined in this thesis. Section 1.5 described the mechanisms currently offered for removal of phenols by activated carbon. The evidence presented in the literature relates the mechanisms to the chemical and physical interaction between the adsorbent and pollutant. The surface chemistry of the particular carbon is critical to its adsorption ability. This knowledge should help explain the experimental results.

The work of Donald Weiss provides the fundamental basis for the project. The first objectives of the project are to reproduce his work as closely as possible - particularly the generation of stabilised bubbles. The reports detail some of the technical difficulties of the project that can be expected, as well as the adsorption properties of modified activated carbons and shell adsorbents which are an integral part of the project.
Chapter 2 - Process Development

2.1 Introduction

The aim of the project was to develop a pilot-scale process by which the capacity of thin-shelled adsorbents (in the form of air bubbles stabilised by a thin coating of powdered activated carbon for pollution treatment) could be assessed. The project was originally developed by Dr. Donald Weiss, who made the first forays into this area of research (as described in Chapter 1). Hence, the basic design for the process was already available. The aims of this particular project were as follows:

- Reproduce the early findings of Weiss, i.e. generate stabilised air bubbles
- Assess the adsorptive potential of stabilised air bubbles for pollution control by developing a suitable contactor
- Document process difficulties for scale-up and make recommendations to overcome these problems

One area that was not covered in the project was the mechanism of coating the bubble. This was thought to be a project in itself and so the major focus became technological development. The literature survey did cover possible mechanisms of particle-bubble attachment as an aid for bubble generator development, but contact angle measurements and other investigative techniques were avoided.

In the 1950’s, Weiss successfully produced carbon-coated bubbles using an impeller to entrain air into a tank. The air bubbles formed in this way were rolled around the inside of the tank wall by rotational shear. This helped to coat the air bubbles with activated carbon. Particle-bubble attachment was only possible with the aid of a spreading agent to render the activated carbon hydrophobic, in this case oleyl alcohol (Moir et al, 1953). The product was then pumped to a column containing water which flowed countercurrently to the coated bubbles. Weiss termed any particle that had an impervious core...
but a thin porous outer layer as a shell adsorbent (Weiss, 1953). Due to the nature of the coated bubbles, they could be classified as shell adsorbents. The benefit of shell adsorbents is that the time to reach equilibrium is much shorter than a conventional porous particle, plus desorption of the adsorbed material is much easier (see Chapters 1 and 5). Despite Weiss’ belief, the project was abandoned in 1953 and not revived until 1988.

The method of generating bubbles using shear was revisited. However, the impeller technique would not work. The reasons for this were not established, but it was thought that the energy requirement to rotate an impeller on a large scale would render this process inefficient anyway (Weiss, 1989 [a], [b]). Weiss looked for other ways of generating shear and successfully developed a louvre system to coat the bubbles (Weiss, 1990 [a], [b]). At this point, the idea needed further backing and the project was transferred to Loughborough University with the help of Severn Trent Water Ltd. This thesis describes the findings of the project.

This chapter covers the development of the process, from the initial design through to the final pilot-scale plant. The bubble generator is considered first. Although the essential design of the generator has not changed significantly throughout the project, the design has been developed to improve bubble production, reduce down time and prolong the useful life-time. The bubble contactor has seen several different designs throughout the life span of the project and the reasons behind this are discussed here. Chapter 3 describes how the contactor was used to assess bubble hydrodynamics and Chapter 5 summarises the effectiveness of the technology for pollution control.

The process can be divided into two sections. The first section is the bubble generation process. The philosophy underlying this equipment was inherited from Weiss, but the project provided an opportunity for greater understanding of the process and allowed necessary refinements to be made. The second section was the stabilised bubble - pollutant contacting column. The primary goal in designing the column was that the column should facilitate assessment of the properties of the coated bubbles, both sorptive and hydrodynamic. Stabilisation of the bubbles was also a major priority. Hence, more
traditional engineering principles were required here. The way the two sections interrelate is conveyed in Fig. 2.1. Initially, the bubble generator and column were connected by a tube containing a stop-cock (V3). However, as the development progressed and the process was scaled-up, the transfer of bubbles between the two major items of equipment became more difficult and eventually, a lot of attention was focused on how this could be achieved. This will be explained in greater detail later in this chapter.

Essentially, the process operates as follows: the materials for generating the coated bubbles, powdered activated carbon (PAC), oleyl alcohol and water are mixed in a tank (T2), see Fig. 2.1. The carbon and water are mixed together while the oleyl alcohol is metered out at a specific flow rate to aid bubble generation. The exact quantities of each are given in the next section. The slurry is pumped to the bubble generator (BG) at a flow rate of 9 l/min. The slurry is recycled back to tank T2. Tank T1 is used for cleaning purposes. Air is supplied via a pressurised cylinder (AI). As well as providing the air for the bubbles, the air supply also regulates the height of the slurry in the generator. This is achieved by using a submerged dip tube. If the dip tube is raised, less air pressure is forced into the generator and the level rises. If the dip tube is lowered, more air is forced into the generator and the slurry level falls. The importance of the slurry level is explained later.

The slurry pumped to the generator is divided into a series of jets upon entering the vessel by a distributor plate. The jets impinge upon the surface of the slurry and entrain air in the form of bubbles. The bubbles are gradually coated with the activated carbon which is rendered hydrophobic by the spreading agent, oleyl alcohol. Once the generator is full of stabilised bubbles, they can be transferred to the contacting column.

The column into which the bubbles are transferred (BC1) must be full of water which flows counter-currently to the bubbles. This is essential since the bubbles, coated with PAC, only remain stable while submerged. Contact with an air interface causes the bubbles to collapse. The water required for this is provided from tank T3. Although this tank contains water, it can be dosed with pollutant to test the adsorptive capacity of the
Figure 2.1 - Schematic of the Process (key overleaf)
KEY TO FIGURE 2.1

T1, T2 - Feed tanks to Bubble Generator
T3 - Feed Tank to Contacting Column
BG - Bubble Generator
P1, P2 - Pumps
BC1 - Contacting Column
F1, F2 - Flowmeters
AI - Air supply from compressed cylinder
V1 - Three way valve
V2 - Diaphragm valve to adjust flow rate to generator
V3 - Stopcock between generator and column
V4 - Start-up recycle valve
V5, V6 - Column outlet valves
V7 - Diaphragm valve to adjust flow rate to column
V8 - By-pass valve
VT1, VT2 - Bubble Generator Vents
VT3 - Column vent
B1, B2 - Plate bleeds
bubbles. A retaining plate is also necessary to prevent bubbles rising to the top of the column and collapsing. In this manner, coated bubbles are collected in a deep bed whilst the counter-current flow of water is distributed sufficiently to agitate and fluidise the bubbles and prevent their coalescence.

This chapter discusses the process in more detail. The materials used in generating stabilised air bubbles are considered first, followed by a discussion of the properties of the bubble generator - specifically, how the design helps it work and what underlies the physical process. The contacting column is considered after that and finally the mechanism of bubble transfer is described and how the problems were overcome.

2.2 Stabilised Bubble Generation Materials

2.2.1 Powdered Activated Carbon (PAC)

The properties of activated carbon have been described comprehensively in Chapter 1. In this section, the properties of the particular type of PAC used are given. In any conventional water treatment process using activated carbon, the main operating expense is the carbon itself. To make the process economically viable, the spent carbon must be regenerated. Granular activated carbon (GAC) is more expensive than its counterpart PAC, hence any process that can utilise PAC effectively holds a distinct advantage. Another advantage, is that the time to reach equilibrium for PAC is smaller than that for GAC. The adsorption capacity will not differ, but the fast kinetics mean that PAC can be used more efficiently.

This explains why PAC is ideal for producing shell adsorbents and the process can be intensified. PAC will adsorb micropollutants and reach saturation quickly provided that large quantities of carbon-coated bubbles can be produced and moved counter-currently to the contaminated liquid. In theory, the PAC should be used so efficiently that regeneration is not required. The use of oleyl alcohol as the stabilising agent means regeneration would be difficult in any case.
The PAC used for the project was NORIT SA4. This is a steam activated carbon with a large internal surface area, traditionally used for odour and taste removal, particularly low molecular weight organic material (e.g. phenols and chlorinated hydrocarbons) and micro-pollutants (e.g. pesticides, dyes and detergents). This carbon can be regenerated by steam activation or alternatively by thermal reactivation in kilns at 800-1000 °C. Technical information supplied by NORIT is given in Table 2.1:

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Peat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation Method</td>
<td>Steam</td>
</tr>
<tr>
<td>Apparent density</td>
<td>490 kg m⁻³</td>
</tr>
<tr>
<td>Internal surface area</td>
<td>650 - 750 m² g⁻¹</td>
</tr>
<tr>
<td>Total pore volume</td>
<td>0.80 cm³ g⁻¹</td>
</tr>
<tr>
<td>Micropore volume</td>
<td>0.25 cm³ g⁻¹</td>
</tr>
<tr>
<td>Mesopore volume</td>
<td>0.19 cm³ g⁻¹</td>
</tr>
<tr>
<td>Macropore volume</td>
<td>0.36 cm³ g⁻¹</td>
</tr>
<tr>
<td>pH</td>
<td>10</td>
</tr>
</tbody>
</table>

The particle size range by wet sieving:

<table>
<thead>
<tr>
<th>Size Range</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;10 µm</td>
<td>80%</td>
</tr>
<tr>
<td>&gt;44 µm</td>
<td>37%</td>
</tr>
<tr>
<td>&gt;74 µm</td>
<td>20%</td>
</tr>
<tr>
<td>&gt;150 µm</td>
<td>5%</td>
</tr>
</tbody>
</table>

A study performed within the department showed that the particle size range varied from 0.5 to 1000 µm. For the purposes of bubble generation this was not a problem. Eventually, the PAC was sieved to a size range 0.5 - 53 µm as this was thought to improve the adsorption characteristics of the coated bubbles, i.e. improve equilibration times. This had no detrimental effect upon generating stable bubbles.
2.2.2 Oleyl Alcohol

This spreading agent was used by Weiss and colleagues at the start of the project in the 1950's. It was chosen for its spreading efficiency, i.e. the ability to spread at an air-water interface. Weiss believed that this would maximise the area available for adsorption within the pores of the activated carbon.

The molecular formula for oleyl alcohol is \( C_{18}H_{35}OH \). The 18 C backbone means it is insoluble in water, a property that is vital in rendering the surface of the carbon hydrophobic. It is non-toxic and principally used in cosmetics as a binder for perfume in cologne sticks, a valve lubricant for spray deodorants and a penetration and spreading agent for skin-care preparations. Technical information supplied by Croda Chemicals is given in Table 2.2:-

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solidification range</td>
<td>&lt;4°C</td>
</tr>
<tr>
<td>Boiling Point at 1 atm</td>
<td>205°C</td>
</tr>
<tr>
<td>Density (at 40°C)</td>
<td>830 - 840 kg/m³</td>
</tr>
<tr>
<td>Viscosity</td>
<td>24 - 32 Ns m⁻²</td>
</tr>
</tbody>
</table>

2.2.3 Air and Water

The air supplied from the compressed cylinder was assumed to be of atmospheric quality and the water was regular tap grade.

2.3 The Stabilised Bubble Generator

2.3.1 Description of the Generator

The dimensions of the generator are shown in Fig. 2.2. Originally, the generator was constructed from clear perspex. A series of holes drilled through the perspex allowed the
Figure 2.2 - Dimensions of the bubble generator

Figure 2.4 - Views of the a) top 3 louvres, b) bottom 3 louvres
three sections shown in Fig. 2.2 to be bolted together. This arrangement was not sufficient to make the system water-tight and silicone was applied to seal the generator properly. The problem with using perspex as the material of construction is that it is not very robust. To prolong the life of the generator, the nuts and bolts had to be applied as evenly as possible. Any over-tightening of the nuts would warp the perspex, making it increasingly difficult to obtain an effective seal with the silicone. The outlets from the generator were also made of perspex. They had an outer diameter of 12 mm and were only 1 - 2 mm thick. Continuous removal and reapplication of tubing meant that they would frequently break, requiring a hole to be re-drilled before a new outlet could be fixed.

These factors meant an improvement in the quality of the design of the generator was required. Firstly, an alternative material of construction was found. Polycarbonate provided the robustness required, but was still malleable enough to make construction easy. Instead of using silicone, a less permanent but equally effective seal was required. Common draught exclusion tape was used. The rubber material used allowed the tape to be compressed as the bolts were applied, plus an adhesive backing meant the tape could be secured firmly in place. The tape proved to be very successful. The outlet pipes were not constructed from polycarbonate. Instead, stainless steel was used. No problems were ever encountered. If the pipes ever worked loose, they were simply re-glued.

Fig. 2.3 shows a section through the bubble generator. The slurry, containing PAC, water and oleyl alcohol, is pumped to the feed inlet. The slurry then passes through a distributor plate. This is a polycarbonate block, 160 mm long x 25 mm wide x 10 mm deep, through which a series of holes were drilled, 2 mm in diameter. Twenty-eight holes were drilled in a straight line through the middle of the block. The slurry passes through the holes creating a number of plunging jets. Just below the distributor plate is the air inlet, which supplies the air to be entrained by the plunging jets.

The generator is divided into an array of sections - each section divided by a louvre plate. Fig. 2.4 shows the design of the louvre plates. All louvres were of dimensions 160 mm x 20 mm x 20 mm, but the channels within the plates were of different dimensions. The
Figure 2.3 - Section through the bubble generator (all dimensions in mm)
Chapter 2 - Process Development

top three plates were constructed from perspex greenhouse roofing. This material contained channels 11 mm x 9 mm but they were cut at an angle of 30° to the vertical to provide the inclination shown in Figs. 2.3 and 2.4. Two layers of these louvres were glued back-to-back so that each layer faced in an opposite direction to the other (see Fig. 2.4). Each layer consisted of 11 channels, giving an overall free area of 69%.

The bottom three louvres were made of PVC and were constructed using the same principle, except the channels were slightly smaller (9 mm x 7.5 mm) and the walls were thicker (see Fig. 2.4). Each layer consisted of 10 channels, giving an overall free area of 42%. The reason for the difference between the louvres is that this enables the generator to behave as a classifier, i.e. smaller bubbles are retained in the lower sections of the generator whilst larger bubbles are retained in the top sections. The free area controls the velocity of the slurry through the plates, hence a smaller free area produces a higher velocity which retains the smaller bubbles more easily.

Fig. 2.3 shows a series of outlets from the bottom four sections. This is to enable bubble transfer from any section as required. In practice, the bubbles were removed from the third section from the bottom and transferred to the contacting column. During operation, the slurry would leave the generator via the outlets at the bottom and be recycled to the feed tanks.

Later experiments called for a greater volume of stabilised bubbles to be generated and so a larger generator was constructed. Essentially, it was of the same dimensions as the original generator except it was now twice as wide - 50 mm compared with 25 mm (see Fig. 2.5). This necessitated several changes to the design. In this generator, all the louvres were constructed of PVC and consisted of four layers of channels, inclined at 30° to the vertical, positioned in opposite directions alternatively. In designing the new louvres a similar approach to the original generator was adopted. The slurry velocity through a louvre channel was calculated and this was taken to be the defining criterion for the new louvre plates. Calculations revealed that the velocity through the top three louvre plates was 0.068 ms\(^{-1}\) and 0.108 ms\(^{-1}\) in the bottom plates. The louvre plates were designed in order to reproduce these velocities as closely as possible.
Figure 2.5 - Dimensions of the enlarged generator

Figure 2.6 - Views of the a) top 3 louvres  b) bottom 3 louvre plates
Fig. 2.6 shows the designs of the new plates. Each plate had dimensions 160 mm long x 49 mm wide x 20 mm deep. In the top three plates, the plan channel dimensions were 7.5 mm x 7.0 mm, each layer consisting of 13 channels producing a total free area of 36.4% and a channel velocity of 0.065 m s\(^{-1}\). The bottom three plates consisted of four layers, each layer containing 12 channels, producing a total free area of 23.8%. Each channel had cross-sectional dimensions of 6.5 mm x 6.0 mm.

Similarly, the distributor plate that created the plunging jets of slurry, had to be re-designed. The distributor plate was designed to produce the same jet velocity as in previous attempts, except that to produce coated bubbles effectively, the jets should plunge over the whole cross-sectional area of the generator. Fig. 2.7 shows the designs considered. Each plate was drilled with 28 holes, 3 mm in diameter. The jet velocity produced by this plate was 0.89 m s\(^{-1}\). The bottom plate shown in Fig. 2.7 was chosen as the standard distributor plate as it covered the entire cross-sectional area of the generator.
Figure 2.7 - Distributor plate designs considered for the enlarged bubble generator
Plate b) was used in all experiments involving this generator
(all dimensions in mm)
most effectively. Fig 2.8 shows the bubble generator as it would appear before the start of an experiment.

2.3.2 Method of generating stabilised carbon-coated bubbles

The important parameters in generating stabilised bubbles are slurry flow rate, oleyl alcohol addition rate, amount of carbon and oleyl alcohol/carbon ratio. The air flow rate is less important as this is self-regulating. The characteristics of the plunging jet are also vitally important but this aspect is discussed in the next section. Preliminary experiments established the ideal amounts of each material for stable bubble generation. These are given in Table 2.3:-

<table>
<thead>
<tr>
<th>Table 2.3 - Bubble generation requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Activated carbon</td>
</tr>
<tr>
<td>Slurry flow rate</td>
</tr>
<tr>
<td>Oleyl alcohol addition rate</td>
</tr>
<tr>
<td>Total quantity of oleyl alcohol</td>
</tr>
<tr>
<td>Oleyl/carbon ratio</td>
</tr>
</tbody>
</table>

The method of generating carbon-coated bubbles was as follows. Clean water in feed tank (T2) was pumped to the generator. Despite the outlet valves remaining open, the level of water rose in the generator. The level of water is critical to the entrainment of air bubbles. Research on air entrainment showed that there are many factors which dictate the amount of air entrained and the size of bubbles produced. These factors include jet length, jet diameter and jet velocity, i.e. In plain terms, the momentum of the jet is crucial to bubble formation. Hence, a large jet momentum means more bubbles are formed. For this reason, the level of water remained just below the air inlet pipe (see Fig. 2.3). By reducing the jet length, the kinetic energy within the jet remained high and so could entrain and retain bubbles to the required standard. This mechanism is explained in more detail later.
When the liquid level reached the required height, a vent on the air inlet supply was closed and the level stopped rising. This was due to the air pressure in the space above the water. The air inlet was connected to a cylinder of compressed air via a dip tube suspended in a 25 mm glass column containing a head of water. This was used to control the level in the generator during bubble generation. Air was supplied to the generator at a pressure of 10 psi gauge and the air rate was sufficient that excess air was directed to the dip tube. When this happened, the air pressure exceeded the head of water in the dip tube and bubbles sparged into the head of water. Lowering the dip tube into the water caused more air to flow to the generator as it could no longer overcome the head of water in the column. This increased the air pressure in the head space and the water level dropped until the pressure in the system equilibrated. Similarly, raising the dip tube out of the head of water, lowered the air pressure in the generator and the level would rise. This meant control over the generation conditions was possible.

Once at the required height, the finely divided activated carbon was added to the feed tank and stirred continuously. This was necessary to ensure mixing of the hydrophobic carbon with the water and with the added oleyl alcohol. Baffles lined the tank walls to prevent vortex formation which could entrain air and damage the pump. Once the carbon was mixed, the oleyl alcohol was added dropwise via a pipette. For an unknown reason, the oleyl alcohol must be added continuously for a certain period of time, not in one batch dosing. The appearance of coated bubbles is as follows:-

<table>
<thead>
<tr>
<th>Time</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mins</td>
<td>Oleyl alcohol added to feed tank</td>
</tr>
<tr>
<td>30 seconds</td>
<td>Immediate effect upon slurry. The bubbles which form during entrainment by jet impingement are immediately stabilised to a degree. Bubbles continue to form and are retained within the channels of the top louvre plate. These bubbles provide a buffer zone for newly formed bubbles and protect them from the air-water interface at which they collapse. More bubbles are generated than destroyed at the interface.</td>
</tr>
</tbody>
</table>
# Chapter 2 - Process Development

<table>
<thead>
<tr>
<th>Time</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mins</td>
<td>Top section below first louvre plate is full of bubbles. Generator filling up with bubbles which are only partially coated with carbon.</td>
</tr>
<tr>
<td>7 mins</td>
<td>Oleyl alcohol addition stopped. Top two sections filled with bubbles</td>
</tr>
<tr>
<td>10 mins</td>
<td>All sections contain bubbles. A size gradation is seen in the generator with the smallest bubbles in the bottom sections.</td>
</tr>
<tr>
<td>15 mins</td>
<td>The bottom two sections have bubbles which appear fully coated with PAC. They have a matt grey appearance. The larger bubbles in the other sections are black but shiny, indicating the bubbles are not completely coated.</td>
</tr>
<tr>
<td>30 - 40 mins</td>
<td>The bubbles in the bottom four sections are matt grey in appearance, denoting full coating and stabilisation. The top section acts as a buffer zone between the stabilised bubbles and the air-water interface. Bubbles are constantly being formed and collapsed in this area. Hence, the louvre plates serve to transport the bubbles away from this area as quickly as possible.</td>
</tr>
</tbody>
</table>

The generation process as described above did not always go according to plan however. Bubbles would not form quickly enough and so more would collapse than form. The level in the generator was sometimes difficult to control due to blockage of the air supply pipe by the slurry. Activated carbon would sometimes line the wall of the generator making it impossible to see if bubble generation was occurring. Extra oleyl alcohol and/or activated carbon was sometimes added to propagate the process.

Many of these faults however, were caused by contamination with carbon. The holes in the distributor plate that formed the plunging jets were often blocked by the carbon, reducing the entrainment efficiency. The carbon that lined the inner walls of the generator affected the production of bubbles - how so is uncertain, but it could have adsorbed some of the oleyl alcohol used in the generation process.

The generation process involves several factors that cause the production of stabilised bubbles:-
Chapter 2 - Process Development

- Carbon/water slurry flow rate
- Oleyl alcohol flow rate
- Air flow rate and pressure
- Number of plunging jets
- Velocity and shear rate within the louvre plates

If any of these factors are adversely affected, then bubble production is impaired. Hence, the bubble generator must be regularly cleaned. The cleaning process was a laborious and tiresome task, hence the design of the generator had to be improved. The improvements made are described in Section 2.3.1, but the most significant was changing the material of construction to polycarbonate. As well as the inherent robustness of the material, the other major advantage was that the activated carbon no longer deposited on the inner wall. Blockage of the distributor plate by particles of carbon became the primary shut down factor.

Despite the many problems associated with stabilised bubble generation, the process was successful on the vast majority of occasions. Fig. 2.9 shows a typical collected bed of stabilised bubbles. Note the size gradation of the bubbles from the top of the bed to the bottom. From observation, typical bubble sizes range from 0.5 mm to 3 mm plus. The gradation of the bubbles is dictated by their buoyancy - the largest bubbles have the greater buoyancy and so are retained at the top of the bed, just below the distributor plate. The buoyancy of the bubbles means they needed to be retained for observation. However, retention in a liquid medium is insufficient and the bubbles need to stabilised by flowing liquid (in this case water). Fig. 2.9 shows the water flowing counter-currently, against the buoyancy of the bubbles.

Under these conditions, the stability of the bubbles was remarkable. The bubbles would remain intact for many hours with little coalescence. Beds of bubbles were retained for several hours without collapsing, provided there were no uncoated air bubbles in the system. Fig. 2.9 shows the bed of bubbles collected in a specially constructed two-dimensional flat-walled column which was designed specifically for photographing the bubbles. The bed was retained by a sieve plate which can be seen at the top of Fig. 2.9.
Fig. 2.9 A typical fluidised bed of stabilised bubbles

Direction of water flow
Chapter 2 - Process Development

The problem with the sieve plate was that uncoated air bubbles were retained at the surface of the plate as the column was being filled. The effect of these bubbles is to collapse the coated bubbles, hence it was a requirement to remove the air bubbles. Air bleeds at the plate solved this problem, although it was a tricky operation. As will be seen later, with scale-up of the column, this problem became more difficult and the effects of entrained air on the bed of bubbles became more dramatic.

The observed behaviour of the bed of stabilised bubbles appeared to be that of an inverted fluidised bed, i.e. the density of the fluidised particles is less than the fluidising medium. Hence, the flow of liquid must be from top to bottom of the bed. Chapter 1 describes the work of various authors in this field. The present work differs significantly since the fluidising particles (the bubbles) are not robust and do not retain their integrity. Also, the density difference between the fluidising medium (water) and the bubbles is significant. Chapter 3 describes the results of these experiments and attempts to correlate them.

Fig. 2.5 shows the enlarged version of the generator. Initially, the quantity of materials required to generate stabilised bubbles was investigated. The amount of water used was increased to 18 litres. The amount of carbon was increased to 30 g and the oleyl alcohol was added at the same rate, keeping the alcohol/carbon ratio at 0.2 ml/g. The flow rate had to be kept the same as 10 l/min was the upper limit on the pump. Initial trials showed that the concentration of PAC in the water was too low (0.16 % w/w basis) and the slurry was very opaque. Another 30 g was added. However, generation of the stable bubbles did not occur.

With the slurry level below the air inlet, it became obvious that not enough bubbles were being generated and retained. The vast majority were simply rising against the slurry flow and collapsing at the air-water interface. The distributor plate had been specifically designed to reproduce the jet velocities associated with the first generator (Fig. 2.7) and so this was not considered a contributing factor. More jets could have been introduced as a wider area was now covered by the same number of jets, but this would have reduced the velocity of the jets. The louvre plates were designed to reproduce the same
velocities in each channel and hence the same shear rate. The only significant difference was the slurry velocity in each section. In the previous generator, this was 0.047 m s\(^{-1}\), but due to the increase in cross-sectional area, this was reduced to 0.024 m s\(^{-1}\) in the new generator. Hence it was more difficult to prevent bubbles rising to the interface.

Figure 2.10 - Generating stabilised bubbles in the enlarged generator

There were two possible alternatives to overcome this. One was to increase the flow rate within the generator. This would have required installing a more powerful pump, which was not possible due to time and financial restrictions. The other alternative was to increase the rate of air entrainment, so a buffer layer would form preventing newly formed bubbles to rise to the interface. This was achieved by lowering the slurry level to the top of the third section, as shown in Fig. 2.10. This had the effect of increasing the jet length and also disrupting the surface of the jet, both contributing factors in increased air entrainment rate (see section 2.3.3). At increased entrainment rates, larger bubbles form. Soon, the upper section was full of large bubbles which protected the newly
formed bubbles from the interface. The rate of bubble formation surpassed that of bubble collapse and within 45 minutes, the generator was full of bubbles. Eventually, the larger bubbles collapse, but they were replaced by stable smaller bubbles.

Collection of these bubbles showed that the size distribution was narrower than the previous generator, although the size range was never measured for accuracy. This is thought to be due to a combination of the air entrainment rate and the shearing and retention effect of the louvre plates. The increased number of channels per louvre plate may increase the shear and so smaller bubbles are formed from larger ones. Also, the bubble size retained by the plates may have been less. It must be pointed out that there was still a degree of classification throughout the generator.

2.3.3 Factors affecting bubble entrainment

The literature, reviewed by Bin (1993), shows that air entrainment rates are dictated primarily by nozzle geometry, jet diameter, jet velocity, liquid viscosity and surface roughness. Other factors that contribute include surface tension and angle of inclination. The many parameters that define entrainment mean that experimental conditions within the literature vary considerably, and so no correlations exist that define all parameters.

The conditions used for producing bubbles in this experiment are very specific. According to van de Sande and Smith (1976), the upper limit for low velocity jets is 5 ms\(^{-1}\). The jet velocity produced at the nozzle outlet in the distributor plate is only 2 ms\(^{-1}\) for the bubble generators, well within the low velocity range. The liquid viscosity is low (water - 0.001 kg(ms\(^{-1}\)).

With each generator, different conditions were used. For the first generator, the slurry level was high, hence jet length, \(L_j\), jet diameter, \(d_j\), and surface roughness, \(\varepsilon\), were small. To produce bubbles in the scaled-up generator, the slurry level needed to be lowered, resulting in higher values of \(L_j\), \(d_j\), and \(\varepsilon\). Why was this so?
Consider the first generator, shown in Fig. 2.2. The conditions satisfied the criteria that the minimum entrainment velocity was exceeded. If this had not been the case then bubbles would not have formed. Low viscosity jets have surface disturbances on them and it is the interaction between these disturbances and the surface upon which the jets impinge that causes entrainment (see Chapter 1) (Bin, 1993).

The jet velocity is defined by the Bernoulli equation:

\[ V_j = \left( V_o + 2gL_j \right)^{1/2} \]  

where, \( V_o \) is the jet velocity at the nozzle outlet (ms\(^{-1}\))

In most circumstances, this is an oversimplified equation as there are usually energy losses associated with the jet passing through an air space. However, in the present case, it can be assumed to be reasonably accurate as the jet length is only approximately 3 cm. The jet length may be low but energy losses are small, meaning all the momentum of the jet is transferred to the surface of the slurry below. This means that the bubbles will entrain to greater depths. This was shown by Kumagai et al (1993) as they correlated the data in terms of jet momentum (\( V_o d_o \)), and jet characteristics (\( L_j/d_o \)):

\[ H_p = 50 \left( V_o d_o \right)^{0.55} \frac{\left( L_j/d_o \right)^{1.5}}{(\sin \alpha)} \]  

where \( H_p \) is the depth of penetration (m) \( \alpha \) is the angle of inclination

The depth of penetration is proportional to the momentum and inversely proportional to the jet length. Hence, the system used in the first generator means the bubbles are quickly removed from the aeration zone where they can be retained by the louvre plates.

The process takes place within a confined space, and this has an effect upon the entrainment process. A rotameter was installed between the air inlet and supply cylinder. During the generation process, the air flow rate would rise to 0.1 l/min, remain there for approximately 5 seconds and then gradually drop back to zero. After a few seconds the cycle would start again. The cycle is attributed to the fact that the plunging jets entrain the air comfortably. When the pressure in the head space lowers more air is drawn into the generator (the rise to 0.1 l/min). As the system equilibrates again, the air flow to the system stops. If the jets could not entrain air quickly enough, then the level in the
generator would fall, until the jet length was sufficient to entrain air. These observations agree with those of Evans et al (1996).

The literature supports the findings from these observations and so it can be explained why bubbles form, but does not explain why these conditions did not work for the scaled-up generator. In the literature, there is general agreement that there are two distinct regions of bubble size created by the shear forces of a plunging jet (Ervine et al, 1980; McKeogh and Ervine, 1981; Bin, 1988, 1993; Evans and Jameson, 1995). The first consists of a conical zone containing fine bubbles of diameter 1 mm or less. These bubbles can penetrate relatively deeply due to momentum. The second region comprises larger bubbles which are subject to larger buoyancy forces.

In the second generator, all the conditions for entrainment were duplicated except for the fact that the velocity of the slurry in the open cross-section of each section was lowered. Under conditions where the slurry level was high, the bubbles were being entrained as expected, however, the number of jets was the same and so the rate of air entrainment per unit area had decreased. Hence air could not be entrained quickly enough to form the required bubble buffer layer.

Fig 2.11 shows a photograph of entrainment using clear water. The photograph shows many fine bubbles within the water, however, the larger bubbles are negligible in comparison; they only exist in the louvre channels where the flow is sufficient to stabilise them. To overcome this problem, the rate of entrainment had to be increased. The observations seen with the first generator and confirmed by Evans et al (1996) provided the answer. Bin (1993) stated that air entrainment rates are improved using longer jets with more surface disturbances. Experimental findings have supported this claim. By reducing the level in the generator to the height shown in Fig. 2.10, the jet length was sufficiently increased to improve air entrainment. The kinetic energy of the jet was dissipated by hitting the louvre plates, but not to a significant extent. This served to disrupt the jet surface which upon impact with the bulk slurry, created more interactions and so more air was entrained.
Many authors also believe that surface disturbed jets entrain air into the confines of the jet as they pass through a gaseous atmosphere (Burgess et al., 1972, Ervine et al., 1980, McKeogh and Ervine, 1981; Kusabiraki et al., 1992; Bonetto et al., 1994). This will also improve entrainment rates.

In this way, larger bubbles are formed more quickly and so can provide a buffer layer to protect newly formed bubbles from the air-water interface. This also means a lot of the generator space is wasted, but the increased size of the generator compensates.

The attempts to create stabilised bubbles were only on a small scale and dependent upon Weiss' original design. Smaller and larger quantities of bubbles could, in all probability,
be made using higher jet velocities, larger jet lengths and diameters. The main finding of these experiments on generator scale-up is that in any increase in size, the flow rate of the slurry supplied to the generator should also be increased proportionally.

However, it must be remembered that simply entraining air is insufficient to create stable bubbles. To do this requires a spreading agent (oleyl alcohol) and finely divided material (powdered activated carbon).

2.3.4 Bubble Stabilisation

The most important property of bubbles coated with activated carbon is that they retain their identity under conditions where they are constantly agitated by flowing water. The only methods of breaking the stabilised bubbles are by stopping the water flow - the bubbles coalesce at rates much slower than ordinary bubbles - or by introducing uncoated air bubbles which can interact with the coated ones - a chain reaction occurs, gradually collapsing the bubbles.

The method of creating air bubbles has been outlined previously. The durable nature of the bubbles is due to the coating of activated carbon upon the surface of the bubble. This phenomenon is only possible with the addition of oleyl alcohol.

In processes, such as dispersed-air flotation, there is a conditioning stage where the mineral to be floated is rendered hydrophobic by treating it with a hydrophobic spreading agent. This does not occur with the bubble generation process. The slurry is already pumping around the system before the oleyl alcohol is added. Hence, the conditioning of the activated carbon is in situ. Observation of the bubble generation process showed that the effect of adding oleyl alcohol is instantaneous. The air bubbles retain their integrity for longer than they normally would.

The initial bubbles that are formed are semi-stable, i.e., the bubbles are stable enough to prevent collapse at the air-slurry interface, but they are not fully coated and do eventually collapse. These bubbles are generally larger than those used in the process, and provide
the buffer zone to protect the smaller bubbles. The semi-stable bubbles must be coated with some particles to protect them from the rigours of generation.

Without oleyl alcohol, carbon coating is not possible, therefore it is a reasonable assumption that the oleyl alcohol is adsorbed by the PAC and renders it sufficiently hydrophobic to attach to the bubble. Activated carbon contains many sites available for adsorption and so as long as the alcohol molecule can enter the pores of the particle, the -OH functional group can attach to the available sites. The straight chain hydrocarbon backbone of the molecule provides the hydrophobic character to attract the carbon particle to the bubble surface. Why oleyl alcohol needs to be added dropwise has not been ascertained. This author speculates that it may be because the oleyl alcohol adsorbs onto a large number of particles, rather than a smaller number which may aggregate together.

In aqueous conditions, both the bubbles and carbon particles are negatively charged. By electrical double layer theory, the two negatively charged components should repel each other upon approach. This effect can be reduced by lowering the charge on one of the surfaces and the oleyl alcohol may perform this function to some degree. Several authors have claimed that such electrostatic forces cannot be the dominant mechanism and proclaim a preference for hydrophobic forces (Kitchener, 1984; Laskowski, 1986; Lu, 1991). The actual mechanism of hydrophobic attraction is unknown, but upon attachment it is known that the hydrocarbon backbone penetrates into the bubble. Results published by several authors have indicated that bubble-particle interaction cannot be explained by electrostatic and hydrophobic forces alone; there must be a reconciliation between the two mechanisms. A full understanding of this process is not yet available.

As well as the attractive forces that bind bubble and particle together, one must also consider the hydrodynamic forces that exist in the generator. The louvre channels create zones of shear below the plate which roll the bubbles in elliptical orbits before escaping. In this manner, the carbon particles are also coerced into approaching the bubble surface until the particle is at the critical distance at which the attractive forces interact.
According to Luttrell and Yoon (1992), the water film between the particle and bubble must be thinned in order for adhesion to occur. The hydrocarbon chains adsorbed on the particle surface would facilitate this process. The authors believed that the particle is mobile on the bubble surface before full attachment occurs. Under conditions of shear, this is certainly likely and so, the particles have to overcome the same shear forces to avoid detachment. This is possible if the contact angle of the particle is lower than the critical contact angle. Above this value, the disruptive forces would be too strong and the particle would be torn away from the bubble.

2.4 The Stable Bubble Contacting Column

2.4.1 Aims and Objectives

Stable bubble generation is a significant stage in the process. Collection of the bubbles in a two-dimensional column had shown that the bubbles were stable (see Fig. 2.9) and coalescence was negligible despite numerous collisions. Powdered activated carbon is a porous, versatile adsorbent, hence it seemed obvious to try and utilise carbon-coated bubbles for the removal of micropollutants from water. Weiss envisaged that adsorption on an industrial scale would be possible if the adsorbent exhibited fast kinetics and could be moved counter-currently to a polluted stream. Stabilised bubbles have a thin surface layer of adsorbent material and so will reach equilibrium much faster than a bed of granulated particles. Hence, higher throughput rates can be achieved. The underlying theory is covered in more depth in Chapter 5.

A quick test on a fluidised bed of coated bubbles in the two-dimensional column showed that negligible amount of pollutant (in this case phenol) was adsorbed by the carbon. This was attributed to the small amount of carbon inventory available at the bubble surface. It was decided that a new contactor was needed that could hold a larger volume of stable bubbles and hence a greater carbon inventory.
Chapter 2 - Process Development

A problem identified with the two-dimensional contactor was that carbon slurry was introduced from the generator during bubble transfer. The contactor would fill up with carbon slurry unless the flow rate was high enough to sweep the suspension out. It is obvious that a treated stream must not be contaminated by carbon suspension since this would negate any potential advantage of the process. This means that the new contactor must be designed to remove all the slurry before it is dosed with the polluted stream. It was assumed that coated bubbles would load with pollutant fairly quickly and therefore a method of removing exhausted bubbles (before new bubbles are introduced) must be devised. The distributor plate in the contactor must retain the bubbles efficiently and not allow air bubbles to form upon filling of the contactor with water. The next sections look at how these points were addressed.

2.4.2 The 50 mm diameter column

This contactor was made of 50 mm internal diameter QVF glass column sections, held together by bolted flanges. Using individual sections aided dismantling for cleaning and/or exchanging distributor plates. The dimensions of the column are shown in Fig. 2.12. In order to fluidise the bubbles successfully, the water must enter from the top. The top of the column was domed, consisting of an inlet pipe, internal diameter 17 mm, and two venting pipes, 10 mm in internal diameter. Before the bubbles can be collected, the column must be pre-filled with water. The domed section facilitated removal of the vented air near the top of the column, which proved more difficult with a flat top section.

The domed section was bolted to a section 300 mm in length, which was bolted to the housing for the distributor plate. The housing was a short cylindrical section made of PVC. The internal diameter was such that it fitted the glass sections above and below. The distributor plate sat on a ledge mid-point in the housing which was turned to fit snugly with the plate. A 10 mm i.d. PVC pipe was inserted into the wall of the section. The function of this pipe was to remove bubbles from the column as required. O-rings in the inner wall provided the seal. The base of the section was bolted to a long glass section, 800 mm in length.

111
Figure 2.12 - Diagram of the 50 mm diameter contacting column (all dimensions in mm)
Chapter 2 - Process Development

The long section was bolted to a glass expansion section, which increased the column diameter to 100 mm. This was attached to a PVC cylinder, 100 mm in diameter and 200 mm long. Inserted into the wall of the cylinder was a 25 mm diameter short length of pipe which served as the outlet to the column. The PVC cylinder was attached to a glass section which reduced the column diameter back to 50 mm. This was bolted to a 300 mm glass section. The base of the column was a 80 mm PVC disk to which was glued a PVC pipe, 25 mm diameter, which was 400 mm long and extended into the expanded section of the column.

Bubble transfer and collection was difficult prior to the installation of the expansion section. The transfer pipe connecting the generator and the column must be free of air, otherwise these air pockets will affect the stability of the bed of stable bubbles. This meant that this pipe must be back-flushed with water from the column before bubble collection. This was easily achieved by fitting a Saunders valve on the outlet of the column. The valve introduced a resistance to flow and increased the back-pressure in the column and forced water into the generator. Collecting the bubbles, however, proved to be more difficult. A flow rate of about 6 l min\(^{-1}\) (0.0001 m\(^3\) s\(^{-1}\)) was required to retain the bubbles beneath the distributor plate, but this flow rate excluded the bubble rise rate due to buoyancy. Bubbles could not overcome the pressure drop and enter the column. To overcome this, the column expansion was fitted. Doubling the column diameter, reduced the superficial flow velocity four-fold and the hydrodynamic pressure at this point in the column. By installing a pipe so that the bubbles entered at the expansion point, collection of the bubbles was readily achieved. When the bubbles entered the 50 mm diameter section of the column, the superficial velocity increases, retaining the bubbles below the distributor plate.

The flow rate range at which the column could operate was limited to 6-10 l min\(^{-1}\) (0.0001 - 0.000167 m\(^3\) s\(^{-1}\)). The process would be more versatile if novel distributor plates could be designed to retain stable bubbles at low flow rates, particularly in hydrodynamic fluidised bed tests and adsorption tests. Initial designs had attempted to use the louvre concept to retain the bubbles. It was thought that the increased superficial velocity and hydraulic shear created by the plate may be sufficient to retain the bubbles.
However, the bubbles easily passed through the plate irrespective of flow rate.

Bubbles were retained in the domed section of the column by the water entering at the inlet. From this observation, it was assumed that the velocity in the column inlet was sufficient to counter-balance the bubble rise velocity. Calculations were made to find the velocity and Reynolds number for flow rates in the range $1 - 10 \text{ l min}^{-1}$ in the inlet. The calculations showed that at flows of $3 \text{ l min}^{-1} (0.00005 \text{ m}^3 \text{s}^{-1})$ and above, the Reynolds number was above 3000. A decision was made that all plates should be designed so that the flow through an individual channel should satisfy the $\text{Re} > 3000$ criteria.

A spreadsheet was constructed to calculate the Reynolds numbers for plate designs with various numbers of holes and hole diameters. The minimum number of holes was four and this was increased up to ten in various combinations. Hole diameters were chosen to be 4, 5 or 6 mm. Calculations showed that the lower the free area of the plate, the higher the Reynolds number. Consequently, a plate consisting only of four 4 mm diameter holes would best retain a bed of coated bubbles. However, this proved not to be the best practical design. It was difficult to fill the column from the top with this design and also it was easy to introduce air bubbles which would interfere with bed stability. More successful designs are shown in Fig. 2.13. Design a) was used for regular experiments as air bubble formation was significantly reduced with this plate.

The column was incorporated into the process as shown in Fig. 2.1 except that there was only one bleed pipe below the plate and one outlet from the column. Tank T3 was increased to hold at least 100 litres of water. Coated bubbles were collected from the generator section above the bottom louvre plate. Care was taken not to collect any bubbles from the buffer zone, as these bubbles were too unstable. A series of hydrodynamic expansion tests were performed on the fluidised beds (see Chapter 3) and preliminary bed adsorption trials (see Chapter 5) were performed with this column.
Figure 2.13 - Various distributor plate designs for the 50 mm diameter column
2.4.3 The 100 mm diameter column

No discernible adsorption took place in the 50mm fluidised bed column. (see Chapter 5). Possible reasons for this are short contact time, inadequate carbon inventory, rapid exhaustion of carbon, excessive pollutant concentration in feed stream and single column operation. It was decided to build a larger column to provide a still larger bed bubble inventory. With this came the realisation that the column had not been operated truly counter-currently. The stream had passed over the stable bubble bed and fluidised it, but as only one stage existed in the column, it could not be operated counter-currently. The option to increase the number of stages was incorporated into the new design.

Fig. 2.14 shows the design of the 100 mm diameter column. The design criteria followed the same philosophy as the 50 mm diameter column. The column must be easy to assemble and dismantle, for cleaning purposes and for inserting new distributor plates. The base of the column included an expansion to 150 mm to aid bubble collection and a 25 mm pipe at the bubble inlet. Unlike the 50 mm column, this was open to atmosphere. This was so that a weir system could be incorporated to collect spent bubbles. The idea was that bubbles passing through the column would eventually reach the air-water interface and collapse, forming a stable froth. By controlling the level in the column, the froth would overflow the weir into a catchment cylinder, 150 mm in diameter. The base of the cylinder was tilted so the froth could be washed out of the system. Then, the froth could be filtered and the amount of carbon utilised assessed. Air bleeds were also positioned below each distributor plate. They were primarily used to remove unwanted air bubbles, but if necessary they could be used to collect beds of stable bubbles.

The entire column was constructed of perspex. The main body was made of four 500 mm lengths of perspex tubing. Two of each length were taken and assembled using drain-pipe connectors. O-rings inside the connector formed a water-tight seal. The two 1000 mm lengths were then combined using a flange through which the two sections could be bolted together. The first distributor plate sat at this flange. The weir section was bolted to the top of the column at the point where the top distributor plate would sit. Two PVC sections were milled to provide the expansion to and reduction from the 150
Figure 2.14 - Diagram of the 100 mm diameter contacting column (all dimensions in mm)
mm diameter cylinder where the column outlet was positioned. The column height was over 3 metres.

Sample points were incorporated in the walls of the column. Silicone rubber seals were push-fitted into the walls at the top of the column, above the bottom plate and at the base of the column. Samples could be taken from various points in the column using hypodermic syringes, which could then be analysed for pollutant concentration.

The distributor plates were designed on the same principle as the plates for the 50 mm column. The free area was assumed e.g. 6%, 8% or 10%. The diameter of a channel was then assumed, e.g. 5 or 6 mm. Using these parameters, the number of holes required to give a specific free area was calculated. Then, the Reynolds number was calculated for each plate at various flow rates from 10 to 20 l min$^{-1}$. The results calculated showed a marked decrease in Reynolds number, i.e. below Re=3000. It was decided to try two particular designs; one being the bottom plate, the other being the top plate. These designs are shown in Figs. 2.15 and 2.16. The lower plate (Fig. 2.15) had 6 mm diameter holes and retained the bubbles well. Stable bubbles were collected at 10 l min$^{-1}$ (0.00016 m$^{3}$s$^{-1}$). At flow rates below this, bubbles would pass through the plate. The upper plate (Fig. 2.16) consisted of channels 5 mm in diameter and so had a smaller free area than the lower plate. This meant, in theory, that bubbles could be retained below this plate at a lower flow rate. This meant bubbles could be passed from one stage to another by lowering the flow rate in the column. Experimental trials on attaining counter-current flow are described in Section 2.5.

The new rig was on a much larger scale and so new pipework to and from the column had to be constructed. Fig. 2.17 shows a schematic of the process. All pipework was 25 mm diameter and made from PVC. To run experiments over a prolonged period, larger feed tanks were required. Two 150 litre tanks (T1 and T2) were piped together to provide the feed. A ball valve (V5) was positioned between the tanks so one could be shut-off if necessary.
Figure 2.15 - A distributor plate design used in the 100 mm diameter contacting column (all dimensions in mm)
Figure 2.16 - A distributor plate design used in the 100 mm diameter column
(all dimensions in mm)
Figure 2.17 - Schematic of the Bubble contacting process constructed for the 100 mm diameter column
Chapter 2 - Process Development

It was imperative that the stable bubbles were collected in clean water and not contaminated since this would affect results by immediate adsorption. The system had to be flexible and allow an additional clean water source. A mains water supply was connected to the column via a stop-cock (V3). A flow meter was also installed in-line to measure the flow rate entering the column. It was difficult, however, to fill the column from the top, so the pipework was adjusted so that the column could be filled from the bottom by the mains water supply. This had the added advantage that air bubble formation at the distributor plates was kept to a minimum during filling of the column.

The weir design at the top of the column meant that the level of water in the column must be kept constant. The water level was controlled by setting the inlet flow rate and throttling the outlet valve (V2). Once the level was steady, collection of the bubbles could begin. There were problems with this system. The entire process was operated manually, as the cost of automatic control could not be justified at this stage. The height of the column and the associated pipework meant that two people were required to operate the process manually. One was positioned at the top of the column to operate the flow into the column and watch the level in the column. The other operated all ground level equipment and, by consultation with the other operator, ensured the level was constant by operating valve V2. This required constant dialogue between the two. Another problem associated with level control, was that the mains water flow fluctuated occasionally. This meant constant vigilance was required to ensure that the level in the column did not drop too low.

Sample points (sp1, sp2 and sp3.) were also installed in the pipework, along with those in the column (sp4, sp5 and sp6). The samples collected from these points were taken to measure the pollutant concentration entering and leaving the column. Samples were collected in small plastic bottles, which were attached to the pipework. Each sampling point was connected to a solenoid valve which when switched on, allowed the sample to enter the bottle.
2.4.4 Transfer of stable bubbles between the generator and the column

Transferring stable bubbles between the generator and the 50 mm diameter column had not caused any problems. The pressure supplied by the compressed air was able to overcome the pressure in the column. By opening the valve in the tube between the two items of equipment, the bubbles would rise up into the column under buoyancy forces. With the 100 mm diameter column, this process was more complicated. The height of water in the column was close to 3 metres. Combining this with the fact that the column was open to atmosphere, there was no possibility of the bubbles transferring in the same manner. The static pressure head was too large. An alternative transfer method was sought.

Mechanical pumps such as centrifugal or piston pumps, would destroy the stabilised bubbles. A less energetic method was required, hence a peristaltic pump was tested. Using a series of rollers, the tube connecting the generator and column was squeezed, sucking the bubbles in one side and forcing them out the other. The pressure at which the bubbles are supplied is set by the width of the gap between the roller and the pin, upon which the tube rests. The smaller the gap, the greater the pressure. The flow rate was set by the speed of revolution of the peristaltic head. It was assumed that if the right combination of gap width and r.p.m. could be found, then the stable bubbles could be pumped without damage to. In practice this proved impossible. If the gap was too small, the bubbles would collapse and a mixture of air bubbles and slurry enters the column. If the gap was opened to a width such that the bubbles would not collapse, the driving pressure was insufficient to force the bubbles into the column. Increasing the peristaltic head speed had no effect.

The most successful method of transferring bubbles used a technique developed for the 50 mm diameter column. Fig. 2.18 shows the apparatus involved. A small column, known as the bubble feed hopper, was made of 50 mm diameter. The domed section of the original column was used as the top piece. The domed section sat on top of a 50 mm diameter PVC cylinder which had a 12 mm diameter pipe protruding out of the side. This pipe was the bubble inlet to the column. Below this was a 300 mm length of QVF
Bubbles enter column by feed pipe

Figure 2.18 - The coated bubble feed hopper used for transferring bubbles to the column

Flow agitates bubbles

Figure 2.19 - The stabilised bubbles are agitated by water supplied to the hopper by a spout
Chapter 2 - Process Development

glass, 50 mm in diameter. A base section was also made from PVC which had two 12 mm diameter outlet pipes. All sections were bolted together. The main inlet to the feed hopper was attached via a 25 mm ball valve to the base of the column by a robust length of plastic piping.

For coated bubbles to remain stable, they must enter the column by buoyancy, i.e. no external force must be used. In order to do this, the bubbles must be able to overcome the pressure in the receiving vessel. The original 50 mm diameter column was enclosed and so the water flowing down the column acted as a siphon. Hence, the pressure in the column was lower than that in the generator and the coated bubbles could enter by buoyancy. This is also true for the bubble feed hopper.

By opening the tap (t1), shown in Fig. 2.18, the bubbles rose into the hopper at the bubble inlet. The bubbles filled up the hopper until the required amount was collected. Naturally the slurry also enters the column, but this is swept out with the down-flowing water. Once ready, the outlet valve (t3) is closed and the ball valve (V) above the hopper is opened simultaneously. This forces the stable bubbles into the column where they are retained by the bottom distributor plate. This cycle was repeated if more bubbles were required.

The bubbles had to be agitated in the hopper to remain stable. For the majority of the bubbles this was achieved by the down-flowing water stream. However, a minority of bubbles sat in a static area of piping just below the ball valve. These bubbles also needed to be agitated otherwise they would coalesce, forming an air-lock in the pipe which would be transferred to the column. This was achieved using the system shown in Fig. 2.19.

The water supply came from mains water, which was attached to the hopper by a length of 12 mm diameter tubing. Inserted into this tubing was a cylindrical PVC adaptor which was bored down the middle to an internal diameter of 5 mm. A length of 5 mm diameter tubing was push-fitted into the adaptor and the tubing was manipulated in the hopper to form a spout below the ball valve. The water feed to the column would have
to enter via this spout which would fluidise the bubbles in this area and reduce the chance of coalescence.

![Figure 2.20 - Stabilised and uncoated bubbles entering the 100 mm diameter column](image)

The system worked reasonably well. The formation of large air-locks which would collapse the bed was prevented. However, the stability of the bubbles was affected to some degree. Fig. 2.20 shows some bubbles which have entered the column and are just about to join the bubbles retained below the plate. The photograph shows a variation in appearance of the bubbles. Some are black, as expected, but the majority show a variation in colour, from grey through to clear. It is therefore reasonable to assume that some of the coating has been stripped from the bubble surface, or uncoated air bubbles, which could not be back-flushed from the pipes, were also entering the column. The effect on bed stability was minimal for the residence times required for an adsorption process, but this would obviously affect the adsorption capacity of the collected bed.
2.5 Examining the possibility of counter-current flow

For a continuous adsorption process to be effective, the adsorbent material must be moved swiftly against the stream to be treated in a vessel. The literature contains several attempts at achieving counter-current flow with granulated material and these were covered in Chapter 1. Loading finely divided material on a low density, non-porous sphere enables movement of the adsorbent material to be achieved more easily. In this process, bubble buoyancy provides the motion against the counter-current water stream. The difficulty arises in retaining bubble integrity during transfer to the column.

Fig. 2.18 shows a diagram of the equipment used to transfer the bubbles. This method was partially successful; bubble transfer was possible but uncoated bubbles were entering the column also (see Fig. 2.20). Hydrodynamic experiments were performed on the fluidised bed of bubbles collected (see Chapter 3). The next aim was to see if the bubbles could be moved continuously through the column. Fig. 2.21 shows how a typical bed of bubbles would appear in the column. The bubbles are retained at plate dp2 (lower stage) and quickly classify with the largest bubbles (diameter approximately 2 mm) retained just beneath the plate and the smallest bubbles (approximately 0.5 mm in diameter) furthest away from the plate. An interesting phenomenon was that the smallest bubbles did not join the fluidised bed, but were continuously moving up and down the column, as shown in Fig. 2.21.

Fig. 2.22 shows a photograph of how a collected fluidised bed appears. The scale to the right of the photograph was used to measure the bed depth at various flow rates. The movement of the bubbles can be seen in the swirling patterns at the walls of the column. Below the bed, many tiny bubbles can be seen which do not become part of the fluidised bed, but a good interface can be seen at the bottom of the fluidised bed, enabling readings to be taken more easily.

An ideal method of moving the bubbles counter-currently would be to continuously feed them to the column. Unfortunately, the transfer of the carbon suspension into the column with the bubbles ruled out that possibility.
Figure 2.21 - The appearance of a fluidised bed of stabilised bubbles
Hence, the stabilised bubbles had to be collected in batches. Collected fluidised beds were of the depth, 13 - 18 cm, insufficient to effectively treat large quantities of contaminated water. Attempts were made to increase the bed size by loading more batches of bubbles. As a result, the bed depth would increase marginally, but not by a significant amount. This was due to uncoated air bubbles destabilising the coated bubbles. Trials had shown that addition of new bubbles from the feed hopper, to current fluidised bubbles exacerbated bed instability. An alternative was to transfer the fluidised bed to the next stage and then allow a new batch to enter the column, i.e. the fluidised bed is retained in the bottom stage, then transferred to the top stage and then new bubbles enter the bottom stage. This method of moving the bubbles is called a semi-batch cycle.
Initially, the method was attempted by lowering the flow rate. It was thought that at a certain flow rate, buoyancy would prevent the bubbles being retained at the plate and they would rise through. However, once the flow rate was lowered, the column began to drain. To compensate, the outlet valve V2 was throttled. This stopped the column draining and also equalised the pressure on both sides of the plate, hence the bubbles would not pass through. An attempt was made to push the bubbles through the plate, by throttling valve V2 further, but this only served to raise the level in the column and caused flooding.

The only successful method of moving the stable bubbles between the stages was by halting the flow instantaneously in the column. With reference to Fig. 2.17, valves V2 and V3 were simultaneously closed, allowing the bubbles to pass through the plate due to buoyancy. Once the first of these bubbles reached the top plate, both valves were opened and the bubbles were retained once again. This worked well but only a proportion of the bed was transferred to the top stage. This result showed that only small beds could be collected and transferred in this manner. In order to provide sufficient loading, many stages would be required and the bubbles would have to be moved swiftly through the column. This requires the bubble generator to produce large quantities of bubbles quickly. The current design does not allow this.

Hence, for the column adsorption trials, experiments were carried out on a single fluidised bed retained in the bottom stage. Significant water decontamination was not expected, but the adsorption isotherms showed nominal adsorption should occur (see Chapter 4). Experiments were performed to verify this (see Chapter 5). Chapter 6 will include some recommendations on how the problems associated with this particular column might be overcome.
Chapter 3 - The Hydrodynamics of Inverted Fluidised Beds

3.1 Theory

3.1.1 Modification of the standard drag curve

The fundamentals of fluidised bed hydrodynamic behaviour were introduced in Chapter 1 with particular reference to inverted fluidised beds, i.e. liquid-solid systems where the density of the particles, \( \rho_p \), is less than the density of the fluidising liquid, \( \rho_l \). A review of the pertinent literature revealed that inverted fluidised beds can be related to conventional systems by the Richardson-Zaki equation, provided the drag coefficient, \( C_D \), is modified. Only Karamanev and Nikolov have successfully modified the Richardson-Zaki equation for inverse beds. This section will look at the equations describing hydrodynamic behaviour and how they can be used in assessing expansion data.

As explained in Chapter 1, models describing hydrodynamic behaviour come in three types. The type I model relates the dependence between \( \frac{U}{U_i} \) and \( e \) - the Richardson-Zaki (1954) model being the most popular of this type. This equation has already been shown to be:

\[
\frac{U}{U_i} = e^n
\]                                               \hspace{1cm} (1.19)

where \( U \) is the observed fluidising velocity (ms\(^{-1}\))
\( U_i \) is the superficial fluidising velocity at \( e = 1 \) (ms\(^{-1}\))
\( e \) is the voidage (or porosity) of the system
\( n \) is an index.

The unknown values in this equation are \( U_i \) and \( n \). \( U_i \) was found to correspond closely to the particle terminal velocity, \( U_t \) for sedimentation and was related by the following expression for fluidisation by Richardson and Zaki (1954):

\[ U_i = U_t e^n \]
Chapter 3 - Bed Hydrodynamics

\[ \log_{10} U_i = \log_{10} U_t - \frac{d}{D} \]  \hspace{1cm} (3.1)

where \( d \) is the particle diameter (m) and \( D \) is the tube or column diameter (m). The value of \( U_t \) is calculated by equating the gravitational force (\( F_g \)) to the drag force (\( F_d \)) on the particle, i.e.

At the terminal velocity \( U_t \), \( F_g = F_d \)

\[ \pi d \left( \frac{\rho_p - \rho_l}{6} \right) g = \frac{C_D}{2} \left( \pi d^2 \right) \rho_l U_t^2 \]  \hspace{1cm} (3.2)

By rearranging in terms of \( U_t \), the result is:-

\[ U_t = \sqrt{\frac{4 \left( \frac{\rho_p - \rho_l}{3 C_D \rho_l} \right)}{g d}} \]  \hspace{1cm} (3.3)

The drag coefficient, \( C_D \) is determined from the standard drag curve which is shown in Fig. 3.1 - the dependence \( \ln(C_D) - \ln(Re_t) \), where \( Re_t \) is the particle Reynolds number at the terminal settling velocity, as defined by \( (d U_t \rho_l / \mu) \).

\[ \text{Figure 3.1 - The standard drag curve for settling (continuous line) and rising spheres (dotted line)} \]

(Source - Karamanov and Nikolov, 1992[a])

132
Richardson and Zaki found, by dimensional analysis, that the value of the index, $n$, is dependent upon $Re_t$ and the ratio $d/D$ for spherical particles. The index, $n$ is given by the following correlations:

\begin{align*}
\text{for } 1 < Re_t < 200 & \quad n = \left( 4.4 + 18 \frac{d}{D} \right) Re_t^{-0.1} \quad (3.4) \\
\text{for } 200 < Re_t < 500 & \quad n = 4.4 Re_t^{-0.1} \quad (3.5) \\
\text{for } Re_t > 500 & \quad n = 2.4 \quad (3.6)
\end{align*}

By plotting values of $\log(e)$ against $\log(U)$, the bed expansion characteristics of a fluidised bed can be illustrated. If the experimental data lies on a straight line, then the expansion behaviour obeys the Richardson - Zaki model (Eq. 1.19). It is worth noting that the Richardson - Zaki model applies best to monosized particles (due to the ratio $d/D$). During fluidisation experiments involving a bed of a significant size range, stratification occurs with the largest particles forming a bed of low voidage near the bottom and the smallest particles a bed of high voidage near the top. Segregation becomes virtually complete with well defined size ranges, and in effect, a bed is produced which consists of a series of fluidised beds of different voidages, one on top of the other.

The key component in the success of the Richardson-Zaki model is the accuracy of the value of the drag coefficient, $C_D$. The standard drag curve is experimentally determined for systems where settling occurs when $\rho_p > \rho_l$ and so the accuracy of the model is assured for particles of density greater than 1000 kgm$^{-3}$ when fluidised by water. As an alternative method of calculating the value of $U_t$, Eq. 3.7 is often used as a correlation for the standard drag curve in the range $12.2 < Re_t < 6350$ (Clift et al, 1978):

\[
\log(Re_t) = -1.814 + 1.347 \log(N_D) - 0.1243(\log(N_D))^2 + 0.00634(\log(N_D))^3 \quad (3.7)
\]

where $N_D$, the Best number, is defined as :-
\[ N_D = C_D \text{Re}_t^2 = \frac{4}{3} \rho_i \left( \frac{\rho_p - \rho_i}{\mu^2} \right) g d^3 = \frac{4}{3} Ga \] \hspace{1cm} (3.8a)

where Ga is the Galileo number.

The earliest attributed attempt at using the type I model to correlate inverted fluidised beds is due to Fan et al (1982). They redefined the correlations for \( n \), but do not mention how \( U_t \) was calculated. It is assumed that Eq. 3.7 (i.e. the standard drag curve) was used to calculate \( U_t \) with the modification that \( \rho_p < \rho_i \). In this case Eq. 3.8a becomes:

\[ N_D = \frac{4}{3} \rho_i \left( \frac{\rho_p - \rho_i}{\mu^2} \right) g d^3 = \frac{4}{3} Ar \] \hspace{1cm} (3.8b)

where Ar is the Archimedes number, for systems where \( \rho_p < \rho_i \) (note reversal of terms in Eq. 3.8b).

Fan and co-workers found that their correlation predicted bed expansion in the range \( \text{Re}_t < 500 \) and the coefficient of variation for \( n \) was 8%. Nikolov and Karamanev attempted to predict bed expansion in a series of papers (Nikolov and Karamanev, 1992 [a], [b]) but found it necessary to experimentally determine the standard drag curve for particles less dense than water. The authors found that "light" particles (i.e. those with a density less than water) with a density greater than 900 kgm\(^{-3}\) still obeyed the standard drag curve, but those particles with a density less than 300 kgm\(^{-3}\) deviated radically from the drag curve. This deviation is shown in Fig. 3.1. In the range \( 130 < \text{Re}_t < 9 \times 10^4 \), the value of \( C_D \) remained constant at 0.95. Nikolov and Karamanev then attempted to predict the expansion of an inverted bed using this modification in order to find \( U_t \). They propose that the standard drag curve for rising spheres with a density below 300 kgm\(^{-3}\) is given by the expression:

\[ \log(\text{Re}_t) = -1.814 + 1.347 \log(N_D) - 0.1243(\log(N_D))^2 + 0.00634(\log(N_D))^3 \] \hspace{1cm} (3.7)

for \( 12.2 < \text{Re}_t < 130 \)
and by manipulating Eq. 3.8a,

\[ \text{Re}_r = \sqrt{\frac{N_D}{0.95}} \]  

(3.9)

for \( 130 < \text{Re}_r < 9 \times 10^4 \).

Karamanev and Nikolov fluidised a series of inverted beds consisting of mono-sized polystyrene spheres. They found that the experimental data followed the values predicted by the correlation closely, especially the experimental and predicted values of \( U_i \), confirming the legitimacy of using a modified drag curve for rising spheres (see Fig. 3.2). In this manner, Karamanev and Nikolov proved that inverted fluidised beds can be characterised by Richardson-Zaki, provided the hydrodynamic properties of rising spheres are taken into consideration.

![Graph](image)

**Figure 3.2** - A comparison, by Karamanev and Nikolov, of the expansion data for an inverted stabilised bubble bed and the modified Richardson-Zaki equation. Mean particle Size - 3.46 mm, Particle density - 75 kg m\(^{-3}\), Column Diameter - 80 mm (Source - Karamanev and Nikolov, 1992 [6])
3.1.2 Stabilised air bubbles

Observation of the collected beds of stabilised, carbon-coated air bubbles led this author to believe that the stabilised bubbles were behaving as an inverted fluidised bed. An increase in the liquid flow rate produced an increase in the bed depth, as expected of a fluidised bed. This led to a question: can stabilised bubbles be characterised by the Richardson-Zaki model? A model was developed, based upon the theory proposed by Karamanev and Nikolov, for various inverted beds of mono-sized spheres, fluidised in columns of differing diameters (i.e. D = 50, 67 and 100 mm). The results of this model are shown in Figs. 3.5, 3.9 and 3.12. In order to assess the hydrodynamic characteristics of the bubbles, the experimental data must be compared with this model.

However, the data from the experiments is collected in terms of the fluidised bed depth. In order to satisfactorily compare the data and model, the data must be converted into the bed voidage, \( e \). Measurement of the bed voidage is difficult for the following reasons:

- the fragile nature of the bubbles means no probes or devices can be inserted into the column
- the bubbles cannot be collected at zero flow rate as they will not be retained by the distributor plate
- or, if the plate has small enough holes to retain the bubbles, coalescence of the bubbles will occur rapidly under static conditions. Hence no measurement of the minimum bed depth can occur

(Note: the difficulties of retaining the stabilised bubbles are discussed in Chapter 2).

In each experiment, the bed of stabilised bubbles was collected at a minimum allowable flow rate. The bed depth at this flow rate is referred to as the initial bed depth, \( h_0 \). However, in order to calculate the voidage of the bed under conditions of increasing liquid velocity, an assumption had to be made as to what the voidage of the bed is at \( h_0 \).

This can be achieved by considering the packing arrangement of the bubbles in the bed. In conventional fluidised beds, the initial packing array is dependent upon the shape, surface roughness and rate of addition to the column of the particles. According to Leva...
(1959), the resulting bed is more dense when the particles are added slowly to the
column and the particles are smoother. In this experiment, the stabilised bubbles are
added reasonably slowly, are spherical once collected and relatively smooth in
comparison to granular particles.

Zenz and Othmer (1960) also stated that the initial voidage of a fluidised bed is
dependent upon the packing array. They described the value as falling between two
extremes. The most open form of packing of a bed of uniform spheres occurs when they
are arranged in a square array with each layer directly above the other (see Fig. 3.3).

![Figure 3.3 - A number of spheres packed in a square array. This arrangement produces the maximum voidage](image)

In this arrangement, the void fraction is approximately 48 percent. The closest packing
occurs when the particles are arranged in a triangular array. Each layer of particles is
offset from the one below so that each particle sits in a pocket formed by the particles
below (see Fig. 3.4).

![Figure 3.4 - Rhombohedral packing. This arrangement produces the closest packing](image)
This arrangement is called rhombohedral packing and produces a void fraction of 26 percent. The larger the particles and the closer they are to spheres, the greater the likelihood that they will exhibit a voidage between 26 and 48 percent. If, however, the size range of the particles varies considerably, there is a greater chance that the voidage will exceed either range extreme.

Further evidence for the value of voidage required is provided by Leva (1959). He provided a chart showing the voidage as a function of the particle and column diameters (d/D), for various materials including smooth uniform spheres. In the range $0.05 < d/D < 0.2$, the void fraction varies from 0.35 - 0.41. The majority of $d/D$ values used in the Richardson-Zaki model are within the range $0.05 - 0.2$.

In the model used to compare the experimental data with Richardson-Zaki, the value of $e=0.4$ has been chosen. This is for several reasons:-

- It lies within the range 26-48%.

- The spherical nature of the bubbles, the slow rate of charging of the bed and their natural buoyancy means the bubbles will form a close packing formation. However, the bed is collected at a minimum flow rate which means that the bubbles will be gently fluidised, resulting in expansion above the minimum possible bed volume.

- The collected bed contains a gradation of bubble sizes which will increase the value of $e$.

- In their paper on liquid-solid inverse fluidised beds, Karamanev and Nikolov (1992[b]) found that their polystyrene spheres retained a minimum voidage of 0.4 or 0.41. It must be noted, however, that the fluidised beds in this case were mono-sized.

It is realised that the value of 0.4 is empirical but it is a reasonable estimate of voidage at the point of collection.
In order to calculate the voidage for each bed depth, the volume of the bubbles must be considered. At a bed depth of $h_0$, the volume of bubbles must be equal to the volume at a bed depth of $h_1$, i.e.,

$$A_h(1-e_o) = A_h(1-e_1)$$  \hspace{1cm} (3.10)

where $A$ = the cross-sectional area of the column ($m^2$)

$h_0, h_1$ = the initial and current bed depth respectively ($m$)

$e_o, e_1$ = the bed voidages at $h_0$ and $h_1$ respectively.

Equating,

$$\frac{h_o}{h_i} = \frac{(1-e_i)}{(1-e_o)}$$  \hspace{1cm} (3.11)

Therefore,

$$e_i = 1 - \frac{h_o}{h_i}(1-e_o)$$  \hspace{1cm} (3.12)

Values of $h_o$ and $h_i$ are gathered during the experiment and $e_o$ is taken as 0.4. Therefore at any bed depth, the voidage can be calculated. An example of this is shown in Appendix 2 along with other sample calculations, including how to calculate the Richardson-Zaki model.

3.2 Experimental Method

3.2.1 Experimental apparatus and materials

The bed hydrodynamic experiments were performed in three contacting columns. The 50 mm and 100 mm diameter columns are described comprehensively in Chapter 2, but
there was also a flat-walled column, known as the 2D column, which was used primarily for observation and photography of the bubbles and consisted of a rectangular perspex box, 140 mm by 25 mm by 500 mm. To make things simpler regarding the calculations, the cross-sectional area was calculated and based on a cylindrical geometry, the 2D column was given an effective diameter of $D = 67$ mm. The 2D column was superseded by the 50 mm and 100 mm diameter columns. To read the depth of the fluidised bed, a scale was fixed to each column and calibrated for the purposes of accuracy.

The only materials used were those required for generating stable bubbles, i.e. finely divided powdered activated carbon (sieved to a size range 0 - 53 μm), oleyl alcohol and mains water to prepare the slurry and fluidise the bubbles in the column. The physical properties of each substance are given in Chapter 2.

### 3.2.2 Experimental Method

The process schematic for the experiment is shown in Fig. 2.1. The stabilised bubbles were generated in the bubble generator (BG) in the usual manner. Once ready they were transferred to the contacting column and retained below the distributor plate. Transfer of the bubbles from the 2D and 50 mm column required opening valve V3 - the bubbles moved to the column due to their buoyancy. Transfer to the 100 mm column was more complex and required transferal to a feed hopper first before moving to the column. This apparatus is shown in Fig. 2.18 in Chapter 2.

The bubbles were collected at a minimum flow rate. For the 2D column this varied from 0.5 - 3.8 l min$^{-1}$. For the 50 mm column this was 3 l min$^{-1}$ and for the 100 mm column this was 10 l min$^{-1}$. This flow rate was the lowest at which the bubbles could be transferred without passing through the retaining plate. A reading was taken of the depth of the fluidised bed at this flow rate via the calibrated scale. The experiment proceeded with the flow rate increased incrementally and the bed depth observed at each point.
Chapter 3 - Bed Hydrodynamics

Various initial bed depths were tried to see if this affected the bed hydrodynamics. After each experiment the stable bubbles were removed via the bleeds in each column, which were positioned beneath the distributor plate.

From the data compiled, graphs were produced plotting the voidage of a bed, e, against the liquid velocity, $U \text{ (ms}^{-1})$ of the fluidising water. This enabled direct comparison of the results from all the columns.

3.3 Results

This section provides the results for the expansion of beds of various depths in different columns. The results are produced as follows:-

Figs. 3.5 - 3.8 - expansion results for beds in the 2-D column
Figs. 3.9 - 3.11 - expansion results for beds in 50 mm diameter column
Figs. 3.12 - 3.15 - expansion results for beds in 100 mm diameter column

The cross-sectional shape of the 2-D column was rectangular, of dimensions length - 14 cm and width - 2.5 cm. In order to calculate the Richardson-Zaki model for Figs. 3.5 - 3.8, an effective hydraulic diameter was calculated based on the cross-sectional area. Hence, for the model the 2-D column was considered to be cylindrical with an effective diameter of $D = 67 \text{ mm}$.

Sample calculations of how the figures were produced are shown in Appendix 2.
Figure 3.5 - Predicted inverted bed expansion for monosized spheres in the 2-D column (D = 67 mm) using Richardson-Zaki

![Graph showing predicted inverted bed expansion for monosized spheres in a 2-D column. The graph plots voidage (e) against liquid velocity (U) for different particle sizes (d). The particle sizes are indicated as: 0.5 mm (solid line), 1.0 mm (dashed line), 1.5 mm (long-dashed line), 2.0 mm (dash-dot line), and 4.0 mm (dotted line).]
Figure 3.6 - Comparison of experimental data and Richardson-Zaki correlation for an inverted fluidised bed (initial depth = 14.3 cm) in the 2-D Contactor (D = 67 mm)
Figure 3.7 - Comparison of experimental data and Richardson-Zaki correlation for an inverted fluidised bed (initial depth = 13.5 cm) in the 2-D contactor (D = 67 mm)
Figure 3.8 - Comparison of experimental data and Richardson-Zaki correlation for an inverted fluidised bed (initial depth = 9.5 cm) in the 2-D Contactor (D = 67 mm)
Figure 3.9 - Predicted inverted bed expansion for monosized spheres in a column of diameter (D) 50 mm using Richardson-Zaki

- Liquid Velocity, $U$ (ms$^{-1}$) vs. Voids, $e$
- Particle Size (d) vs. Voids, $e$
  - 0.8 mm
  - 1.0 mm
  - 2.0 mm
  - 3.0 mm
  - 4.0 mm
  - 6.0 mm
Figure 3.10 - Comparison of experimental data and Richardson-Zaki correlation for an inverted fluidised bed (initial depth = 13.0 cm) in a column of diameter (D) 50 mm.
Figure 3.11 - Comparison of experimental data and Richardson-Zaki correlation for several inverted fluidised beds in a column of diameter (D) 50 mm
Figure 3.12 - Predicted inverted bed expansion for monosized spheres in a column of diameter (D) 100 mm using Richardson-Zaki

Particle Size (d)
- 0.5 mm
- 1.0 mm
- 2.0 mm
- 3.0 mm
- 6.0 mm
Figure 3.13 - Comparison of experimental data and Richardson-Zaki correlation for an inverted fluidised bed (initial depth = 14.6 cm) in a column of diameter (D) 100 mm
Figure 3.14 - Comparison of experimental data and Richardson-Zaki correlation for an inverted fluidised bed (initial depth = 12.9 cm) in a column of diameter (D) 100 mm
Figure 3.15 - Comparison of experimental data and Richardson-Zaki correlation for an inverted fluidised bed (initial depth = 4.7 cm) in a column of diameter (D) 100 mm
3.4 Evaluation of the expansion data for inverted fluidised beds

Figs. 3.5, 3.9 and 3.12 show how fluidised beds of particles are predicted to behave according to the Richardson-Zaki model. The model predicts the expected behaviour; the smaller stabilised bubbles are expanded further than the larger bubbles due to their lower buoyancy forces. The packing arrangement of the bubbles would also dictate that a bed of larger bubbles would produce a lower voidage (Zenz and Othmer, 1960). Each particle size is represented by a straight line (on log-log paper) with the smaller bubbles showing the largest voidage.

The slope of each line represents the exponent, n. Hence, the variation in slope for particles up to 3.0 mm in diameter. Above 3.0 mm, the slope is independent of bubble size, representing an n value of 2.4. All the lines therefore lie very close and parallel to each other. The distance between each line depends upon the variation in the superficial velocity, $U_i$, which represents the intercept at e = 1.

In their series of papers, Karamanev and Nikolov (1992, [a],[b]) compared their expansion data with the results predicted by Richardson-Zaki. By using polystyrene spheres as particles, they were able to produce beds of particles within a very narrow size range. Comparing the data, they found excellent agreement between the predicted and experimental results. The aim of the series of expansion tests performed in this thesis is to see if the bed of stabilised air bubbles can be represented by the Richardson-Zaki model.

By studying all the results as a whole, the variation in bed voidage with fluidising velocity behaves as expected. The Richardson-Zaki model describes the expansion behaviour for mono-sized fluidised beds, hence the success of Karamanev and Nikolov’s results. However, as can be seen from the photographs in Chapter 2, the bubble generator produces stabilised bubbles in a range of sizes. In agreement with the behaviour of conventional fluidised beds, the bubbles segregate into bands of a similar size. For inverted beds, however, the larger bubbles are fluidised at the top of the bed while the smaller bubbles are fluidised near the bottom.
According to Zenz and Othmer, such fluidised beds can be considered to consist of a multiple of fluidised beds stacked one upon the other. Each band or zone of fluidised bed has a particular voidage. Hence, the voidage of the bed varies with depth. As predicted by Richardson and Zaki, the larger bubbles will have a lower bed voidage than the small bubbles at a particular fluidising velocity.

This behaviour is seen in the results of the expansion data (Figs. 3.6-3.8, 3.10, 3.11, 3.13-3.15). The data points drift from the line predicting the behaviour of larger bubbles and tend towards the line representing the smaller-sized bubbles. Hence, one can postulate that each data point represents a particular band of bubble size in the fluidised bed and this corresponds to a particular voidage. In almost all the cases shown, the expansion data approaches the line representing the smallest bubbles and it is believed that if further readings at higher velocities were measured then the expansion data would continue to follow this line. In each graph, the lines representing the Richardson-Zaki model have been specifically chosen as the best fit data.

In Figs. 3.7, 3.8 and 3.14, the expansion data almost fits a straight line as seen in the Karamanev and Nikolov data. This can be explained by the fact that the data points lie between narrow particle sizes, e.g. in Fig. 3.7, the points lie between predicted data for particles 1.0 and 2.0 mm in diameter, in Fig. 3.8 between 0.5 and 1.0 mm and in Fig. 3.14 on the 2.5 mm line. Hence, a small error in the experiment can correspond to a large shift in the data. It should also be noted that these experiments were performed in the 2-D and 100 mm columns. Both pieces of equipment suffered from problems due to the presence of uncoated air bubbles (see Chapter 2). These bubbles led to incidents of coalescence which could have affected the hydrodynamic characteristics of the fluidised bed.

In general, the hydrodynamic behaviour of the beds is similar, regardless of the size of column used. Another parameter that has been investigated is bed depth. Fig. 3.11 shows the data for three different beds of similar depth (approximately 13.0 cm). As expected, the data points all follow each other closely, highlighting the reproducibility of good beds of stable bubbles. If these beds are compared to those of similar depth in
other columns (see Fig. 3.16), all the data shows a similar trend with the exception of a few points. Hence, column diameter is not a factor in determining the hydrodynamic behaviour.

![Diagram showing correlation between liquid velocity and bed depth with column diameter](image)

**Figure 3.16 - A comparison of expansion data of beds of similar depth (12.9-14.6 cm) in columns of various diameters (50, 67 and 100 mm)**

If hydrodynamic behaviour is independent of column diameter, is there an effect of bed depth? Fig. 3.17 compares two beds of widely different bed depths, 4.7 and 13.0 cm.

![Diagram showing correlation between liquid velocity and bed depth](image)

**Figure 3.17 - A comparison of the expansion of beds of different bed depths**
The data shows clearly that despite the difference in bed depth, the variation between the data is not that significant. The trend is similar to that seen in Fig. 3.16. The expansion data for the bed of depth 4.7 cm, is not as comprehensive as for the other data due to limitations of the equipment. But it is clear, that the data would follow the 13.0 cm bed if the expansion were to continue.

The trend in expansion must therefore be related to the bubble size distribution of the fluidised beds. If each experiment is considered in turn, one can see that in Figs. 3.6, 3.7 and 3.8, the expansion data falls in a band predicted for bubble sizes 0.5-2.5 mm, in Fig. 3.11, in a range for 0.8-6.0 mm and in Figs. 3.13-3.15, in a range for 1.0-3.0 mm. The bubble size distributions represented here are not attributable to the column diameter, but rather to the bubble generator. The experiments in Figs. 3.6-3.11, used the same bubble generator. In later experiments (Figs. 3.13-3.15), a new bubble generator, double the width of the previous generator and with a different distributor plate design, was used.

As described in Chapter 2, observation of the stabilised bubbles produced from the new generator indicated that bubble size was uniform, i.e. they appeared to have a narrow size range. This would explain why Figs. 3.13-3.15 can be modeled by a narrow size range, but this does not explain the size difference for the other experiments. This author believes that the narrow size range predicted by the model in Figs. 3.6-3.8, is attributable to the low volume of bubbles required to collect a bed of appreciable depth. The 2-D column is only 25 mm thick, compared to the 50 mm diameter of the first column trial. Hence, less bubbles are required to produce a bed of similar depth. In the bubble generator, the bubbles segregate into bands of similar size - the smaller bubbles in the lower compartments, the larger ones higher up. When the valve is opened between the generator and 2-D column, the first bubbles to enter are the smaller ones from the lower compartments. Once the required bed depth is reached, the tap is closed. Hence, there is a reduced chance of larger bubbles entering the column.
The results show clearly the dependence of bed voidage upon bubble size and fluidising velocity, and how it is independent of bed depth and column diameter. With this knowledge, is it possible to predict the hydrodynamic behaviour? The literature is almost devoid of research into predicting bed voidage for conventional fluidised beds with a large particle size distribution. The difficulty in predicting the voidage for such beds is that it varies with bed height. According to Zenz and Othmer (1960), large particles pack tighter than smaller ones. Segregation of particles occurs in conventional fluidised beds and so the bed can be visualised as a series of fluidised beds of different particle sizes and voidage, stacked one upon the other. In a similar manner, the inverted fluidised bed segregates the bubbles by size. Hence, it can be simplified to a series of mono-sized fluidised beds of bubble size, \( d_i \) and voidage, \( e_i \) (see Fig. 3.18).

![Figure 3.18 - Segregation of the bubbles allows the bed to be visualised as a series of mono-sized fluidised beds](image)

In the inverted bed, \( d_1 \) represents the largest bubble size and hence the lowest voidage, \( e_1 \). The converse is true at the bottom of the bed for \( d_9 \) and \( e_9 \) in Fig. 3.18. The fragile nature of the stabilised bubbles means it is difficult to measure the voidage at various depths. Any intrusions into the bed would act as interfaces which could disrupt the surface coating and lead to coalescence and formation of air locks beneath the distributor.
The homogeneous nature of the bed and the complexity in gathering information on voidage has meant that predictive equations or empirical correlations have been difficult to develop. However, an empirical curve to fit the data produced for homogeneous beds is easily calculated. One method is to use the modified Richardson-Zaki.

Consider, the experimental data from Fig. 3.10, which shows the expansion data for a bed of bubbles of initial depth 13.0 cm in a column of diameter 50 mm. The results show how the data lies between the predicted expansion for beds of bubbles 0.8 mm and 6.0 mm respectively. However, the predicted values of Richardson-Zaki are calculated specifically for a column 50 mm in diameter. It has been shown that the column diameter does not significantly affect the bed hydrodynamics, hence it is more convenient to calculate Richardson-Zaki for a column of infinite width. Hence, all experimental data could be compared, regardless of the column diameter. In this case, the assumptions are that \( D = \infty \) and \( U_i = U_t \). Hence the Richardson-Zaki equation becomes

\[
\frac{U}{U_t} = e^n
\]

where

\[
n = 4.4 \text{Re}_t^{0.1}
\]

for \( 1 < \text{Re}_t < 500 \)

and

\[
n = 2.4
\]

for \( \text{Re}_t > 500 \)

Calculation of Richardson and Zaki for \( D = \infty \) for values in the range \( d = 0.8 - 3.6 \) mm produces a series of lines as shown in Fig. 3.19. The values of \( \rho_b, \rho, \mu_t \) are as expected. The numbers around the top right-hand corner of the frame represent the bubble sizes.
Chapter 3 - Bed Hydrodynamics

Figure 3.19 - Richardson-Zaki predictions for various mono-sized beds, assuming a column of infinite width.

If the experimental data from Fig. 3.10 is super-imposed over the predictions, the result is Fig. 3.20.

Figure 3.20 - Comparison of experimental data for a bed of initial depth 13.0 cm and Richardson-Zaki
Fig. 3.20 shows the experimental data lies between the predictive data for 0.8 and 3.6 mm sized bubbles - a more realistic size range than shown in Fig. 3.10. Each experimental data point crosses a line representing Richardson-Zaki at a particular bubble size. In real terms, this means that at a particular fluidising velocity, the expansion of the bed is governed by bubbles of a particular size. For example, at 0.025 m s\(^{-1}\), expansion of the larger bubbles occurs, while expansion of the smaller bubbles at the bottom of the bed is hindered by the larger bubbles. As the fluidising velocity increases, the expansion is governed by differing bubble sizes until a point is reached where the smallest bubbles dictate the hydrodynamics and the bed follows the expansion predicted by Richardson-Zaki. Hence, the model of a fluidised bed as shown in Fig. 3.18 appears valid.

In order to use Richardson-Zaki to fit a curve to the data, it is assumed that at a particular velocity, the hydrodynamics are governed by bubbles of a particular size. A good estimate of this size can be made by consulting Fig. 3.20. Values of \( U \) and \( d_i \) are entered into Eq. 3.13, and this produces a voidage, \( e \), for the entire bed. This continues for differing values of \( U \) and the corresponding \( d_i \), until enough points are calculated to fit the entire range of experimental data (Fig. 3.21).

Using this method, the Richardson-Zaki equation can be expressed as:-

\[
\sum_{i=1}^{n} e = \left( \frac{U}{U_i} \right)^{1/n}
\]

where \( U_i = \frac{\text{Re}_i \mu}{\rho_i d_i} \)

and \( \text{Re}_i \) is based upon Eqs. 3.7, 3.8b and 3.9

and \( n \) is based upon Eqs. 3.5 and 3.6

160
Chapter 3 - Bed Hydrodynamics

Figure 3.21 - Experimental data points fitted by Richardson-Zaki

It should be stressed that this is not a predictive method and is entirely empirical because an estimate of the bubble size is required. The curve illustrates how bubble size affects the hydrodynamic behaviour of the fluidised bed.

Hartman et al (1992) proposed an alternative correlation to estimate the voidage in a liquid-solid fluidised bed. By considering the balance of forces acting on a single particle in a fluidised bed, they suggested a general relationship as follows:

\[ k_1 \text{Re}^{k_2} + k_3 \text{Re} - e^{k_4} \text{Ar} = 0 \]

where \( k_1 - k_4 \) are constants. The constants were determined by considering values of \( \text{Ar} \) and \( \text{Re} \), varying the values of \( \text{Re} \) from \( \text{Re}_{mf} \) to \( \text{Re}_t \). The constants were calculated by using the Richardson-Zaki equation (Eq. 1.19), except they used the n correlation proposed by Garside and Al-Dibouni (1977):

\[ n = \frac{5.09 + 0.2839 \text{Re}_t^{0.877}}{1 + 0.104 \text{Re}_t^{0.877}} \]

for \( 10^3 < \text{Re}_t < 3 \times 10^4 \)
To calculate $Re_{mf}$, they used the Ergun equation for spherical particles at $e_{mf} = 0.41$:

$$Re_{mf}^2 + 50.5715 Re_{mf} - 0.0393834 Ar = 0 \quad 3.16$$

and to calculate $Re_t$ they used a correlation similar to Eq. 3.7:

$$\log Re_t = P(A) + \log R(A) \quad 3.17$$

where

$$P(A) = ((0.0017795A - 0.0573)A + 1.0315)A - 1.26222$$

$$R(A) = 0.99947 + 0.01853\sin(1.848A - 3.14)$$

and $$A = \log Ar$$

The resulting best-fit equation was:

$$1.4402 Re^{1.8045} + 20.359 Re - e^{4.7296} Ar = 0 \quad 3.18$$

Using exactly the same method as before, Eq. 3.18 was tested with the experimental data. Values of $Re$ and $Ar$ were calculated, based upon the value of $U$ and the corresponding $d_i$ value. It should be noted that the powers calculated by Hartman are too accurate and values of 1.8 and 4.7 would suffice. Again, the Richardson-Zaki model for a column of infinite width was employed, and the results are shown in Figs. 3.22, 3.23.

Fig. 3.22 shows the results for the 13.0 cm bed from Fig. 3.10. In comparison with Fig. 3.21, the results are very similar and the correlation shows a good fit. In reality, the techniques employed are very similar as both are based on Richardson-Zaki and so one would expect similar results. The Hartman correlation is slightly easier to use in calculating the data fit. Fig 3.23 compares all the data from Fig. 3.16 and fits the Hartman correlation to that data. Hartman and colleagues used their correlation to predict the voidage for mono-sized beds of fluidised particles. Hence, it must be used like the Richardson-Zaki equation and can be expressed as:

$$e^{4.7296} = \sum_{i=1}^{14402} \frac{Re^{1.8045} + 20.359 Re}{Ar} \quad 3.19$$
Figure 3.22 - The data for a 13.0 cm fluidised bed can be fitted by the correlation of Hartman et al (1992)

Figure 3.23 - All data for beds 13.0 - 14.6 cm fitted by the Hartman correlation
The experimental data raises a final question: how accurate are the Richardson-Zaki predictions? This question cannot be satisfactorily answered. If the predictions are accurate, then the results could be used to calculate the bubble size range of a fluidised bed. Unfortunately, the experimental data is calculated on the assumption that at the velocity of collection, the bed voidage is 0.40. Reflecting on the results of Karamanev and Nikolov (1992) and Hartman et al (1992), who both used 0.41, this is not a bad assumption. Section 3.1 gives several reasons why this is a reasonable estimate. However, until a method of measuring the voidage in such a fragile environment is available, too much credence cannot be given to the data. The results do show that a bubble size distribution exists and the values of bubble size involved are a reasonable estimate, particularly using Richardson-Zaki with $D = \infty$. Visual measurement of the bed is possible using a computer, however no photographs exist for the experiments shown here and hence no proper evaluation is possible.

The findings of the bed expansion experiments can be summarised as follows:-

- The inverted fluidised beds replicate the hydrodynamic behaviour associated with beds of varying particle size. The beds can be visualised as consisting of a series of beds of different bubble size and voidage, stacked one upon the other.

- The expansion behaviour is independent of the depth of the fluidised bed.

- Without visual measurement of the bed, the bubble size distribution is unknown. However, a reasonable estimate can be obtained by comparing the expansion data with the Richardson-Zaki model.

- Fluidised beds consisting of stable bubbles can effectively reproduce data. Collection of uncoated air bubbles should be avoided as they can affect the expansion behaviour.

- The narrower size distribution estimated in later experiments (Figs. 3.12-3.15) is confirmed by observation of a narrower size range produced by the new generator.

The complexity of the flow patterns through the fluidised bed means a prediction of the hydrodynamic behaviour is ruled out. However, the data can be approximated empirically using the Richardson-Zaki or the Hartman correlation.
Chapter 4 - Batch Adsorption Trials

4.1. Introduction

The capacity of activated carbon for adsorbing aromatics is well documented in the literature and the important aspects of this phenomenon are reviewed in Chapter 1. Harrap (1950) produced a particularly interesting study on adsorption that is strictly relevant to the stabilised bubble process. A mixture of aniline and oleyl alcohol was adsorbed onto the surface of activated carbon and the relevant quantities of each substance adsorbed were measured. Harrap discovered that equal amounts of both substances were adsorbed, suggesting that the same adsorption sites are available to both molecules. In fact, the affinity of oleyl alcohol for adsorption is stronger than that of aniline and the oleyl alcohol molecule displaces the aniline molecule from the adsorption sites.

This finding has serious implications for pollution treatment using the carbon-coated bubbles. Oleyl alcohol is a necessary additive in the mechanism for producing coated bubbles. If the oleyl alcohol behaves similarly in the presence of phenol or para-chlorophenol, the adsorption capacity of the fluidised bed could be seriously impaired. This chapter describes a series of batch adsorption experiments to investigate the extent of impairment of adsorption capacity by oleyl alcohol.

4.2 Liquid-solid adsorption theory for dilute systems

Adsorption at a liquid-solid interface is attributed to an attraction between the adsorbate molecule and the solid surface. This attraction is due to either physical forces, e.g. hydrogen-bonds or van der Waals forces which temporarily hold the molecule at the surface, or chemical forces, i.e. a chemical reaction forms a bond between the sorbate molecule and the surface. Obviously, the strong affinity of a molecule for adsorption is an asset. However, there are other factors which affect the adsorption capacity of a
substance; namely, the surface area available for adsorption, the pore size distribution and the orientation of the adsorbate molecule at the surface.

A solid must have a large surface area available to adsorb large quantities of adsorbate. This surface is usually provided by an extensive microporous network within the solid particle. However, the adsorbate molecule must have access to this surface and this is provided by a series of macro- and meso-pores within the particle. The orientation of the molecule is also important as depending on the interaction between the sorbate and sorbent, a sorbate molecule can adsorb perpendicular or parallel to the surface. If a molecule adsorbs flatly against the surface, it will cover a greater area than if it is adsorbed perpendicularly. This limits the surface area available for adsorption. These factors have been discussed extensively in Chapter 1, but they must be considered when quantifying a material's capacity for adsorption.

Once all the adsorption sites have been filled, the system is in a state of equilibrium. This does not mean that the process is in stasis. At equilibrium, the adsorption process is still dynamic, with some molecules desorbing from the surface while others replace them. The overall picture is that all the adsorption sites have been filled. The concentration of the bulk solution at this point is known as the Equilibrium concentration, $C_e$ (mg l$^{-1}$). This value allows the amount of pollutant adsorbed onto the material to be calculated. The performance of a substance is characterised by its adsorption isotherm. In general, an adsorption isotherm consists of a plot of the equilibrium concentration of the sorbate on the solute (mg g$^{-1}$) against the bulk equilibrium concentration, $C_e$ (mg l$^{-1}$). This is shown below in Fig. 4.1.

![Figure 4.1 - The L2 (Langmuirian) isotherm](image)

**Figure 4.1 - The L2 (Langmuirian) isotherm**
According to the classification system adopted by Giles and colleagues (1960), Fig. 4.1 is known as the L2 or Langmuirian isotherm. The shape of the isotherm reveals the method of adsorption. In this case, the rate of adsorption decreases with an increase in the bulk concentration which means that it is becoming increasingly more difficult to find a suitable site for adsorption. This infers that the molecules adsorb parallel to the sorbent surface.

The Langmuir isotherm has a firm theoretical basis (Langmuir, 1918), and is characterised by the following equation:

\[ q_e = \frac{q_{\text{max}}aC_e}{1 + aC_e} \]  \hspace{1cm} (4.1)

where \( q_e \) is the mass of sorbate adsorbed per unit mass of sorbent (mg g\(^{-1}\)),

- \( q_{\text{max}} \) corresponds to the surface concentration at monolayer coverage and represents the maximum value of \( q_e \) that can be achieved (mg g\(^{-1}\))
- \( a \) is related to the energy of adsorption and increases as the strength of the adsorption bond increases (J g\(^{-1}\))

The values of \( q_{\text{max}} \) and \( a \) can be determined from plotting a linearised form of Eq. 4.1,

\[ \frac{1}{q_e} = \frac{1}{q_{\text{max}}aC_e} + \frac{1}{q_{\text{max}}} \]  \hspace{1cm} (4.2)

or in a modified form,

\[ \frac{C_e}{q_e} = \frac{1}{q_{\text{max}}a} + \frac{C_e}{q_{\text{max}}} \]  \hspace{1cm} (4.3)

A plot of \( C_e/q_e \) vs. \( C_e \) using Eq. 4.3, the slope of the line corresponds to \((1/q_{\text{max}})\) and the intercept \((1/q_{\text{max}}a)\). The problem with the Langmuir model is that it cannot describe data accurately over a large concentration range. Experimentally determined values of \( q_{\text{max}} \) and \( a \) are not constant due to the heterogeneous nature of the surface and interaction between adsorbed molecules. In the model, it has been assumed that the adsorbent surface is homogeneous and there is no interaction between the sorbate molecules. However, for dilute systems, the Langmuir model is a reasonable estimate.
Chapter 4 - Batch adsorption

For organic systems, the Freundlich equation is commonly used. This is an entirely empirical formula and so describes accurately much adsorption data. This equation has the form:

\[ q_e = KC_e^{1/n} \]  \hspace{1cm} (4.4)

where \( K \) is related to the capacity of the adsorbent \((\text{mg g}^{-1})(\text{l mg}^{-1})^{1/n}\)

\( n \) is a function of the strength of adsorption

For fixed values of \( C_e \) and \( 1/n \), the larger the value of \( K \), the larger the adsorption capacity. For fixed values of \( C_e \) and \( K \), the smaller the value of \( 1/n \), the stronger the adsorption bond. If \( 1/n \) is large, the bond is weak and \( q_e \) changes markedly with small changes in \( C_e \).

The values of \( K \) and \( n \) can be calculated by plotting the linearised form of Eq. 4.4 on a log-log scale, i.e.:-

\[ \log q_e = \log K + \frac{1}{n} \log C_e \]  \hspace{1cm} (4.5)

Like the Langmuir, the Freundlich works best at dilute concentrations because at saturation, \( q_e \) is independent of further increases in concentration and the equation no longer applies.

In this chapter, the adsorption capacity of activated carbon for phenol and p-chlorophenol will be characterised using the Langmuir and Freundlich equations. In this manner, the effect of adding the spreading agents can be assessed. Examples of how the isotherms are calculated are shown in Appendix 2.
4.3 Experimental Method

4.3.1 Materials

The amounts of each material used in the batch trials were chosen to reflect as closely as possible the quantities used to generate the stabilised bubbles. The activated carbon (NORIT SA4) was sieved to a particle size < 53μm. It had been shown in bubble generation trials that using a narrower particle size range did not affect production of stabilised bubbles. The advantage of using smaller adsorbent particles is that equilibrium is attained quickly - a distinct advantage in any continuous process.

The adsorption capacity of activated carbon for phenol is widely documented, hence its inclusion as a model adsorbent. The electron-withdrawing influence on the benzene ring observed with the chlorine substituent group on p-chlorophenol means it has a greater affinity for adsorption than phenol. This should be reflected in the isotherms as a greater adsorption capacity.

Two spreading agents were used in this series of trials. Oleyl alcohol is used as a binding agent in the production of stabilised bubbles. The effect it has upon adsorption capacity must be assessed in terms of potential to be used as a counter-current continuous process. Oleic acid was also studied, as it has similar properties to oleyl alcohol but also shows a degree of functionality which may aid adsorption of the pollutants.

4.3.2 Method

Each batch experiment was performed in a one litre flask. Two flasks were used simultaneously and the temperature within each flask was regulated using a water bath set at a temperature of 21 ± 1°C. The water used in the experiments was from the same
source that was to be used in the bed adsorption trials. Stock solutions of phenol and p-chlorophenol were made and then diluted so each flask contained 500 ml of a 20 mg l⁻¹ solution of the required pollutant.

Oleyl alcohol and oleic acid were added using a Pasteur pipette. The volume of each drop was calculated to ensure that the exact amount of spreading agent required was added. In the bubble generation process, oleyl alcohol is added such that there is 0.2 ml of oleyl alcohol per gram of carbon. The spreading agents were added to the flask in this ratio, to try and keep the system as close to that in the adsorption column as possible. Knowing the amount of carbon that was to be added to the flask, the required amount of spreading agent could be added.

The adsorption isotherms were obtained by placing differing amounts of sieved NORIT SA4 in each batch. Adsorption was aided by mixing the batch using a stirrer. This was to ensure continuous contact between the carbon and the competing molecules. The rotational speed was kept as low as possible (300 - 400 rpm) so that no break-up of the carbon particles occurred which would affect the results. Each batch was in contact for 4 hours. This was because the finely divided nature of the carbon meant that it would reach equilibrium quickly. The isotherms produced would be sufficient for predicting the capacity of a stabilised bed of bubbles which does not have such a long contact time.

After this time, a sample of the solution was withdrawn and centrifuged to remove the carbon. Finer particles were then removed by passing the sample through a Whatman 0.8 μm filter. The pseudo-equilibrium concentrations for each sample were measured with UV light using a Perkin-Elmer Lambda II Spectrophotometer. The advantage of this machine is that it can find the best wavelength to measure the concentrations and hold it there with a minimum of fluctuation. Phenol concentrations were measured at 269.5 nm and p-chlorophenol at 279.9 nm. Previously installed calibration curves were used to measure the concentration at the corresponding absorbance value.
4.4 Results

The data collected from the experiments were used to calculate adsorption isotherms. The Freundlich isotherm (Eq. 4.4) and the modified Langmuir isotherm (Eq. 4.3) were used to characterise the activated carbon. Figs. 4.2 and 4.3 show the Freundlich isotherms for phenol and p-chlorophenol respectively, and figs. 4.4 and 4.5 show the modified Langmuir isotherms.

Each graph shows three sets of data and the respective isotherms that best fit each set of data. The data represents the experimental results for three separate systems:-

- Activated carbon and a pollutant (phenol or p-chlorophenol) in the absence of a spreading agent
- Activated carbon and pollutant in the presence of oleyl alcohol
- Activated carbon and pollutant in the presence of oleic acid

From the data, the values of $K$, $1/n$, $q_{max}$ and $a$ can be calculated.

### Table 4.1 - Freundlich constants for phenol and p-chlorophenol

<table>
<thead>
<tr>
<th>Description of system</th>
<th>$K$ (mg g$^{-1}$)(l mg$^{-1}$)$^{1/n}$</th>
<th>$1/n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenol / no surfactant</td>
<td>36.76</td>
<td>0.287</td>
<td>0.99</td>
</tr>
<tr>
<td>phenol / oleyl alcohol</td>
<td>20.29</td>
<td>0.299</td>
<td>0.90</td>
</tr>
<tr>
<td>phenol / oleic acid</td>
<td>19.36</td>
<td>0.333</td>
<td>0.95</td>
</tr>
<tr>
<td>p-chlorophenol / no surfactant</td>
<td>78.96</td>
<td>0.334</td>
<td>0.99</td>
</tr>
<tr>
<td>p-chlorophenol / oleyl alcohol</td>
<td>47.03</td>
<td>0.241</td>
<td>0.95</td>
</tr>
<tr>
<td>p-chlorophenol / oleic acid</td>
<td>38.95</td>
<td>0.233</td>
<td>0.89</td>
</tr>
</tbody>
</table>
Table 4.2 - Langmuir constants for phenol and p-chlorophenol

<table>
<thead>
<tr>
<th>Description of system</th>
<th>q_{max} (mg g^{-1})</th>
<th>a (l g^{-1})</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenol / no surfactant</td>
<td>81.21</td>
<td>0.852</td>
<td>0.98</td>
</tr>
<tr>
<td>phenol / oleyl alcohol</td>
<td>49.56</td>
<td>0.492</td>
<td>0.98</td>
</tr>
<tr>
<td>phenol / oleic acid</td>
<td>58.78</td>
<td>0.300</td>
<td>0.94</td>
</tr>
<tr>
<td>p-chlorophenol / no surfactant</td>
<td>195.19</td>
<td>0.790</td>
<td>0.98</td>
</tr>
<tr>
<td>p-chlorophenol / oleyl alcohol</td>
<td>87.94</td>
<td>1.062</td>
<td>0.99</td>
</tr>
<tr>
<td>p-chlorophenol / oleic acid</td>
<td>72.38</td>
<td>0.963</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Tables 4.1 and 4.2 show the findings from the Freundlich and Langmuir isotherms. The value R^2 is calculated from the regressions used to calculate the best fit data and is a measure of the accuracy of the fit.

The raw data behind the isotherms in Figs. 4.2 - 4.5 is in Appendix 1. Sample calculations are in Appendix 2.
Figure 4.2 - Freundlich isotherms for phenol batch adsorption

Effect of adding surfactants

Experimental conditions

- Temperature = 21°C
- Contact Time = 4 hrs
- Initial concentration = 20 mg l⁻¹
- Surfactant/carbon ratio = 0.2 ml g⁻¹
- Stirrer speed = 300 - 400 rpm

- phenol with no surfactant
- phenol with oleyl alcohol
- phenol with oleic acid
- Freundlich isotherms
Figure 4.3 - Freundlich isotherms for para-chlorophenol batch adsorption
Effect of adding surfactants

Experimental conditions
- Temperature = 21 C
- Contact Time = 4 hrs
- Initial concentration = 20 mg l⁻¹
- Surfactant/carbon ratio = 0.2 ml g⁻¹
- Stirrer speed = 300 - 400 rpm
Figure 4.4 - Modified Langmuir isotherms for phenol batch adsorption

Effect of surfactants

Experimental conditions

- Temperature = 21 C
- Contact Time = 4 hrs
- Initial concentration = 20 mg l⁻¹
- Surfactant/carbon ratio = 0.2 ml g⁻¹
- Stirrer speed = 300 - 400 rpm
Figure 4.5 - Modified Langmuir isotherms for para-chlorophenol batch adsorption
Effect of surfactants

Equilibrium concentration, $C_e$ (mg l$^{-1}$)

Experimental conditions
- Temperature = 21 C
- Contact Time = 4 hrs
- Initial concentration = 20 mg l$^{-1}$
- Surfactant/carbon ratio = 0.2 ml g$^{-1}$
- Stirrer speed = 300 - 400 rpm

- p-chlorophenol with no surfactant
- p-chlorophenol with oleyl alcohol
- p-chlorophenol with oleic acid
4.5 Discussion

NORIT SA4 is a thermally-activated porous carbon which is alkaline in nature (pH = 10) and so the number of surface-oxygen compounds present on the surface is expected to be low. According to some authors, surface-oxygen compounds, due to their weakly acidic nature, reduce the capacity for phenols (Drago et al., 1964; Coughlin and Ezra, 1968; Mattson et al., 1969; Cookson Jr., 1975; Koganovskii et al., 1987). Mattson and colleagues (1969) believed that the mechanism of adsorption was that the $\pi$-electrons of the benzene ring and the carbon basal plane formed a donor-acceptor complex. The surface-oxygen groups are less likely to form such a complex due to their electron-donating properties. Conversely, basic activated carbons contain carbonyl groups which are electron-withdrawing and so form stronger donor-acceptor complexes.

Other authors found that the presence of molecular oxygen at the surface improved the adsorption capacity (Vidic et al., 1993; Abuzald and Nakhla, 1994; de Jonge et al., 1996). The mechanism theory proposed by these authors is that the surface oxygen reacts with the phenolic compound to form a phenoxy radical. This reacts with other phenol molecules to form dimers and trimers. The mechanism is known as oxidative coupling.

de Jonge and colleagues (1996) performed a series of batch experiments using NORIT SA4 and 2-methylphenol and 3-chlorobenzoic acid. They found that the SA4 absorbed these compounds strongly and desorption was negligible. This result is indicative of oxidative coupling. Several reasons were proposed to explain this. SA4 is prepared by thermal activation during exclusion of oxygen. This means that the resulting carbon is more reactive towards oxygen and the surface chemistry could alter dramatically upon exposure to air. de Jonge also found that oxidative coupling can also occur under micro-aerophilic conditions, i.e. there is still sufficient oxygen available for coupling to occur.

What do these findings mean in terms of adsorption of phenol and p-chlorophenol? de Jonge found that adsorption of 2-methylphenol increased with the presence of surface oxygen. This is probably as much to do with the functionality of the substituent groups as to do with the surface chemistry. The electron-donating methyl- group means that it is
not as strong an acid as phenol. However, it can still form the phenoxy radical for coupling. This is thought to be due to the methyl group which promotes oxidation and hence the formation of the radical. Abuzald and Nakhla (1994) showed that both phenol and 2-methylphenol improved their adsorption capacity with increased levels of oxygen. Their Freundlich isotherms showed that the carbon had a greater affinity for 2-methylphenol, which lends credence to the theory that it can form couplings easier. The chlorine group associated with p-chlorophenol is very electron withdrawing and so the benzene ring is more susceptible to attack from a nucleophilic substance such as surface molecular oxygen. Hence, its improved performance over phenol.

What is still unclear is why the discrepancy between earlier authors and the more recent work? The reason for this must lie with the activated carbon itself. With so many types available with correspondingly different activation mechanisms, it is a certainty that the behaviour could differ so radically. It should also be noted that the surface of activated carbon is very heterogeneous. Both basic and acidic areas can exist simultaneously which means the mechanism of adsorption can differ depending on the conditions at the adsorption site.

de Jonge and colleagues (1996) have shown that NORIT SA4 is a good adsorber of phenolic compounds, hence it is a good choice for the process. Whatever the actual mechanism is, all authors agree that the phenol molecules adsorb parallel to the carbon surface and so one would expect the isotherm to be a Langmuirian curve. The results shown in Figs. 4.2 - 4.5 and in Tables 4.1 and 4.2 confirm this. As expected, p-chlorophenol shows a higher affinity for activated carbon than phenol. In the presence of no additive agents, the $K$ value for p-chlorophenol is twice that of phenol and $q_{\text{max}}$ is 195.19 mg g$^{-1}$ compared with 81.21 mg g$^{-1}$ for phenol.

The main aim of the batch tests was to see the effect of adding a spreading agent to the system. Harrap (1950) had shown that a state of competitive adsorption exists between the spreading agent and pollutant. As the loading of oleyl alcohol increased, it displaced the pollutant (in this case aniline) from the surface of the activated carbon and was adsorbed. Oleyl alcohol is a vital part of the stabilised bubble generation process and its
effect upon the carbon adsorption capacity could be crucial. Oleic acid was also tested. It is very similar to oleyl alcohol but is a stronger acid, hence its functionality could make a difference.

Fig. 4.2 shows the effect on phenol adsorption and Fig. 4.3 shows the effect on p-chlorophenol. In agreement with Harrap's findings, there is a significant reduction in the level of adsorption for both pollutants. Using the $q_{\text{max}}$ values from Table 4.2 as a tool to compare the adsorption capacity, the monolayer coverage of phenol is reduced by 40% for oleyl alcohol and by 28% for oleic acid. A comparison of the Freundlich isotherms in Fig. 4.2 shows that there is not much difference between using oleyl alcohol and oleic acid, with the performance of oleic acid being slightly better. For p-chlorophenol, the effect of using oleyl alcohol is to reduce the $q_{\text{max}}$ value by 55% and by 63% using oleic acid. Despite the increased reduction using p-chlorophenol, the carbon's adsorption capacity is, on average, 1.5 times greater than for phenol.

Oleyl alcohol and oleic acid both have a C$_{18}$ hydrocarbon backbone which means that the molecule is very long in comparison with the phenolic compounds. The pollutants and spreading agents were added together before the introduction of activated carbon in the batch to allow both an equal chance to adsorb. Harrap proposed that oleyl alcohol and phenolic compounds occupy the same adsorption sites and oleyl alcohol had a stronger affinity for carbon, hence it was able to displace aniline. The results of these experiments prove that oleyl alcohol and oleic acid have a strong affinity for carbon, yet there is still a significant proportion of the surface available for phenols. As well as occupying sites that the pollutants would otherwise occupy, the spreading agents may also block pores that the pollutants could enter. This would significantly reduce the adsorption capacity.

In terms of evaluating this effect on the bubble process, it means that a larger proportion of coated bubbles are required to treat a polluted stream. Provided the generator can produce a large enough volume at a quick rate then, in theory, the process could work. This would require spent bubbles to be replaced quickly by fresh ones.
Chapter 4 - Batch adsorption

There are still several questions unanswered by these experiments. A further study could ascertain more information on the adsorption of oleyl alcohol. For example, was all the oleyl alcohol adsorbed during the experiment? If not, what proportion? In essence, a series of isotherms could be produced for oleyl alcohol, enabling the equilibrium relationship between carbon, pollutant and spreading agent to be understood.

From this study, it was decided that p-chlorophenol should be used in preference to phenol, due to the greater affinity for adsorption. In both Figs. 4.2 and 4.3, the slope of the Freundlich isotherms beyond 5 mg l$^{-1}$ do not change so rapidly. Hence, it was decided to dose the polluted stream to an initial concentration of only 5 mg l$^{-1}$ in the column trials. In this way, a large bed of coated bubbles would be able to adsorb a similar quantity of pollutant to that at a higher initial concentration.
Chapter 5 - Column Adsorption Trials

5.1 Introduction

Conventional adsorption techniques normally use packed beds of granular material to achieve the desired pollutant abatement. This method, though highly effective, is handicapped by relatively low throughput and the need to invest in extra capital equipment to regenerate the spent adsorbent. Hence, there is an opportunity for process intensification. An ideal process would permit higher throughputs, require smaller adsorbent inventory and eliminate the extra unit process required for regeneration.

Weiss and colleagues (Swinton and Weiss, 1953; Moir et al, 1953) believed that this was possible if counter-current movement between a waste stream and adsorbent occurred. They envisaged a method involving flotation of an adsorbent against a contaminated liquid stream, e.g. by attaching the adsorbent to an air bubble. If the adsorbent was finely divided, a high surface area would be achieved and the rate of adsorption would increase allowing significantly higher throughputs.

Chapter 2 described how attachment of powdered activated carbon (PAC) to air bubbles was possible using a spreading agent, oleyl alcohol, and a system of plunging jets and rotational shear. These coated bubbles were stabilised by PAC as long as they were fluidised by flowing water. The next step was to examine the adsorption potential of the bubbles. If they could be produced in significant quantities and moved counter-currently to the polluted liquid stream, then adsorption would be highly likely. However, transferring and moving the bubbles proved very difficult, due to the nature of the air bubbles (see Chapter 2). Hence, it was only possible to collect batches of stabilised bubbles. Although significant adsorption was not expected, it was hoped that some adsorption would occur. This chapter explains the theory behind shell adsorbents and describes the experimentation involved in assessing adsorption potential. Results are shown for different fluidised bed conditions.
5.2 Shell Adsorption Theory

Sorption theory for a shell adsorbent is based upon the diffusion of a substance into a homogeneous porous sphere. Consider first the general diffusion equation according to Crank (1975):

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left( D \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left( D \frac{\partial C}{\partial z} \right)
\]

where \( D \) is the adsorbate diffusion coefficient and varies from point to point, \( C \) is the solute concentration and \( x, y, z \) are space co-ordinates. Eq. 5.1 can be manipulated to define diffusion in different geometries, e.g. plates, cylinders or spheres. The corresponding equation for a sphere is obtained by considering a volume element of a sphere with sides of length \( dr, r \, d\theta, r \sin\theta \, d\phi \). To transfer to spherical co-ordinates, \( r, \theta, \phi \), we write:

\[
x = r \sin \theta \cos \phi \]

\[
y = r \sin \theta \sin \phi \]

\[
z = r \cos \theta
\]

Eq. 5.1 becomes:

\[
\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D r^2 \frac{\partial C}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( D \sin \theta \frac{\partial C}{\partial \theta} \right) + \frac{D}{\sin^2 \theta} \frac{\partial^2 C}{\partial \phi^2}
\]

If diffusion into the sphere is radial and the diffusion coefficient is constant, Eq. 5.5 can be simplified to:

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{2 C}{r} \frac{\partial C}{\partial r} \right)
\]

Substituting \( u = C \, r \)

182
Eq. 5.6 becomes:

\[ \frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial r^2} \]

5.7

This equation can be solved by setting boundary conditions:

\[
\begin{align*}
  u &= 0, & r &= 0, & t > 0 \\
  u &= a C_0, & r &= a, & t > 0 \\
  u &= r f(r), & t &= 0, & 0 < r < a
\end{align*}
\]

where \(C_0\) is the constant concentration at the sphere surface and \(a\) is the radius of the sphere.

By separation of variables or Laplace transformation, Eq. 5.7 can be solved to obtain a general solution:

\[
 C = C_1 + (C_2 - C_1) \frac{r}{a} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_2 \cos n\pi - C_1}{n} \sin \frac{n\pi r}{a} \exp \left( -\frac{Dn^2\pi^2 t}{a^2} \right) \\
 + \frac{2}{a} \sum_{n=1}^{\infty} \sin \frac{n\pi r}{\pi} \exp \left( -\frac{Dn^2\pi^2 t}{a^2} \right) \int_0^r f(r') \sin \frac{n\pi r'}{a} dr'
\]

5.8

If the sphere is initially at a uniform concentration \(C_1\) and the surface concentration is maintained at \(C_0\), the solution becomes:

\[
 \frac{C - C_1}{C_0 - C_1} = 1 + \frac{2a}{\pi} \sum_{n=1}^{\infty} (-1)^n \sin \frac{n\pi r}{a} \exp \left( -\frac{Dn^2\pi^2 t}{a^2} \right)
\]

5.9

The concentration at the centre is given by the limit as \(r \to 0\) :-

\[
 \frac{C - C_1}{C_0 - C_1} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left( -\frac{Dn^2\pi^2 t}{a^2} \right)
\]

5.10
Hence, the total amount of diffusing substance entering (or leaving) a sphere is:

\[
\frac{Q}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{Dn^2 \pi^2 t}{a^2} \right)
\]

where \(Q\) is the amount of adsorbate retained by unit amount of adsorbent after it has been in contact with a solution for time \(t\), and \(Q_\infty\) is the amount adsorbed after infinite time. The ratio \(Q/Q_\infty\) is a measure of the degree of saturation.

The diffusion equation for a porous spherical shell of external radius, \(a\), with an impervious core of radius, \(b\), can also be derived using Eq. 5.6. In this case, \(r\) is defined as \(b < r < a\), the concentration \(C\) is maintained constant, \(C_0\) at the outer surface \(r = a\), and no flux through the inner surface \(r = b\). The variables are:

\[
\begin{align*}
\theta &= \frac{D}{(a - b)^2} \\
&= U_0 \\
x &= \frac{a - r}{a - b} \\
\theta &= \left(1 - \frac{q x}{(q + 1)}\right) - U_0 \sum_{n=1}^{\infty} A_n \exp(-\beta_n^2 \theta) \sin \beta_n x
\end{align*}
\]

where \(q = (a - b)/b\), and \(U_0 = a C_0\).

The solution takes the form:

\[
U = U_0 \left[ 1 - \frac{q x}{(q + 1)} \right] - U_0 \sum_{n=1}^{\infty} A_n \exp(-\beta_n^2 \theta) \sin \beta_n x
\]

where \(\beta_n\) are the positive roots of the equation:
By multiplying Eq. 5.12 by \( \sin(nx) \) and integrating, the coefficients \( A_n \) are found to be:

\[
A_n = \frac{2(\beta_n^2 + q^2)}{\beta_n (\beta_n^2 + q^2 + q)}
\]

Substituting Eq. 5.14 into Eq. 5.12 and returning to the original variables gives:

\[
\frac{C}{C_0} = 1 - \alpha \sum_n \frac{2(\beta_n^2 + q^2)}{\beta_n (\beta_n^2 + q^2 + q)} \exp\left[-\beta_n^2 \frac{Dt}{(a-b)^2}\right] \sin\left[\beta_n (a-r)\right]
\]

Similarly to Eq. 5.11, the level of saturation can be determined at a time, \( t \):

\[
\frac{Q}{Q_w} = 1 - \frac{6(1+q)^2}{(3+3q+q^2)} \sum_n \frac{(\beta_n^2 + q^2)}{\beta_n^2 (q+q^2+\beta_n^2)} \exp\left[-\beta_n^2 \frac{Dt}{(a-b)^2}\right]
\]

Eq. 5.16 is used to predict the rate of adsorption for shells of various thickness. The values of \( \beta_n \) (where \( n = 1, 2, ... \)) are given in Carslaw and Jaeger (1959), while the \( q \) values represent the shell thickness, \( a-b \), in relation to the core radius, \( b \). By plotting the level of saturation, \( \frac{Q}{Q_w} \), against dimensionless time, \( Dt/a^2 \), for various \( q' \) values (where \( q' = (a-b)/a \text{ : note the difference between } q \text{ and } q' \)), one can see how the time to reach saturation is affected by the shell thickness. Fig. 5.1 shows the results of plotting Eq. 5.16. One can see that the thinnest shell adsorbent \( (q' = 0.091) \) reaches saturation \( \left( \frac{Q}{Q_w} = 1 \right) \) quicker than thick shells, particularly those with very small impervious cores \( (e.g. q' = 0.75) \). As a comparison, the diffusion equation for a porous spherical particle with no impervious core \( (b=0) \), Eq. 5.11, is also plotted in Fig. 5.1. This shows that the time taken to reach saturation is much longer than for a shell adsorbent. This argument is particularly relevant to activated carbon, if one considers that a particle consists of a network of meso- and micropores. The pore network within a particle is very tortuous and comprises a large surface area. The conclusion drawn from this analysis is that it would take a long time for a molecule to diffuse into the centre of a homogeneous
Figure 5.1 - Comparison of rates of adsorption for porous shells of varying thickness with a homogeneous porous sphere
particle, or alternatively, much of the internal surface area would be unused in a short time.

The effectiveness of shell adsorbents can be illustrated in another way. Fig. 5.2 plots the dimensionless time ($D t / a^2$) against the dimensionless shell thickness ($q' = (a-b)/a$) for several values of adsorbate loading ($Q/Q_\infty = 0.8, 0.9, 0.98$) calculated from Eq. 5.16 (Weiss, 1953). This plot shows that the residence time $t$ required for the adsorbent to reach the same $Q/Q_\infty$ value will decrease with decreasing shell thickness for adsorbents of the same particle size. This result is in agreement with Weiss’ findings.

Assume that a particular column, cross-sectional area, $S$, and length, $L$, contains $N$ particles per unit volume, $V$ is the volume of one shell and $c$ is the average concentration of the adsorbate in the shell. The number of moles per unit time passing through the column, $W$, is:

\[ W = (N/t) \cdot S \cdot L \cdot V \cdot c \]

\[ = 4\pi/3 (a^3 - b^3) (Nc/t) \cdot SL \quad 5.17 \]

The ratio of $W$ for adsorbent particles having a shell thickness $(a-b)$ to $W$ for completely porous particles when $b=0$ when the same value of $Q/Q_\infty$ is attained in each case, is defined as $W_R$:

\[ W_R = (a^3 - b^3)/a^3 \cdot t_0/t \quad 5.18 \]

which reduces to:

\[ W_R = \left[ 1 - \left( \frac{b}{a} \right)^3 \right] \frac{t_0}{t} \quad 5.19 \]

where $t$ and $t_0$ are the contact times of the adsorbents having values of $b$ and $b=0$ respectively.
Figure 5.2 - The time ($Dt/a^2$ in dimensionless form) to reach a given level of adsorption as a function of the dimensionless shell thickness $(a-b)/a$.
Fig. 5.3 shows Eq. 5.19 plotted as the ratio b/a, the impervious core radius to the particle radius, as a function of the throughput ratio, $W_R$. The values of $t$ and $t_0$ were obtained from Eqs. 5.16 and 5.11 respectively. The figure shows that if thin shell coated particles are used, large increases in throughput are possible in comparison to completely porous particles. For both $Q/Q_\infty$ values of 0.8 and 0.98, the increase in throughput for a shell adsorbent where $b/a = 0.9$ is about 7 times greater than for a porous particle. Hence it is seen that greater volumes of contaminated streams can be treated provided that similar levels of saturation are possible.

It is clear from the evidence presented here that shell adsorbents, in whatever form, have a clear benefit over conventional porous media, provided they are:

- easily and rapidly produced,
- robust
- capable of counter-current flow
Figure 5.3 - Relative increase in throughput $W_R$ (using shell adsorbents) plotted against $b/a$.

The graph shows the relationship between the relative increase in throughput $W_R$ and the ratio $b/a$. The $Q/Q_\text{values}$ are indicated as 0.8 and 0.98, with the corresponding curves for each value.
5.3 Materials and Experimental Method

5.3.1 Materials

The materials used to generate stable air bubbles (PAC and oleyl alcohol) have already been covered in Chapter 2. This section will concentrate on the micropollutants used in the column trials - phenol and p-chlorophenol. Phenol was used in the preliminary trials using the 50 mm diameter column and p-chlorophenol was used in the 100 mm diameter column trials. The chemicals were chosen as model pollutants since the adsorption isotherms were well documented and there is considerable literature on the adsorption mechanisms. The physical properties of the pollutants are as follows:

Table 5.1 - phenol

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (at 760 mm Hg)</td>
<td>40.9 °C</td>
</tr>
<tr>
<td>Boiling point (at 760 mm Hg)</td>
<td>181.8 °C</td>
</tr>
<tr>
<td>Density (at 20 °C)</td>
<td>1.072 gm cc⁻¹</td>
</tr>
<tr>
<td>Water solubility</td>
<td>very soluble</td>
</tr>
</tbody>
</table>

Table 5.2 - p-chlorophenol

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (at 760 mm Hg)</td>
<td>43 °C</td>
</tr>
<tr>
<td>Boiling point (at 760 mm Hg)</td>
<td>220 °C</td>
</tr>
<tr>
<td>Density (at 40 °C)</td>
<td>1.265 gm cc⁻¹</td>
</tr>
<tr>
<td>Water solubility</td>
<td>soluble</td>
</tr>
</tbody>
</table>

The reason p-chlorophenol superseded phenol was its greater affinity for adsorption. The work of Giles et al (1960), Coughlin and Ezra (1968), Mattson et al (1969) and de Jonge et al (1996), all concluded that phenolic molecules adsorbed by interaction between the electrons of the aromatic ring π-system and the surface complexes of the basal plane. These authors also noted the effect of functional groups on adsorption. The Cl atom on p-chlorophenol is electron withdrawing and so reduces the electron density within the π-
system, enabling stronger attraction between the molecule and the carbon surface. \( p \)-chlorophenol is only slightly soluble in water and so would have a greater affinity for a hydrophobic surface, such as activated carbon.

5.3.2 Experimental Method

5.3.2.1 The 50 mm diameter column procedure

This section will describe the method of assessing the adsorptive properties of coated bubbles using the 50 mm diameter column. The apparatus is shown in Fig. 5.4.

Initially, the contacting column was filled with clean water, supplied from the feed tank (150 litres capacity) as shown in Fig. 5.4. When the bubbles were ready to generate, the water in the tank was pumped through the column, where it then passed to drain. The flow rate was set at 3 l min\(^{-1}\) (the rate at which the bubbles were retained below the distributor plate) and the valve between the generator and column opened to allow the bubbles to enter. As soon as the required amount of bubbles were retained, the valve was closed. A small waiting period was necessary to allow the carbon/oil/water suspension, which had entered with the bubbles, to be washed out of the column. This was necessary as the suspension would affect the results and make analysis of the samples difficult.

The flow rate was set at the required level when clear of suspended carbon. The feed tank was then dosed with 1 litre of 2000 mg l\(^{-1}\) phenol concentrate. The phenol was not added until the volume of water was at 100 litres to ensure that the phenol concentration would be at 20 mg l\(^{-1}\) in the tank. The concentrate quickly dispersed due to the actions of a mixer and the recycle loop shown in Fig. 5.4.

Samples of the contaminated stream were taken before and after the column. The time and bed depth at which each sample was taken was noted. Two full experiments were tried with this apparatus and the results are shown in Figs. 5.8 and 5.9 (section 5.4).
Figure 5.4 - The process used in the trials involving the 50 mm diameter column, including the feed tank and sample points.
The bubble bed was collected via the bubble outlet, positioned just below the distributor plate, once enough liquid samples had been taken. The resulting mix of suspension and crud was filtered under vacuum through a 0.8 μm Whatman filter, and the resulting filtrate allowed to dry out in an oven. The filter paper was weighed before and after to ascertain the amount of carbon collected.

5.3.2.2 The 100 mm diameter column procedure

In these trials, the generator and column size were increased and the feed concentration of p-chlorophenol was lowered from 20 to 5 mg l\(^{-1}\). This change was necessary in the light of the batch adsorption trials (see Fig. 4.3). The shape of the Freundlich isotherms indicate that p-chlorophenol loading does not increase significantly beyond an equilibrium concentration of 5 mg l\(^{-1}\). Hence, the carbon has the same adsorptive capacity but, the reduced concentration extends bed life.

The apparatus is shown in Fig. 5.5. The general procedure is similar to that for the 50 mm diameter column, i.e. the bubbles enter the column, they are dosed with the pollutant at a specific flow rate and samples are taken before and after the fluidised bed. The method of transfer between the generator and column was more complicated and is described in Chapter 2. The larger diameter meant that the stabilised bubbles had to be collected at 10 l min\(^{-1}\) in order to be retained at the bottom distributor plate, dp2. Trials, described in Chapter 2, had shown that insufficient bubbles were generated to allow truly counter-current flow. Hence, the column could only be loaded with stabilised air bubbles in a batchwise mode.

Dosing of the column with p-chlorophenol was not possible until the carbon/oil suspension was washed out. Once clear of the suspension, the p-chlorophenol feed was pumped to the column. The flow rate was kept as close to 10 l min\(^{-1}\) as possible, but there were some fluctuations caused by the pump. Sometimes the flow would drop to 8 l min\(^{-1}\), and on one occasion 6 l min\(^{-1}\). Samples were taken from the column inlet (sp4), just above the bottom plate (sp5) and at the column outlet (sp6) (see Fig. 5.5). Samples were withdrawn using syringes. Where possible, the fluidised beds of stable bubbles

194
Figure 5.5 - Adsorption process apparatus for the 100 mm diameter column
were collected, filtered and dried to obtain the activated carbon loading. Several experiments were performed using different experimental conditions and fluidised bed depths.

5.3.2.3 Sample Analysis

All samples were analysed using a Perkin-Elmer Lambda II UV Spectrophotometer. Phenol samples were measured at a wavelength of 269.5 nm, while p-chlorophenol was measured at 279.9 nm. Each sample was analysed in a cuvette and compared with a blank sample of mains water. The concentration of the sample was determined using previously stored calibration curves. The calibration curves for phenol and p-chlorophenol, including the calibration equation, are shown in Figs. 5.6 and 5.7 respectively.
Calibration equation: \[ C = 62.81A + 0.0041 \]

where \( C \) = concentration (mg l\(^{-1}\))
\( A \) = absorbance
Fig 5.7 - p-chlorophenol calibration curve

Calibration equation: \[ C = 86.6 \, A + 0.001 \]

where \( C \) = concentration (mg l\(^{-1}\))
and \( A \) = absorbance
5.4 Results

The results of the column adsorption trials are shown in Figs. 5.8 - 5.15. Figs 5.8 and 5.9 show the results of the trial using the 50 mm diameter column. The remaining results relate to the 100 mm column. Each figure indicates the experimental conditions; the size of the bed, the amount of carbon collected (where possible), the flow rate, velocity and p-chlorophenol concentration.

Each figure shows an inlet stream of variable composition which rises up to the final stream concentration. Samples taken from the middle of the column before the fluidised bed and at the outlet after the bed, show how this initial trace varies through the column. The fluidised bed of stable bubbles only contains a nominal amount of activated carbon. Hence, it is not possible to tell if any adsorption occurs by comparing the inlet and outlet traces. In order to do this, one must first consider Fig. 5.13 which shows the trace of p-chlorophenol through the column at various points with no stabilised bubbles present. It is obvious from this figure that dispersion is the dominant effect, because the slopes of the traces at the mid-point and outlet from the column differ from the inlet.

It is possible to calculate the mass of p-chlorophenol passing through the column using these curves. Comparing the masses for experiments where no bubbles are present to those which contain a fluidised bed will show how much p-chlorophenol, if any, is adsorbed.

For the purposes of analysis, Fig. 5.13 was compared with Fig. 5.11. Both experiments were performed under the same conditions and so were directly comparable. For this reason, the other experiments were not comparable, but they do highlight the fact that the bubbles appear to inhibit the dispersion effect. The next section elaborates on this further and explains how the mass of p-chlorophenol passing through the system can be calculated.
Figure 5.8 - Stable fluidised bubble bed adsorption trial No. 1 - 50 mm diameter column

Experimental conditions

- Bed depth = 36 cm
- Flow rate = 2 l min⁻¹
- Flow velocity = 1.7 cm s⁻¹
- Carbon loading in bed = 800 mg
- Loading per unit volume = 1.13 mg cm⁻³
Figure 5.9 - Stable fluidised bubble bed adsorption trial No. 2 - 50 mm diameter column

Experimental conditions

- Bed depth = 40 cm
- Flow rate = 3.5 l min⁻¹
- Flow velocity = 3 cm s⁻¹
- Carbon loading in bed = 1000 mg
- Loading per unit volume = 1.27 mg cm⁻³
Figure 5.10 - Stable fluidised bubble bed adsorption trial No. 3 - 100 mm diameter column

Experimental conditions

- Bed depth = 9.9 cm (7.7 + 2.2)
- Flow rate = 6 l min⁻¹
- Flow velocity = 1.3 cm s⁻¹
- Carbon loading in bed = 374 mg (4 cm collected)
- Loading per unit volume = 1.19 mg cm⁻³
Figure 5.11 - Stable fluidised bubble bed adsorption trial No. 4 - 100 mm diameter column

Experimental conditions:
- Bed depth = 11.2 cm
- Flow rate = 8 l min⁻¹
- Flow velocity = 1.7 cm s⁻¹
- Carbon loading in bed = 473 mg
  (8.5 cm collected)
- Loading per unit volume = 0.71 mg cm⁻³
Figure 5.12 - Stable fluidised bubble bed adsorption trial No. 5 - 100 mm diameter column

Experimental conditions

- Bed depth = 12.5 cm
- Flow rate = 7 l min\(^{-1}\)
- Flow velocity = 1.5 cm s\(^{-1}\)
- Carbon loading in bed = 385 mg (11 cm collected)
- Loading per unit volume = 0.45 mg cm\(^{-3}\)
Figure 5.13 - Dispersion of p-chlorophenol through column in the absence of bubbles
- 100 mm diameter column

[Graph showing concentration (mg l⁻¹) vs. time (seconds) with various data points and lines indicating inlet, mid-column, and outlet concentrations, as well as final concentration.]
Figure 5.14 - Stable fluidised bubble bed adsorption trial No. 6 - 100 mm diameter column p-chlorophenol dispersion in presence of stabilised bubbles

Experimental conditions:
- Bed depth = 9.7 cm
- Flow rate = 8 l min⁻¹
- Flow velocity = 1.7 cm s⁻¹
- No carbon collected
Figure 5.15 - Stable fluidised bubble bed trial No. 7 - 100 mm diameter column

Experimental conditions

Bed depth = 12 cm
Flow rate = 10 l min\(^{-1}\)
Flow velocity = 2.1 cm s\(^{-1}\)
No carbon collected
5.5 Discussion

5.5.1 Analysis of the results

The results show, in all cases, that the outlet concentration increases with time until the inlet concentration is reached. Considering the results of the batch adsorption trials in Chapter 4 and those produced by Harrap (1951), adsorption of phenol and p-chlorophenol can occur in the presence of a spreading agent, such as oleyl alcohol. Hence, one would deduce that a proportion of the carbon surface was available for adsorption. It now remains to prove that adsorption occurs and the extent of that adsorption.

Consider the results shown in Fig. 5.11. In this particular experiment, the inlet concentration was measured at sampling point 5 (sp5), which is located in the middle of the 100 mm diameter column, just above the bottom plate (see Fig. 5.5). The coated bubble bed depth was 11.2 cm and after the experiment, 8.5 cm of the bed was collected. After filtration and drying, the amount of carbon collected was 473 mg. The inlet and outlet concentrations were measured, and were found to rise to approximately 4.9 mg l⁻¹.

The adsorption isotherm for p-chlorophenol on activated carbon in the presence of oleyl alcohol (Fig. 4.3, see Chapter 4) shows that one gram of carbon can adsorb approximately 70 mg of p-chlorophenol in equilibrium with a solution concentration of 5 mg l⁻¹. A fluidised bed (11.2 cm depth) contains 623 mg of carbon and can adsorb 44 mg of p-chlorophenol (based on a carbon loading of 0.71 mg cm⁻³) assuming plug flow in the liquid stream.

Figs. 5.8 - 5.15 show that the feed to the column is not in plug flow. The inlet trace is variable, rising up to approximately 4.9 mg l⁻¹. Hence, the fluidised bed in Fig. 5.11 will not attain the theoretical adsorption of 44 mg of p-chlorophenol. To establish if p-chlorophenol is adsorbed it is necessary to compare this trial with a similar experiment in the absence of stabilised bubbles. The actual amount of p-chlorophenol that has passed
through the bed can be calculated for each experiment. The difference corresponds to the amount of $p$-chlorophenol adsorbed on the carbon coated bubbles.

![Micropollutant concentration (mg l$^{-1}$)](image)

**Figure 5.16 - The shaded area represents the mass of pollutant passing through the bed**

The curves shown in Figs. 5.11 and 5.13 must be plotted as $C$ (mg l$^{-1}$) against $V$, the volume of effluent that has passed through (litres) to calculate the mass of $p$-chlorophenol that has passed through the system. The mass of pollutant is represented by the shaded area in Fig. 5.16. This procedure was performed for the two experiments in question and the results compared.

Figs. 5.17 and 5.18 show the inlet and outlet traces for Figs. 5.11 and 5.13 respectively, plotted as $C$ against $V$. By calculating the areas under the curves, the mass of $p$-chlorophenol passing through a system with no bubbles present was 25.44 mg (Fig. 5.18). With the fluidised bed present, this value was 24.65 mg (Fig. 5.17). The likely explanation for this difference of 0.79 mg is that the pollutant must be present on the surface of the carbon. This trace uptake of $p$-chlorophenol is not surprising since the carbon loading in the bed is low and oleyl alcohol is present in the pores suppressing micropollutant adsorption.
Figure 5.17 - Inlet and outlet traces from Fig. 5.11, plotted as C against V. This is used to calculate the mass of p-chlorophenol passing through the fluidised bed.

Figure 5.18 - Traces seen at inlet and outlet with no bubbles present. Both curves were extrapolated to calculate the mass of p-chlorophenol passing through. This result does not offer conclusive proof of the ability of carbon coated bubbles to adsorb trace organic micropollutants. A more accurate result would be obtained if more data points had been collected. The initial shape of the curves are represented by a few points, leading to inaccuracies in the area calculations. The samples were collected.
manually and so it was not possible to collect them swiftly and regularly. In-line data logging would have solved this problem, but there were fears that contamination with carbon from the bubble transfer process would make this process inoperable.

The other experiments show the effect of bubbles on dispersion. In Fig. 5.13, in the absence of bubbles, the concentration response curves change with distance along the column indicating longitudinal dispersion. However, in the presence of a fluidised bed of bubbles, the shape of the inlet and outlet curves are similar, indicating that dispersion is suppressed. According to Danckwerts (1953), if dispersion is suppressed, then the flow through the bed must be piston-flow. This is caused by intimate mixing of the bubbles within the system. Complete piston-flow is not possible in Newtonian fluids and so there will always be some longitudinal mixing.

5.5.2 Activated carbon loading

Several reasons contribute to the level of performance of the stabilised bubbles. The low carbon inventory in the fluidised bed is a major factor. Table 5.3 (overleaf) shows the carbon loading for various bed depths.
### Table 5.3 - Carbon loading on various fluidised beds of coated bubbles

<table>
<thead>
<tr>
<th>Column diameter (mm)</th>
<th>Bed depth (cm)</th>
<th>Carbon loading (mg)</th>
<th>Loading per unit volume (mg cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>4.0</td>
<td>374</td>
<td>1.19</td>
</tr>
<tr>
<td>100</td>
<td>5.0</td>
<td>428</td>
<td>1.08</td>
</tr>
<tr>
<td>100</td>
<td>6.6</td>
<td>540</td>
<td>1.04</td>
</tr>
<tr>
<td>100</td>
<td>8.5</td>
<td>473</td>
<td>0.71</td>
</tr>
<tr>
<td>100</td>
<td>11.0</td>
<td>385</td>
<td>0.45</td>
</tr>
<tr>
<td>100</td>
<td>12.2</td>
<td>910</td>
<td>0.95</td>
</tr>
<tr>
<td>100</td>
<td>13.9</td>
<td>913</td>
<td>0.84</td>
</tr>
<tr>
<td>100</td>
<td>34.2</td>
<td>1372</td>
<td>0.51</td>
</tr>
<tr>
<td>50</td>
<td>36.0</td>
<td>800</td>
<td>1.13</td>
</tr>
<tr>
<td>50</td>
<td>40.0</td>
<td>1000</td>
<td>1.27</td>
</tr>
</tbody>
</table>

One must distinguish between the results for the 50 mm and 100 mm diameter columns when considering the carbon inventory in each bed. This is because different techniques were used to transfer the stable bubbles from the generator to the column.

Table 5.3 reveals that the carbon loading in each fluidised bed is low, less than 1 gram in most cases. The general trend in the 100 mm diameter column is for the carbon loading to increase with bed depth, the only exception being the beds depths of 8.5 and 11.0 cm. However, if the amount of carbon present is considered per unit volume, this value decreases with bed depth. It is believed the reason for this (and the unusual results with the 8.5 and 11.0 cm beds) is due to the chosen method of bubble transfer.
Chapter 5 - Column Adsorption Trials

The technique by which bubbles were transferred between the generator and the 100 mm diameter column involved collecting the bubbles in an intermediate hopper. Continual agitation of the bubbles ensured their stability. However, a small proportion of the bubbles near the connecting valve could not be agitated. These bubbles slowly coalesced, leading to the formation of uncoated air bubbles. When the valve was opened, the uncoated bubbles were seen entering the column. It is believed that the uncoated bubbles interacted with the stable bubbles and stripped them of their carbon coating. Small fluidised beds (which only require one transfer of bubbles from the generator to the column) were less susceptible to this phenomenon and so have a larger loading per unit volume.

The bubbles transferred to the 50 mm diameter column had the largest loading per unit volume because the enclosed nature of the column meant the bubbles could enter by buoyancy, therefore requiring no intricate transfer process. Hence, these bubbles were inherently more stable and less carbon was stripped.

It must also be pointed out that the usage efficiency of the carbon was low. The first generator used 30 grams of carbon to generate the stable bubbles, while the larger generator used 60 grams. Comparing these values with the carbon loading on each bed, one can see that utilisation of the activated carbon was poor. The result of this is the recommendation that improvements in the coating technique are required.

5.5.3 The role of oleyl alcohol

Several authors have shown that oleyl alcohol impairs the adsorption of a pollutant on activated carbon (Weiss, 1949; Harrap, 1951). This result has also been replicated in this study (see Chapter 4). Oleyl alcohol is required to bind the carbon particles to the surface of the air bubble. A fundamental study of the coating mechanism was not undertaken here, but it is thought that the attachment mechanism is a combination of the electrostatic
and hydrophobic forces acting between the bubble and particle (Kitchener, 1984; Laskowski, 1986; Lu, 1991; Gregory, 1993; Paulson and Pugh, 1996).

Harrap (1951) discovered that oleyl alcohol and aniline occupy the same adsorption sites and that oleyl alcohol has a greater binding affinity, i.e. oleyl alcohol can displace aniline from the adsorption sites. From this conclusion, it can be assumed that it can displace phenol and p-chlorophenol. However, in a stable bubble, the oleyl alcohol is present before contact with the micropollutant. For adsorption to take place:

1. Some adsorption sites must be available
2. The pollutant molecule must approach the bubble close enough to enter the micropores of the particle and find an active site. This requires a finite contact time.
3. If no adsorption sites are available, i.e. the oleyl alcohol occupies all the sites or blocks the entrance to the micropores, the pollutant molecule must displace oleyl alcohol.

The results indicate that some adsorption does occur, hence there is sufficient contact time. However, oleyl alcohol significantly reduces the sorption capacity and cannot be displaced in such short times. Low carbon inventory in the fluidised bed means that only trace quantities of micropollutant can be adsorbed. One can, therefore, logically deduce that if significant levels of carbon can be introduced to the process, contaminated streams containing trace quantities of micropollutant can be treated to required levels.

5.5.4 The counter-current process

To ensure that adsorption takes place, large quantities of coated bubbles are required. This would require coated bubbles to be generated and transferred continuously between the generator and the column. This has proved difficult for two reasons:-
1. It takes at least 30 minutes to generate enough bubbles to initiate a transfer. Bubble production is not continuous, and trials have shown that extra oleyl alcohol and carbon need to be added to instigate further production.

2. Bubble transfer is impeded by the simultaneous transfer of the carbon/oleyl alcohol suspension. This carbon needs to be removed otherwise it will contaminate the outlet of the column.

This meant that all the column adsorption trials had to be performed on a batch basis. Stage-to-stage movement of the bubbles in the column proved difficult as the rise velocity of the bubbles dictated that only small quantities of bubbles could be moved (see Chapter 2). Hence, semi-batch trials were too difficult. Large beds of coated bubbles were not obtained in the 100 mm diameter column because the bubbles were insufficiently robust to cope with the transfer method employed. One can deduce that the 50 mm diameter column system was more successful as the bubbles were exposed to less hydrodynamic stress.

Weiss and co-workers have suggested that niche applications are possible if a counter-current adsorption process can be successfully developed (Swinton and Weiss, 1953; Weiss, 1953; Moir et al; 1953). The problem with carbon-coated air bubbles as adsorbents is that they are difficult to handle. At present the bubble generation method is inefficient, with large quantities of carbon being wasted. If all the carbon could be utilised on the surface of many bubbles, that would reduce the complexity. However, the generation method would still have to produce bubbles more efficiently and more rapidly than at present. Only when these technical difficulties are overcome, can true counter-current movement occur and hence a proper evaluation of the adsorption properties of stable, coated air bubbles be performed.
5.5.5 Summary

- Mass transfer theory predicts that if the adsorptive property of a particle is limited to a porous outer shell, the particle will reach equilibrium more rapidly, enabling significant increases in throughput compared to conventional adsorption techniques.

- Inverted fluidised beds of stabilised bubbles coated with activated carbon, were generated and collected in 50 mm and 100 mm diameter columns. Each fluidised bed varied in depth and was contacted with of phenol (50 mm) or p-chlorophenol (100 mm).

- Samples were taken at the inlet and outlet of each column, and analysed for pollutant concentration.

- Analysis of the results indicated that adsorption occurred but not at significant levels. This result was a combination of poor carbon loading in the beds, impairment of the adsorptive capacity of the activated carbon by oleyl alcohol and the inability to operate in counter current flow.

- A faster, more efficient generation method would make the process viable. Transfer of bubbles between stages is possible if the beds are small. A large number of stages would allow large quantities of bubbles to be moved counter-currently, increasing the carbon loading to the system.
Chapter 6 - Conclusions and Recommendations

6.1 Conclusions

The aim of this project was to investigate aspects of stabilised bubble generation, equipment design, hydrodynamic properties of inverted fluidised bed of bubbles and the adsorbtent properties of the stabilised bubbles. In summary, the conclusions are as follows:-

Stable bubble generation, as described by Weiss, was successfully achieved. The bubble generator relies on plunging liquid jets to initially entrain air while a series of louvre plates generate rotational shear to promote attachment of the carbon particles to the bubble surface. The literature demonstrated that bubble entrainment is dependent on jet and nozzle geometry, jet velocity and physical properties of the liquid. The conditions required in each generator to entrain air could be explained by these factors. The formation of a bubble buffer layer was also critical as this protected newly entrained bubbles from the surface of the slurry where they would collapse. The original generator worked better with short jets which transferred most of their momentum to the entrainment process, causing good bubble penetration into the slurry. The larger generator operated with the same number of jets and so the rate of air entrainment was increased by using longer jets, successfully developing the required buffer layer.

The attachment of carbon particles to the bubble was facilitated by the addition of oleyl alcohol. The hydrocarbon chain renders the particles sufficiently hydrophobic to overcome any electrostatic repulsion. Conditions of shear within the generator promotes collision of the particles and bubbles. It is believed that initially the particles skim around the bubble surface, resisting detachment by thinning the film surrounding the bubble. The hydrocarbon chains facilitate this process and eventually they penetrate into the bubble, anchoring the particle at the surface.
Chapter 6 - Conclusions and Recommendations

An intriguing facet of coated bubbles is their stability if constantly agitated and submerged in a flowing stream of water. Trials concluded that minimising the presence of uncoated air bubbles allows the bubbles to remain stable for several hours with minimal coalescence. Hence, columns were constructed to fluidise the bubbles and keep them stable, while assessing them for adsorption potential. Two columns were constructed - one 50 mm in diameter, the other 100 mm.

Transfer of the bubbles between the generator and the column was a key step of the process. This operation was easily performed using the 50 mm column as the buoyancy of the bubbles was sufficient to allow transfer via a connecting tube. A drawback was that the carbon/oleyl alcohol suspension used to coat the bubbles was also transferred. The suspension was washed out before any trials could begin. Transfer of the bubbles was more difficult using the 100 mm column. The pressure head in the column was too high for the bubbles to rise up the connecting tube and an alternative method was sought. This was achieved by allowing the stabilised bubbles to enter a short column prior to transfer. The bubbles could enter this feed hopper under buoyancy forces, where they were kept stable by fluidising conditions. Once sufficient bubbles were collected, a valve was opened between the hopper and column and the bubbles entered the column where they were retained at a distributor plate.

An advantage of this system was that the majority of the suspension could be removed from the hopper before the bubbles entered the column. A major disadvantage was that it was difficult to fluidise the bubbles properly in the hopper and some bubbles would coalesce. Air bubbles would enter the column with the coated bubbles reducing the stability of the entire fluidised bed.

A further aim of the project was to promote counter-current flow between the stable bubbles and the contaminated stream. Counter-current flow was possible between stages by halting the flow momentarily - bubble buoyancy causing the bubbles to rise through the retaining plate. True counter-current flow requires numerous stages and large quantities of stable bubbles to work effectively. Unfortunately, the generator could not
produce bubbles in sufficient quantities. Hence, adsorption trials were restricted to batch collections of bubbles.

The hydrodynamic properties of the inverted fluidised bed were investigated in the various columns using beds of different depths. The bed depth was measured at each flow rate which enabled the expansion of the bed to be calculated. The experiments concluded that inverted beds possess similar hydrodynamic properties to conventional fluidised beds and obey the Richardson-Zaki model. The fluidised beds of bubbles collected here consist of beds of varying particle size. The Richardson-Zaki model is based on beds of mono-sized particles and a comparison of the experimental data with the Richardson-Zaki predictions emphasise the size distribution of the coated bubbles. It is speculated here that inverted fluidised bubble beds can be seen as a series of segregated beds of different particle size and voidage. Successful prediction of the expansion behaviour of fluidised beds with a wide particle size distribution is difficult and no examples have been found in the literature. However, it was possible to correlate the data empirically using the Hartman correlation.

A concern was expressed at the effect of oleyl alcohol on the adsorption properties of activated carbon. The affinity of oleyl alcohol for carbon is strong and hence a reduction in the adsorption capacity was expected. A series of batch adsorption trials were performed using phenol and \( p \)-chlorophenol in the presence of oleyl alcohol or oleic acid. The results showed that oleyl alcohol and oleic acid both reduced the adsorption capacity but there was negligible difference between the two spreading agents. The effect of using oleyl alcohol was to reduce the adsorption capacity for phenol by 40% and for \( p \)-chlorophenol by 55%. The adsorption capacity for \( p \)-chlorophenol was still 1.5 times greater than that for phenol. Despite this result, it was hoped that the bed still had sufficient capacity to demonstrate adsorption of trace quantities of \( p \)-chlorophenol.

The effectiveness of shell adsorbents for counter-current adsorption was demonstrated by modelling the diffusion of a substance into a particle with an impervious core and a porous outer shell. The model revealed that restricting the porous shell to a thin layer improved the rates of adsorption and increased the throughput through the bed - an
obvious advantage over conventional bed techniques. However, trials revealed that minimal adsorption was taking place on the beds of coated bubbles. The reason for this is believed to be due to a combination of pore blinding by the oleyl alcohol, poor carbon inventory on the fluidised beds and the inability to move the bubbles counter-currently.

In summary, the important factors affecting stable bubble production and utilisation have been identified. The coated bubbles can be easily produced and the probable mechanisms involved have been identified. Using air bubbles, however, limits their robustness, which makes them difficult to control and generate large quantities quickly. There is certainly scope for improvement and further study, and this should concentrate on making vast quantities of bubbles and moving them counter-currently.

6.2 Recommendations

The whole crux of the process is in the successful development of the counter-current process. In order to do this, large quantities of bubbles must move continuously against a contaminated stream. This is only possible if bubbles can be generated continuously. This may only be possible if a much larger generator is constructed which entrains air and coats bubbles more rapidly. To entrain large quantities of air, the generator would need more plunging jets of larger diameter, operating at higher velocities and longer jet lengths. Whether it is possible to coat bubbles quickly is unknown. It is understood that a minimum induction time is required to allow the particle to rupture the film and attach to the bubble. Investigation of this property could allow an estimation of the minimum generation time.

Collection of the fluidised bubbles revealed the poor utilisation of activated carbon, i.e. the amount of carbon collected in comparison to the amount of carbon added to the slurry is low. This problem also manifested itself in the large quantities of carbon/oleyl alcohol suspension transferred to the column with the stable bubbles. Not only did the suspension have to be removed, it was also wasteful of a valuable resource. An ideal process would utilise as much of the activated carbon as possible. If all the activated
carbon could be utilised then this would simplify the transfer process. Therefore, there is a lot of scope for optimisation of the generation process. Initial trials failed to improve the efficiency of carbon capture.

Further understanding of the adsorption process could be attained by adsorbing oleyl alcohol onto activated carbon. This would reveal the amount of oleyl alcohol that could be adsorbed in comparison to the amount of phenol or \( p \)-chlorophenol. Further trials could then discover if it is possible for phenol or \( p \)-chlorophenol to displace oleyl alcohol from the carbon pores.

If the contaminant was soluble in the spreading agent, then adsorption might still be viable even if all the pores were blocked. Initial trials could assess whether phenol or \( p \)-chlorophenol are soluble in oleyl alcohol. If not, other systems should be found which allow solubility but retain the ability to stabilise bubbles.

An ideal system would allow a spreading oil to be adsorbed onto the surface of a particle with little reduction in the sorption capacity. Many adsorbents are available which have better sorption characteristics than activated carbon. Alternative systems could utilise zeolites, ion exchange resins or polymers. These materials are expensive to produce and so economic viability has to be considered.

Industrial effluents contain many pollutants, which the water industry has to treat before recirculation to the domestic water supply. This means that different adsorbents may be required to treat specific pollutants. Hence, for the counter-current adsorption process to be successful, it must be shown to be versatile, in terms of the adsorbents it can handle.

Most of the recommendations made here allude to improving the stable bubble generation process. With the evidence provided, it should be possible to design a more efficient process, but complete success is not possible until the chemistry of coating air bubbles with particles is resolved and true counter-current movement is achieved.
References


BYRNE, J.F. and MARSH, H., Porosity in Carbons, chapter 1, (ed. PATRICK, J.W.), Edward Arnold, 1995

222
References


CERNY, S., Chapter 3, Active Carbon, (ed. CERNY, S. and SMISEK, M.), Elsevier, 1967


CUMMING, I.W., Ph.D. Thesis, Loughborough University of Technology, 1975


DECKWER, W.D., Bubble Column Reactors, Wiley, 1992

DEITZ, V.R., Bibliography of Solid Adsorbents, United States Cane Sugar Refiners and Bone Char Manufacturers and National Bureau of Standards, 1944

223
References


HASSLER, J.W.[a], Chapter 1, Activated Carbon, Leonard-Hill, 1967

HASSLER, J.W.[b], Chapter 8, Activated Carbon, Leonard-Hill, 1967

HASSLER, J.W. [c], Chapter 9, Activated Carbon, Leonard-Hill, 1967


References


KLASSEN, V.I. and MOKROUSOV, V.A, An Introduction to the Theory of Flotation, Butterworths, 1963


226
References


LEVA, M., Fluidization, McGraw-Hill, 1959


LIN, T.J., Ph.D. Thesis, Wayne State University, 1963

LONDONG, D., Ph.D. Thesis, Technische Universität Aachen, 1973


NORIT, Introduction to Activated Carbon, Public Information Booklet, NORIT N.V., Netherlands


PLAKSIN, I.N., (1960) International Mining and Processing Congress, pg 253


SEBBA, F., (1985) Chemistry and Industry, pg 91


SHAW, D.J., Chapter 4, Colloid and Surface Chemistry, Butterworth-Heinemann, 1994


STEENBERG, B., *Adsorption and Exchange of Ions on Activated Carbon*, Uppsala, 1944


229
References


WEISS, D.E., (1990 [b]) Internal Communication, R.M.I.T.


ZENZ, F.A. and OTHMER, D.F., Fluidization and Fluid-Particle Systems, Reinhold, 1960


Appendix 1 - Raw Data

A) Data for Figs. 3.5 - 3.15

1) Data for Fig. 3.5

<table>
<thead>
<tr>
<th>Liquid Velocity (ms$^{-1}$)</th>
<th>Bed Voidage $e$ 0.5 mm</th>
<th>Bed Voidage $e$ 1.0 mm</th>
<th>Bed Voidage $e$ 1.5 mm</th>
<th>Bed Voidage $e$ 2.0 mm</th>
<th>Bed Voidage $e$ 4.0 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>0.595</td>
<td>0.434</td>
<td>0.361</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.015</td>
<td>0.674</td>
<td>0.499</td>
<td>0.424</td>
<td>0.388</td>
<td>-</td>
</tr>
<tr>
<td>0.020</td>
<td>0.736</td>
<td>0.551</td>
<td>0.474</td>
<td>0.436</td>
<td>0.380</td>
</tr>
<tr>
<td>0.025</td>
<td>0.788</td>
<td>0.595</td>
<td>0.517</td>
<td>0.477</td>
<td>0.417</td>
</tr>
<tr>
<td>0.030</td>
<td>0.833</td>
<td>0.634</td>
<td>0.555</td>
<td>0.514</td>
<td>0.450</td>
</tr>
<tr>
<td>0.040</td>
<td>0.910</td>
<td>0.700</td>
<td>0.621</td>
<td>0.577</td>
<td>0.507</td>
</tr>
<tr>
<td>0.050</td>
<td>0.975</td>
<td>0.756</td>
<td>0.677</td>
<td>0.632</td>
<td>0.556</td>
</tr>
<tr>
<td>0.060</td>
<td>1.031</td>
<td>0.805</td>
<td>0.727</td>
<td>0.681</td>
<td>0.600</td>
</tr>
<tr>
<td>0.070</td>
<td>-</td>
<td>0.849</td>
<td>0.771</td>
<td>0.724</td>
<td>0.640</td>
</tr>
<tr>
<td>0.080</td>
<td>-</td>
<td>0.889</td>
<td>0.813</td>
<td>0.765</td>
<td>0.677</td>
</tr>
<tr>
<td>0.090</td>
<td>-</td>
<td>0.926</td>
<td>0.851</td>
<td>0.802</td>
<td>0.711</td>
</tr>
<tr>
<td>0.100</td>
<td>-</td>
<td>0.960</td>
<td>0.886</td>
<td>0.837</td>
<td>0.742</td>
</tr>
</tbody>
</table>

Only the data required to compile Fig. 5.1 is shown. The values of bed voidage, $e$, are calculated from the following equations predicted by Richardson-Zaki:-

- Equation for 0.5 mm bubbles: $U/0.054 = e^{3.25}$
- Equation for 1.0 mm bubbles: $U/0.113 = e^{2.90}$
- Equation for 1.5 mm bubbles: $U/0.136 = e^{2.57}$
- Equation for 2.0 mm bubbles: $U/0.155 = e^{2.46}$
- Equation for 4.0 mm bubbles: $U/0.204 = e^{2.4}$
2) Data for Fig. 3.6

<table>
<thead>
<tr>
<th>Liquid flow rate (l/min)</th>
<th>Liquid Velocity (m/s)</th>
<th>Bed depth (cm)</th>
<th>Bed Voidage e</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8</td>
<td>0.018</td>
<td>14.3</td>
<td>0.40</td>
</tr>
<tr>
<td>5.5</td>
<td>0.026</td>
<td>17.0</td>
<td>0.50</td>
</tr>
<tr>
<td>5.7</td>
<td>0.027</td>
<td>18.0</td>
<td>0.52</td>
</tr>
<tr>
<td>6.7</td>
<td>0.032</td>
<td>21.0</td>
<td>0.59</td>
</tr>
<tr>
<td>8.2</td>
<td>0.039</td>
<td>26.5</td>
<td>0.68</td>
</tr>
<tr>
<td>10.1</td>
<td>0.048</td>
<td>32.5</td>
<td>0.74</td>
</tr>
<tr>
<td>10.4</td>
<td>0.050</td>
<td>33.5</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Predicted data

<table>
<thead>
<tr>
<th>Liquid Velocity (m/s)</th>
<th>Bed Voidage, e 1.0 mm</th>
<th>Bed Voidage, e 2.5 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.434</td>
<td>0.304</td>
</tr>
<tr>
<td>0.02</td>
<td>0.551</td>
<td>0.407</td>
</tr>
<tr>
<td>0.03</td>
<td>0.634</td>
<td>0.483</td>
</tr>
<tr>
<td>0.04</td>
<td>0.700</td>
<td>0.544</td>
</tr>
<tr>
<td>0.05</td>
<td>0.756</td>
<td>0.598</td>
</tr>
<tr>
<td>0.06</td>
<td>0.805</td>
<td>0.646</td>
</tr>
<tr>
<td>0.07</td>
<td>0.849</td>
<td>0.689</td>
</tr>
<tr>
<td>0.08</td>
<td>0.889</td>
<td>0.728</td>
</tr>
<tr>
<td>0.09</td>
<td>0.926</td>
<td>0.765</td>
</tr>
<tr>
<td>0.10</td>
<td>0.960</td>
<td>0.800</td>
</tr>
</tbody>
</table>

The predicted data is based upon the following equations:

Equation for 1.0 mm bubbles:

\[ \frac{U}{0.113} = e^{2.90} \]

Equation for 2.5 mm bubbles:

\[ \frac{U}{0.170} = e^{2.38} \]
3) Data for Fig. 3.7

<table>
<thead>
<tr>
<th>Liquid flow rate (lmin⁻¹)</th>
<th>Liquid Velocity (ms⁻¹)</th>
<th>Bed depth (cm)</th>
<th>Bed Voidage, e</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
<td>0.011</td>
<td>13.5</td>
<td>0.40</td>
</tr>
<tr>
<td>7.8</td>
<td>0.037</td>
<td>20.0</td>
<td>0.60</td>
</tr>
<tr>
<td>10.5</td>
<td>0.050</td>
<td>29.0</td>
<td>0.72</td>
</tr>
<tr>
<td>12.2</td>
<td>0.058</td>
<td>25.0</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Predicted data

<table>
<thead>
<tr>
<th>Liquid Velocity (ms⁻¹)</th>
<th>Bed Voidage, e 1.0 mm</th>
<th>Bed Voidage, e 2.0 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.434</td>
<td>0.329</td>
</tr>
<tr>
<td>0.02</td>
<td>0.551</td>
<td>0.436</td>
</tr>
<tr>
<td>0.03</td>
<td>0.634</td>
<td>0.514</td>
</tr>
<tr>
<td>0.04</td>
<td>0.700</td>
<td>0.577</td>
</tr>
<tr>
<td>0.05</td>
<td>0.756</td>
<td>0.632</td>
</tr>
<tr>
<td>0.06</td>
<td>0.805</td>
<td>0.681</td>
</tr>
<tr>
<td>0.07</td>
<td>0.849</td>
<td>0.724</td>
</tr>
<tr>
<td>0.08</td>
<td>0.889</td>
<td>0.765</td>
</tr>
<tr>
<td>0.09</td>
<td>0.926</td>
<td>0.802</td>
</tr>
<tr>
<td>0.10</td>
<td>0.960</td>
<td>0.837</td>
</tr>
</tbody>
</table>

The predicted data is calculated from the following equations:

Equation for 1.0 mm bubbles: \[ U/0.113 = e^{2.90} \]
Equation for 2.0 mm bubbles: \[ U/0.155 = e^{2.46} \]
4) Data for Fig. 3.8

<table>
<thead>
<tr>
<th>Liquid flow rate (L/min)</th>
<th>Liquid Velocity (ms⁻¹)</th>
<th>Bed depth (cm)</th>
<th>Bed Voidage, e</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.44</td>
<td>0.002</td>
<td>11.0</td>
<td>0.40</td>
</tr>
<tr>
<td>1.16</td>
<td>0.006</td>
<td>12.3</td>
<td>0.46</td>
</tr>
<tr>
<td>1.64</td>
<td>0.008</td>
<td>13.1</td>
<td>0.50</td>
</tr>
<tr>
<td>2.46</td>
<td>0.012</td>
<td>14.3</td>
<td>0.54</td>
</tr>
<tr>
<td>2.52</td>
<td>0.012</td>
<td>15.6</td>
<td>0.58</td>
</tr>
<tr>
<td>3.05</td>
<td>0.015</td>
<td>16.1</td>
<td>0.59</td>
</tr>
</tbody>
</table>

**Predicted Data**

<table>
<thead>
<tr>
<th>Liquid Velocity (ms⁻¹)</th>
<th>Bed Voidage, e 0.5 mm</th>
<th>Bed Voidage, e 1.5 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>0.384</td>
<td>-</td>
</tr>
<tr>
<td>0.004</td>
<td>0.470</td>
<td>0.357</td>
</tr>
<tr>
<td>0.006</td>
<td>0.529</td>
<td>0.405</td>
</tr>
<tr>
<td>0.008</td>
<td>0.576</td>
<td>0.443</td>
</tr>
<tr>
<td>0.010</td>
<td>0.615</td>
<td>0.476</td>
</tr>
<tr>
<td>0.020</td>
<td>0.753</td>
<td>0.591</td>
</tr>
<tr>
<td>0.030</td>
<td>0.848</td>
<td>0.672</td>
</tr>
<tr>
<td>0.040</td>
<td>0.922</td>
<td>0.735</td>
</tr>
<tr>
<td>0.050</td>
<td>0.985</td>
<td>0.789</td>
</tr>
<tr>
<td>0.060</td>
<td>1.039</td>
<td>0.835</td>
</tr>
<tr>
<td>0.070</td>
<td>-</td>
<td>0.877</td>
</tr>
<tr>
<td>0.080</td>
<td>-</td>
<td>0.914</td>
</tr>
<tr>
<td>0.090</td>
<td>-</td>
<td>0.949</td>
</tr>
<tr>
<td>0.100</td>
<td>-</td>
<td>0.981</td>
</tr>
</tbody>
</table>

Equation for 0.5 mm bubbles: \( U/0.054 = e^{3.25} \)
Equation for 1.5 mm bubbles: \( U/0.136 = e^{2.57} \)
5) Data for Fig. 3.9

<table>
<thead>
<tr>
<th>Liquid Velocity (ms⁻¹)</th>
<th>Bed Voidage 0.8 mm</th>
<th>Bed Voidage 1.0 mm</th>
<th>Bed Voidage 2.0 mm</th>
<th>Bed Voidage 3.0 mm</th>
<th>Bed Voidage 4.0 mm</th>
<th>Bed Voidage 6.0 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.485</td>
<td>0.442</td>
<td>0.332</td>
<td>0.302</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.02</td>
<td>0.609</td>
<td>0.559</td>
<td>0.439</td>
<td>0.403</td>
<td>0.387</td>
<td>0.369</td>
</tr>
<tr>
<td>0.03</td>
<td>0.696</td>
<td>0.641</td>
<td>0.518</td>
<td>0.477</td>
<td>0.458</td>
<td>0.437</td>
</tr>
<tr>
<td>0.04</td>
<td>0.765</td>
<td>0.707</td>
<td>0.582</td>
<td>0.538</td>
<td>0.516</td>
<td>0.493</td>
</tr>
<tr>
<td>0.05</td>
<td>0.823</td>
<td>0.762</td>
<td>0.638</td>
<td>0.590</td>
<td>0.566</td>
<td>0.541</td>
</tr>
<tr>
<td>0.06</td>
<td>0.874</td>
<td>0.811</td>
<td>0.687</td>
<td>0.637</td>
<td>0.611</td>
<td>0.583</td>
</tr>
<tr>
<td>0.07</td>
<td>0.920</td>
<td>0.854</td>
<td>0.731</td>
<td>0.679</td>
<td>0.652</td>
<td>0.622</td>
</tr>
<tr>
<td>0.08</td>
<td>0.961</td>
<td>0.894</td>
<td>0.772</td>
<td>0.718</td>
<td>0.689</td>
<td>0.658</td>
</tr>
<tr>
<td>0.09</td>
<td>0.999</td>
<td>0.930</td>
<td>0.809</td>
<td>0.754</td>
<td>0.724</td>
<td>0.691</td>
</tr>
<tr>
<td>0.10</td>
<td>1.034</td>
<td>0.964</td>
<td>0.845</td>
<td>0.788</td>
<td>0.756</td>
<td>0.722</td>
</tr>
</tbody>
</table>

The equations for each bed according to Richardson-Zaki are as follows:

- **Equation for 0.8 mm bubbles:** $\frac{U}{0.09} = e^{3.04}$
- **Equation for 1.0 mm bubbles:** $\frac{U}{0.11} = e^{2.95}$
- **Equation for 2.0 mm bubbles:** $\frac{U}{0.15} = e^{2.46}$
- **Equation for 3.0 mm bubbles:** $\frac{U}{0.18} = e^{2.40}$
- **Equation for 4.0 mm bubbles:** $\frac{U}{0.20} = e^{2.40}$
- **Equation for 6.0 mm bubbles:** $\frac{U}{0.22} = e^{2.40}$
6) Data for Fig. 3.10

<table>
<thead>
<tr>
<th>Liquid flow rate (lmin(^{-1}))</th>
<th>Liquid Velocity (ms(^{-1}))</th>
<th>Bed depth (cm)</th>
<th>Bed Voidage, e</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.00</td>
<td>0.025</td>
<td>13.0</td>
<td>0.40</td>
</tr>
<tr>
<td>3.25</td>
<td>0.027</td>
<td>14.0</td>
<td>0.44</td>
</tr>
<tr>
<td>3.75</td>
<td>0.031</td>
<td>14.9</td>
<td>0.48</td>
</tr>
<tr>
<td>4.10</td>
<td>0.034</td>
<td>16.8</td>
<td>0.54</td>
</tr>
<tr>
<td>4.50</td>
<td>0.037</td>
<td>19.2</td>
<td>0.59</td>
</tr>
<tr>
<td>5.00</td>
<td>0.041</td>
<td>22.2</td>
<td>0.65</td>
</tr>
<tr>
<td>5.50</td>
<td>0.045</td>
<td>26.8</td>
<td>0.71</td>
</tr>
<tr>
<td>6.00</td>
<td>0.049</td>
<td>32.0</td>
<td>0.76</td>
</tr>
<tr>
<td>6.50</td>
<td>0.053</td>
<td>36.9</td>
<td>0.79</td>
</tr>
<tr>
<td>7.00</td>
<td>0.058</td>
<td>44.8</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Predicted Data

<table>
<thead>
<tr>
<th>Liquid Velocity (ms(^{-1}))</th>
<th>Bed Voidage, e</th>
<th>Bed Voidage, e</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.8 mm</td>
<td>6.0 mm</td>
</tr>
<tr>
<td>0.01</td>
<td>0.485</td>
<td>-</td>
</tr>
<tr>
<td>0.02</td>
<td>0.609</td>
<td>0.369</td>
</tr>
<tr>
<td>0.03</td>
<td>0.696</td>
<td>0.437</td>
</tr>
<tr>
<td>0.04</td>
<td>0.765</td>
<td>0.493</td>
</tr>
<tr>
<td>0.05</td>
<td>0.823</td>
<td>0.541</td>
</tr>
<tr>
<td>0.06</td>
<td>0.874</td>
<td>0.583</td>
</tr>
<tr>
<td>0.07</td>
<td>0.920</td>
<td>0.622</td>
</tr>
<tr>
<td>0.08</td>
<td>0.961</td>
<td>0.658</td>
</tr>
<tr>
<td>0.09</td>
<td>0.999</td>
<td>0.691</td>
</tr>
<tr>
<td>0.10</td>
<td>1.034</td>
<td>0.722</td>
</tr>
</tbody>
</table>

Equation for 0.8 mm bubbles: \( U/0.09 = e^{3.04} \)
Equation for 6.0 mm bubbles: \( U/0.22 = e^{2.40} \)
Appendix 1 - Raw Data

7) Data for Fig. 3.11

<table>
<thead>
<tr>
<th>Liquid Flow rate (lmin⁻¹)</th>
<th>Liquid Velocity (ms⁻¹)</th>
<th>Bed depth (cm)</th>
<th>Bed Voidage (cm)</th>
<th>Bed depth (cm)</th>
<th>Bed Voidage</th>
<th>Bed depth (cm)</th>
<th>Bed Voidage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>13.0 cm</td>
<td></td>
<td></td>
<td>13.0 cm</td>
<td></td>
</tr>
<tr>
<td>3.00</td>
<td>0.025</td>
<td>13.0</td>
<td>-0.40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.25</td>
<td>0.027</td>
<td>14.0</td>
<td>0.44</td>
<td>13.3</td>
<td>0.40</td>
<td>13.5</td>
<td>0.40</td>
</tr>
<tr>
<td>3.75</td>
<td>0.031</td>
<td>14.9</td>
<td>0.48</td>
<td>16.2</td>
<td>0.51</td>
<td>15.7</td>
<td>0.48</td>
</tr>
<tr>
<td>4.10</td>
<td>0.034</td>
<td>16.8</td>
<td>0.54</td>
<td>-</td>
<td>-</td>
<td>18.7</td>
<td>0.57</td>
</tr>
<tr>
<td>4.20</td>
<td>0.035</td>
<td>-</td>
<td>-</td>
<td>20.0</td>
<td>0.60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4.50</td>
<td>0.037</td>
<td>19.2</td>
<td>0.59</td>
<td>-</td>
<td>-</td>
<td>21.6</td>
<td>0.63</td>
</tr>
<tr>
<td>4.60</td>
<td>0.038</td>
<td>-</td>
<td>-</td>
<td>22.1</td>
<td>0.64</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5.00</td>
<td>0.041</td>
<td>22.2</td>
<td>0.65</td>
<td>28.0</td>
<td>0.72</td>
<td>26.5</td>
<td>0.69</td>
</tr>
<tr>
<td>5.50</td>
<td>0.045</td>
<td>26.8</td>
<td>0.71</td>
<td>30.0</td>
<td>0.73</td>
<td>32.4</td>
<td>0.75</td>
</tr>
<tr>
<td>6.00</td>
<td>0.049</td>
<td>32.0</td>
<td>0.76</td>
<td>37.3</td>
<td>0.79</td>
<td>35.4</td>
<td>0.77</td>
</tr>
<tr>
<td>6.50</td>
<td>0.053</td>
<td>36.9</td>
<td>0.79</td>
<td>42.2</td>
<td>0.81</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7.00</td>
<td>0.058</td>
<td>44.8</td>
<td>0.83</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Predicted data

<table>
<thead>
<tr>
<th>Liquid Velocity (ms⁻¹)</th>
<th>Bed Voidage, e 0.8 mm</th>
<th>Bed Voidage, e 6.0 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.485</td>
<td>-</td>
</tr>
<tr>
<td>0.02</td>
<td>0.609</td>
<td>0.369</td>
</tr>
<tr>
<td>0.03</td>
<td>0.696</td>
<td>0.437</td>
</tr>
<tr>
<td>0.04</td>
<td>0.765</td>
<td>0.493</td>
</tr>
<tr>
<td>0.05</td>
<td>0.823</td>
<td>0.541</td>
</tr>
<tr>
<td>0.06</td>
<td>0.874</td>
<td>0.583</td>
</tr>
<tr>
<td>0.07</td>
<td>0.920</td>
<td>0.622</td>
</tr>
<tr>
<td>0.08</td>
<td>0.961</td>
<td>0.658</td>
</tr>
<tr>
<td>0.09</td>
<td>0.999</td>
<td>0.691</td>
</tr>
<tr>
<td>0.10</td>
<td>1.034</td>
<td>0.722</td>
</tr>
</tbody>
</table>
8) Data for Fig. 3.12

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5 mm</td>
<td>1.0 mm</td>
<td>2.0 mm</td>
<td>3.0 mm</td>
<td>6.0 mm</td>
</tr>
<tr>
<td>0.01</td>
<td>0.590</td>
<td>0.425</td>
<td>0.326</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>0.732</td>
<td>0.542</td>
<td>0.431</td>
<td>0.392</td>
<td>0.349</td>
</tr>
<tr>
<td>0.03</td>
<td>0.830</td>
<td>0.625</td>
<td>0.509</td>
<td>0.464</td>
<td>0.413</td>
</tr>
<tr>
<td>0.04</td>
<td>0.908</td>
<td>0.692</td>
<td>0.572</td>
<td>0.523</td>
<td>0.465</td>
</tr>
<tr>
<td>0.05</td>
<td>0.973</td>
<td>0.748</td>
<td>0.626</td>
<td>0.574</td>
<td>0.511</td>
</tr>
<tr>
<td>0.06</td>
<td>1.030</td>
<td>0.798</td>
<td>0.674</td>
<td>0.619</td>
<td>0.551</td>
</tr>
<tr>
<td>0.07</td>
<td></td>
<td>0.842</td>
<td>0.718</td>
<td>0.660</td>
<td>0.588</td>
</tr>
<tr>
<td>0.08</td>
<td></td>
<td>0.883</td>
<td>0.758</td>
<td>0.698</td>
<td>0.621</td>
</tr>
<tr>
<td>0.09</td>
<td></td>
<td>0.920</td>
<td>0.795</td>
<td>0.733</td>
<td>0.653</td>
</tr>
<tr>
<td>0.10</td>
<td></td>
<td>0.955</td>
<td>0.829</td>
<td>0.766</td>
<td>0.682</td>
</tr>
</tbody>
</table>

Equations for Richardson-Zaki model,

- Equation for 0.5 mm bubbles: \( \frac{U}{0.055} = e^{1.22} \)
- Equation for 1.0 mm bubbles: \( \frac{U}{0.114} = e^{2.84} \)
- Equation for 2.0 mm bubbles: \( \frac{U}{0.159} = e^{2.46} \)
- Equation for 3.0 mm bubbles: \( \frac{U}{0.190} = e^{2.40} \)
- Equation for 6.0 mm bubbles: \( \frac{U}{0.251} = e^{2.40} \)
9) Data for Fig. 3.13

<table>
<thead>
<tr>
<th>Liquid Flow rate (lmin⁻¹)</th>
<th>Liquid Velocity (ms⁻¹)</th>
<th>Bed depth (cm)</th>
<th>Bed Voidage, ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.021</td>
<td>14.6</td>
<td>0.40</td>
</tr>
<tr>
<td>11</td>
<td>0.023</td>
<td>15.5</td>
<td>0.43</td>
</tr>
<tr>
<td>12</td>
<td>0.025</td>
<td>16.6</td>
<td>0.47</td>
</tr>
<tr>
<td>13</td>
<td>0.027</td>
<td>17.6</td>
<td>0.50</td>
</tr>
<tr>
<td>14</td>
<td>0.029</td>
<td>18.2</td>
<td>0.52</td>
</tr>
<tr>
<td>15</td>
<td>0.031</td>
<td>19.1</td>
<td>0.54</td>
</tr>
<tr>
<td>16</td>
<td>0.033</td>
<td>19.7</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Predicted data

<table>
<thead>
<tr>
<th>Liquid Velocity (lmin⁻¹)</th>
<th>Bed Voidage, ε 1.0 mm</th>
<th>Bed Voidage, ε 3.0 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.425</td>
<td>-</td>
</tr>
<tr>
<td>0.02</td>
<td>0.542</td>
<td>0.392</td>
</tr>
<tr>
<td>0.03</td>
<td>0.625</td>
<td>0.464</td>
</tr>
<tr>
<td>0.04</td>
<td>0.692</td>
<td>0.523</td>
</tr>
<tr>
<td>0.05</td>
<td>0.748</td>
<td>0.574</td>
</tr>
<tr>
<td>0.06</td>
<td>0.798</td>
<td>0.619</td>
</tr>
<tr>
<td>0.07</td>
<td>0.842</td>
<td>0.660</td>
</tr>
<tr>
<td>0.08</td>
<td>0.883</td>
<td>0.698</td>
</tr>
<tr>
<td>0.09</td>
<td>0.920</td>
<td>0.733</td>
</tr>
<tr>
<td>0.10</td>
<td>0.955</td>
<td>0.766</td>
</tr>
</tbody>
</table>

Equation for 1.0 mm bubbles: \( U/0.114 = e^{2.84} \)
Equation for 3.0 mm bubbles: \( U/0.190 = e^{2.40} \)
Appendix 1 - Raw Data

10) Data for Fig. 3.14

<table>
<thead>
<tr>
<th>Liquid Flow rate (l/min⁻¹)</th>
<th>Liquid Velocity (ms⁻¹)</th>
<th>Bed depth (cm)</th>
<th>Bed Voidage, e</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.021</td>
<td>12.9</td>
<td>0.40</td>
</tr>
<tr>
<td>11</td>
<td>0.023</td>
<td>13.5</td>
<td>0.42</td>
</tr>
<tr>
<td>12</td>
<td>0.025</td>
<td>13.7</td>
<td>0.44</td>
</tr>
<tr>
<td>13</td>
<td>0.027</td>
<td>13.8</td>
<td>0.44</td>
</tr>
<tr>
<td>14</td>
<td>0.029</td>
<td>14.2</td>
<td>0.45</td>
</tr>
<tr>
<td>15</td>
<td>0.031</td>
<td>15.0</td>
<td>0.48</td>
</tr>
<tr>
<td>16</td>
<td>0.033</td>
<td>15.2</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Predicted data

<table>
<thead>
<tr>
<th>Liquid Velocity (ms⁻¹)</th>
<th>Bed Voidage, e 2.5 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.300</td>
</tr>
<tr>
<td>0.02</td>
<td>0.401</td>
</tr>
<tr>
<td>0.03</td>
<td>0.477</td>
</tr>
<tr>
<td>0.04</td>
<td>0.538</td>
</tr>
<tr>
<td>0.05</td>
<td>0.591</td>
</tr>
<tr>
<td>0.06</td>
<td>0.638</td>
</tr>
<tr>
<td>0.07</td>
<td>0.680</td>
</tr>
<tr>
<td>0.08</td>
<td>0.719</td>
</tr>
<tr>
<td>0.09</td>
<td>0.756</td>
</tr>
<tr>
<td>0.10</td>
<td>0.790</td>
</tr>
</tbody>
</table>

Equation for 2.5 mm bubbles: \( \frac{U}{0.175} = e^{2.3k} \)
11) Data for Fig. 3.15

<table>
<thead>
<tr>
<th>Liquid Flow rate (lmin⁻¹)</th>
<th>Liquid Velocity (ms⁻¹)</th>
<th>Bed depth (cm)</th>
<th>Bed Voidage, e</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.021</td>
<td>4.7</td>
<td>0.40</td>
</tr>
<tr>
<td>11</td>
<td>0.023</td>
<td>5.2</td>
<td>0.46</td>
</tr>
<tr>
<td>12</td>
<td>0.025</td>
<td>5.2</td>
<td>0.46</td>
</tr>
<tr>
<td>13</td>
<td>0.027</td>
<td>5.5</td>
<td>0.49</td>
</tr>
<tr>
<td>14</td>
<td>0.029</td>
<td>5.8</td>
<td>0.52</td>
</tr>
<tr>
<td>15</td>
<td>0.031</td>
<td>6.2</td>
<td>0.55</td>
</tr>
<tr>
<td>16</td>
<td>0.033</td>
<td>6.5</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Predicted data

<table>
<thead>
<tr>
<th>Liquid Velocity (lmin⁻¹)</th>
<th>Bed Voidage, e 1.0 mm</th>
<th>Bed Voidage, e 3.0 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.425</td>
<td>-</td>
</tr>
<tr>
<td>0.02</td>
<td>0.542</td>
<td>0.392</td>
</tr>
<tr>
<td>0.03</td>
<td>0.625</td>
<td>0.464</td>
</tr>
<tr>
<td>0.04</td>
<td>0.692</td>
<td>0.523</td>
</tr>
<tr>
<td>0.05</td>
<td>0.748</td>
<td>0.574</td>
</tr>
<tr>
<td>0.06</td>
<td>0.798</td>
<td>0.619</td>
</tr>
<tr>
<td>0.07</td>
<td>0.842</td>
<td>0.660</td>
</tr>
<tr>
<td>0.08</td>
<td>0.883</td>
<td>0.698</td>
</tr>
<tr>
<td>0.09</td>
<td>0.920</td>
<td>0.733</td>
</tr>
<tr>
<td>0.10</td>
<td>0.955</td>
<td>0.766</td>
</tr>
</tbody>
</table>

Equation for 1.0 mm bubbles: \( \frac{U}{0.114} = e^{2.84} \)

Equation for 3.0 mm bubbles: \( \frac{U}{0.190} = e^{2.40} \)
Appendix 1 - B) Data for Figs. 4.2 - 4.5

1) Data for Fig. 4.2

phenol in the absence of any surfactant

<table>
<thead>
<tr>
<th>Mass of carbon in batch (mg)</th>
<th>Equilibrium concentration, $C_e$ (mg l$^{-1}$)</th>
<th>Initial concentration (mg l$^{-1}$)</th>
<th>Phenol adsorbed (mg l$^{-1}$)</th>
<th>$q_e$ (mg phenol per gram carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>382.8</td>
<td>0.31</td>
<td>20.07</td>
<td>19.76</td>
<td>25.29</td>
</tr>
<tr>
<td>296.2</td>
<td>0.50</td>
<td>20.00</td>
<td>19.50</td>
<td>32.25</td>
</tr>
<tr>
<td>195.9</td>
<td>2.15</td>
<td>19.78</td>
<td>17.63</td>
<td>44.09</td>
</tr>
<tr>
<td>100.3</td>
<td>7.01</td>
<td>19.97</td>
<td>12.96</td>
<td>63.31</td>
</tr>
<tr>
<td>50.0</td>
<td>12.17</td>
<td>20.05</td>
<td>7.88</td>
<td>77.25</td>
</tr>
</tbody>
</table>

The data in bold type is plotted as the experimental data. A regression of the data produces the constants $K$ and $1/n$ in the Freundlich equation, which is,

$$q_e = 36.76 C_e^{0.287}$$

This is plotted as the best fit of the above data.

phenol in the presence of oleyl alcohol

<table>
<thead>
<tr>
<th>Mass of carbon in batch (mg)</th>
<th>Equilibrium concentration, $C_e$ (mg l$^{-1}$)</th>
<th>Initial concentration (mg l$^{-1}$)</th>
<th>Phenol adsorbed (mg l$^{-1}$)</th>
<th>$q_e$ (mg phenol per gram carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>348.4</td>
<td>1.98</td>
<td>18.80</td>
<td>16.82</td>
<td>23.66</td>
</tr>
<tr>
<td>237.4</td>
<td>4.54</td>
<td>19.88</td>
<td>15.34</td>
<td>31.66</td>
</tr>
<tr>
<td>151.5</td>
<td>6.60</td>
<td>18.80</td>
<td>12.19</td>
<td>39.43</td>
</tr>
<tr>
<td>78.6</td>
<td>12.53</td>
<td>19.94</td>
<td>7.41</td>
<td>46.18</td>
</tr>
<tr>
<td>37.6</td>
<td>17.28</td>
<td>20.56</td>
<td>3.27</td>
<td>42.64</td>
</tr>
</tbody>
</table>
The Freundlich best fit for this data is,

\[ q_e = 20.29 C_e^{0.299} \]

**phenol in the presence of oleic acid**

<table>
<thead>
<tr>
<th>Mass of carbon in batch (mg)</th>
<th>Equilibrium concentration, ( C_e ) (mg l(^{-1}))</th>
<th>Initial concentration (mg l(^{-1}))</th>
<th>Phenol adsorbed (mg l(^{-1}))</th>
<th>( q_e ) (mg phenol per gram carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>407.1</td>
<td>0.96</td>
<td>17.71</td>
<td>16.75</td>
<td>20.16</td>
</tr>
<tr>
<td>258.4</td>
<td>3.48</td>
<td>17.38</td>
<td>13.90</td>
<td>26.35</td>
</tr>
<tr>
<td>185.5</td>
<td>5.24</td>
<td>18.37</td>
<td>13.13</td>
<td>34.69</td>
</tr>
<tr>
<td>111.9</td>
<td>10.30</td>
<td>19.36</td>
<td>9.06</td>
<td>39.67</td>
</tr>
<tr>
<td>38.0</td>
<td>14.96</td>
<td>18.98</td>
<td>4.02</td>
<td>51.80</td>
</tr>
</tbody>
</table>

The Freundlich best fit for this data is,

\[ q_e = 19.36 C_e^{0.333} \]

2) **Data for Fig. 4.3**

**p-chlorophenol in the absence of any surfactant**

<table>
<thead>
<tr>
<th>Mass of carbon in batch (mg)</th>
<th>Equilibrium concentration, ( C_e ) (mg l(^{-1}))</th>
<th>Initial concentration (mg l(^{-1}))</th>
<th>Phenol adsorbed (mg l(^{-1}))</th>
<th>( q_e ) (mg phenol per gram carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.5</td>
<td>12.93</td>
<td>20.72</td>
<td>7.79</td>
<td>186.12</td>
</tr>
<tr>
<td>50.0</td>
<td>6.61</td>
<td>21.10</td>
<td>14.49</td>
<td>142.03</td>
</tr>
<tr>
<td>100.0</td>
<td>1.50</td>
<td>20.77</td>
<td>19.27</td>
<td>94.44</td>
</tr>
<tr>
<td>150.4</td>
<td>0.50</td>
<td>20.90</td>
<td>20.40</td>
<td>66.45</td>
</tr>
<tr>
<td>249.4</td>
<td>0.18</td>
<td>21.44</td>
<td>21.26</td>
<td>41.78</td>
</tr>
</tbody>
</table>

The data in bold type is plotted as the experimental data. A regression of this data produces the \( K \) and \( 1/n \) constants in the Freundlich equation,
This equation is plotted as the best fit curve for the experimental data.

### p-chlorophenol in the presence of oleyl alcohol

<table>
<thead>
<tr>
<th>Mass of carbon in batch (mg)</th>
<th>Equilibrium concentration, $C_e$ (mg l$^{-1}$)</th>
<th>Initial concentration (mg l$^{-1}$)</th>
<th>Phenol adsorbed (mg l$^{-1}$)</th>
<th>$q_e$ (mg phenol per gram carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>233.4</td>
<td>0.71</td>
<td>20.14</td>
<td>19.43</td>
<td>40.80</td>
</tr>
<tr>
<td>191.4</td>
<td>1.32</td>
<td>20.82</td>
<td>19.50</td>
<td>49.93</td>
</tr>
<tr>
<td>155.1</td>
<td>1.70</td>
<td>19.78</td>
<td>18.08</td>
<td>57.11</td>
</tr>
<tr>
<td>117.1</td>
<td>4.26</td>
<td>20.59</td>
<td>16.33</td>
<td>68.32</td>
</tr>
<tr>
<td>79.3</td>
<td>7.66</td>
<td>20.72</td>
<td>13.06</td>
<td>80.73</td>
</tr>
<tr>
<td>40.2</td>
<td>13.28</td>
<td>19.99</td>
<td>6.71</td>
<td>81.76</td>
</tr>
</tbody>
</table>

The Freundlich best fit data is represented by,

$$q_e = 47.03 C_e^{0.241}$$

### p-chlorophenol in the presence of oleic acid

<table>
<thead>
<tr>
<th>Mass of carbon in batch (mg)</th>
<th>Equilibrium concentration, $C_e$ (mg l$^{-1}$)</th>
<th>Initial concentration (mg l$^{-1}$)</th>
<th>Phenol adsorbed (mg l$^{-1}$)</th>
<th>$q_e$ (mg phenol per gram carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>257.9</td>
<td>0.86</td>
<td>18.86</td>
<td>18.00</td>
<td>34.20</td>
</tr>
<tr>
<td>183.5</td>
<td>1.71</td>
<td>18.67</td>
<td>16.95</td>
<td>45.27</td>
</tr>
<tr>
<td>148.7</td>
<td>2.22</td>
<td>18.45</td>
<td>16.23</td>
<td>53.49</td>
</tr>
<tr>
<td>113.0</td>
<td>5.44</td>
<td>18.41</td>
<td>12.96</td>
<td>56.21</td>
</tr>
<tr>
<td>38.8</td>
<td>12.35</td>
<td>17.71</td>
<td>5.36</td>
<td>67.67</td>
</tr>
</tbody>
</table>

The Freundlich best fit curve that represents this data is,

$$q_e = 38.95 C_e^{0.233}$$
3) Data for Fig. 4.4

In order to plot the modified Langmuir isotherms, the data in bold type in the tables above were used.

**phenol in the absence of any surfactant**

<table>
<thead>
<tr>
<th>Equilibrium concentration, $C_e$ (mg l$^{-1}$)</th>
<th>$q_e$ (mg phenol per gram carbon)</th>
<th>$C_e/q_e$ (mg l$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.31</td>
<td>25.29</td>
<td>12.26</td>
</tr>
<tr>
<td>0.50</td>
<td>32.25</td>
<td>15.58</td>
</tr>
<tr>
<td>2.15</td>
<td>44.09</td>
<td>48.82</td>
</tr>
<tr>
<td>7.01</td>
<td>63.31</td>
<td>110.73</td>
</tr>
<tr>
<td>12.17</td>
<td>77.25</td>
<td>157.53</td>
</tr>
</tbody>
</table>

A regression on the above plot produces the values for the constants $q_{\text{max}}$ and $a$. The Langmuir equation for this data is,

$$\frac{C_e}{q_e} = \frac{1}{81.21 \times 0.852} + \frac{C_e}{81.21}$$

**phenol in the presence of oleyl alcohol**

<table>
<thead>
<tr>
<th>Equilibrium concentration, $C_e$ (mg l$^{-1}$)</th>
<th>$q_e$ (mg phenol per gram carbon)</th>
<th>$C_e/q_e$ (mg l$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.98</td>
<td>23.66</td>
<td>83.50</td>
</tr>
<tr>
<td>4.54</td>
<td>31.66</td>
<td>143.30</td>
</tr>
<tr>
<td>6.60</td>
<td>39.43</td>
<td>167.51</td>
</tr>
<tr>
<td>12.53</td>
<td>46.18</td>
<td>271.36</td>
</tr>
<tr>
<td>17.28</td>
<td>42.64</td>
<td>405.39</td>
</tr>
</tbody>
</table>

The Langmuir equation for this data is,
phenol in the presence of oleic acid

\[
\frac{C_e}{q_e} = \frac{1}{(49.56 \times 0.492)} + \frac{C_e}{49.56}
\]

<table>
<thead>
<tr>
<th>Equilibrium concentration, (C_e) (mg (l^1))</th>
<th>(q_e) (mg phenol per gram carbon)</th>
<th>(C_e/q_e) (mg (l^1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.96</td>
<td>20.16</td>
<td>47.68</td>
</tr>
<tr>
<td>3.48</td>
<td>26.35</td>
<td>132.15</td>
</tr>
<tr>
<td>5.24</td>
<td>34.69</td>
<td>151.05</td>
</tr>
<tr>
<td>10.30</td>
<td>39.67</td>
<td>259.52</td>
</tr>
<tr>
<td>14.96</td>
<td>51.80</td>
<td>288.85</td>
</tr>
</tbody>
</table>

The modified Langmuir equation that best fits this data is,

\[
\frac{C_e}{q_e} = \frac{1}{(58.78 \times 0.30)} + \frac{C_e}{58.78}
\]

4) Data for Fig. 4.5

\(p\)-chlorophenol in the absence of any surfactant

<table>
<thead>
<tr>
<th>Equilibrium concentration, (C_e) (mg (l^1))</th>
<th>(q_e) (mg phenol per gram carbon)</th>
<th>(C_e/q_e) (mg (l^1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.93</td>
<td>186.12</td>
<td>69.46</td>
</tr>
<tr>
<td>6.61</td>
<td>142.03</td>
<td>46.50</td>
</tr>
<tr>
<td>1.50</td>
<td>94.44</td>
<td>15.85</td>
</tr>
<tr>
<td>0.50</td>
<td>66.45</td>
<td>7.58</td>
</tr>
<tr>
<td>0.18</td>
<td>41.78</td>
<td>4.25</td>
</tr>
</tbody>
</table>

The modified Langmuir isotherm that best fits this data is,
Appendix 1 - Raw Data

\[
\frac{C_e}{q_e} = \frac{1}{(195.19 \times 0.79)} + \frac{C_e}{195.19}
\]

p-chlorophenol in the presence of oleyl alcohol

<table>
<thead>
<tr>
<th>Equilibrium concentration, ( C_e ) (mg l(^{-1} ))</th>
<th>( q_e ) (mg phenol per gram carbon)</th>
<th>( C_e/q_e ) (mg l(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.71</td>
<td>40.80</td>
<td>17.39</td>
</tr>
<tr>
<td>1.32</td>
<td>49.93</td>
<td>26.35</td>
</tr>
<tr>
<td>1.70</td>
<td>57.11</td>
<td>29.79</td>
</tr>
<tr>
<td>4.26</td>
<td>68.32</td>
<td>62.34</td>
</tr>
<tr>
<td>7.66</td>
<td>80.73</td>
<td>94.84</td>
</tr>
<tr>
<td>13.28</td>
<td>81.76</td>
<td>162.44</td>
</tr>
</tbody>
</table>

The modified Langmuir isotherm that best fits this data is,

\[
\frac{C_e}{q_e} = \frac{1}{(97.94 \times 1.062)} + \frac{C_e}{97.94}
\]

p-chlorophenol in the presence of oleic acid

<table>
<thead>
<tr>
<th>Equilibrium concentration, ( C_e ) (mg l(^{-1} ))</th>
<th>( q_e ) (mg phenol per gram carbon)</th>
<th>( C_e/q_e ) (mg l(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.86</td>
<td>34.20</td>
<td>25.13</td>
</tr>
<tr>
<td>1.71</td>
<td>45.27</td>
<td>37.84</td>
</tr>
<tr>
<td>2.22</td>
<td>53.49</td>
<td>41.47</td>
</tr>
<tr>
<td>5.44</td>
<td>56.21</td>
<td>96.86</td>
</tr>
<tr>
<td>12.35</td>
<td>67.67</td>
<td>182.52</td>
</tr>
</tbody>
</table>

The modified Langmuir equation is,

\[
\frac{C_e}{q_e} = \frac{1}{(72.38 \times 0.963)} + \frac{C_e}{72.38}
\]
Appendix 1 - C) Data for Figs. 5.8 - 5.15

1) Data for Fig. 5.8

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Inlet concentration (mg l⁻¹)</th>
<th>Outlet concentration (mg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>18.7</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>21.1</td>
<td>4.2</td>
</tr>
<tr>
<td>165</td>
<td>22.4</td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>21.6</td>
<td>17.6</td>
</tr>
<tr>
<td>235</td>
<td>21.6</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>21.6</td>
<td>20.5</td>
</tr>
<tr>
<td>600</td>
<td>22.4</td>
<td></td>
</tr>
<tr>
<td>630</td>
<td>22.4</td>
<td>21.6</td>
</tr>
<tr>
<td>900</td>
<td>20.5</td>
<td></td>
</tr>
<tr>
<td>930</td>
<td>20.5</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>21.1</td>
<td></td>
</tr>
<tr>
<td>1230</td>
<td>22.4</td>
<td></td>
</tr>
</tbody>
</table>

Experimental conditions:

Micropollutant - phenol
Column diameter - 50 mm
Bed depth - 36 cm
Flow rate - 2 l min⁻¹
2) Data for Fig. 5.9

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Inlet concentration (mg l⁻¹)</th>
<th>Outlet concentration (mg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>55</td>
<td>17.7</td>
<td></td>
</tr>
<tr>
<td>95</td>
<td></td>
<td>3.1</td>
</tr>
<tr>
<td>150</td>
<td>25.0</td>
<td></td>
</tr>
<tr>
<td>190</td>
<td></td>
<td>19.7</td>
</tr>
<tr>
<td>310</td>
<td>20.4</td>
<td></td>
</tr>
<tr>
<td>335</td>
<td></td>
<td>20.4</td>
</tr>
<tr>
<td>615</td>
<td>20.4</td>
<td></td>
</tr>
<tr>
<td>630</td>
<td></td>
<td>21.8</td>
</tr>
<tr>
<td>1200</td>
<td>21.4</td>
<td></td>
</tr>
<tr>
<td>1230</td>
<td></td>
<td>21.8</td>
</tr>
</tbody>
</table>

Experimental conditions:

Micropollutant - phenol
Column diameter - 50 mm
Bed depth - 40 cm
Flow rate - 3.5 l min⁻¹
3) Data for Fig. 5.10

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Inlet concentration (mg l⁻¹)</th>
<th>Outlet concentration (mg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>2.51</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>5.08</td>
<td>2.74</td>
</tr>
<tr>
<td>90</td>
<td>5.19</td>
<td>2.75</td>
</tr>
<tr>
<td>120</td>
<td>5.36</td>
<td>5.04</td>
</tr>
<tr>
<td>155</td>
<td>5.21</td>
<td>5.94</td>
</tr>
<tr>
<td>190</td>
<td>5.29</td>
<td>6.30</td>
</tr>
<tr>
<td>225</td>
<td>5.37</td>
<td>6.36</td>
</tr>
<tr>
<td>260</td>
<td>5.12</td>
<td>6.01</td>
</tr>
<tr>
<td>360</td>
<td>5.42</td>
<td>6.53</td>
</tr>
<tr>
<td>390</td>
<td>5.09</td>
<td>6.95</td>
</tr>
</tbody>
</table>

Experimental conditions:

Micropollutant - *p*-chlorophenol
Column diameter - 100 mm
Bed depth - 9.9 cm
Flow rate - 6 l min⁻¹
4) Data for Fig. 5.11

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Inlet concentration (mg l⁻¹)</th>
<th>Outlet concentration (mg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>1.08</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>4.65</td>
<td>1.17</td>
</tr>
<tr>
<td>110</td>
<td>4.75</td>
<td>3.87</td>
</tr>
<tr>
<td>140</td>
<td>4.72</td>
<td>4.98</td>
</tr>
<tr>
<td>170</td>
<td>4.81</td>
<td>4.96</td>
</tr>
<tr>
<td>200</td>
<td>4.95</td>
<td>4.96</td>
</tr>
<tr>
<td>230</td>
<td>4.42</td>
<td>4.88</td>
</tr>
<tr>
<td>260</td>
<td>4.95</td>
<td>4.98</td>
</tr>
<tr>
<td>290</td>
<td>4.68</td>
<td>5.16</td>
</tr>
<tr>
<td>320</td>
<td>4.55</td>
<td>5.22</td>
</tr>
<tr>
<td>350</td>
<td>4.43</td>
<td>4.61</td>
</tr>
</tbody>
</table>

Experimental conditions:

- Micropollutant - p-chlorophenol
- Column diameter - 100 mm
- Bed depth - 11.2 cm
- Flow rate - 8 l min⁻¹
5) Data for Fig. 5.12

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Inlet concentration (mg l⁻¹)</th>
<th>Outlet concentration (mg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>1.10</td>
<td>0</td>
</tr>
<tr>
<td>75</td>
<td>4.36</td>
<td>0.72</td>
</tr>
<tr>
<td>105</td>
<td>4.77</td>
<td>3.97</td>
</tr>
<tr>
<td>135</td>
<td>5.04</td>
<td>4.81</td>
</tr>
<tr>
<td>165</td>
<td>5.26</td>
<td>5.06</td>
</tr>
<tr>
<td>195</td>
<td>4.69</td>
<td>5.54</td>
</tr>
<tr>
<td>225</td>
<td>5.06</td>
<td>5.36</td>
</tr>
</tbody>
</table>

Experimental conditions:

Micropollutant - p-chlorophenol
Column diameter - 100 mm
Bed depth - 12.5 cm
Flow rate - 7 l min⁻¹
6) Data for Fig. 5.13

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Inlet concentration (mg l(^{-1}))</th>
<th>Mid column conc (mg l(^{-1}))</th>
<th>Outlet concentration (mg l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0.02</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>3.34</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>4.25</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>4.68</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>50</td>
<td>6.17</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>6.11</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>70</td>
<td>4.93</td>
<td>1.10</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td>2.60</td>
<td>0.46</td>
</tr>
<tr>
<td>90</td>
<td>5.08</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>3.94</td>
<td>1.12</td>
</tr>
<tr>
<td>110</td>
<td></td>
<td>4.28</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td></td>
<td></td>
<td>1.89</td>
</tr>
<tr>
<td>140</td>
<td></td>
<td></td>
<td>4.02</td>
</tr>
<tr>
<td>160</td>
<td></td>
<td></td>
<td>4.40</td>
</tr>
</tbody>
</table>

Experimental conditions:

- Micropollutant - \(p\)-chlorophenol
- Column diameter - 100 mm
- No bed present - dispersion test
- Flow rate - 8 l min\(^{-1}\)
7) Data for Fig. 5.14

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Inlet concentration Bubbles present (mg l⁻¹)</th>
<th>Mid-column conc. Bubbles present (mg l⁻¹)</th>
<th>Outlet concentration Bubbles present (mg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0.40</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>2.38</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>3.52</td>
<td>0.04</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>4.09</td>
<td>0.12</td>
<td>1.38</td>
</tr>
<tr>
<td>50</td>
<td>5.00</td>
<td>1.26</td>
<td>1.91</td>
</tr>
<tr>
<td>60</td>
<td>4.64</td>
<td></td>
<td>0.67</td>
</tr>
<tr>
<td>70</td>
<td>4.91</td>
<td>3.33</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td></td>
<td>3.97</td>
<td>1.31</td>
</tr>
<tr>
<td>90</td>
<td>5.16</td>
<td>4.35</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>4.86</td>
<td>1.61</td>
</tr>
<tr>
<td>110</td>
<td></td>
<td>4.64</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td></td>
<td></td>
<td>3.74</td>
</tr>
<tr>
<td>140</td>
<td></td>
<td></td>
<td>4.66</td>
</tr>
<tr>
<td>160</td>
<td></td>
<td></td>
<td>5.05</td>
</tr>
</tbody>
</table>

Fig. 5.14 plotted in conjunction with data from Fig. 5.13

Experimental conditions:

Micropollutant - p-chlorophenol
Column diameter - 100 mm
Bed depth - 9.7 cm
Flow rate - 8 l min⁻¹
8) Data for Fig. 5.15

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Inlet concentration (mg l⁻¹)</th>
<th>Mid-column conc. (mg l⁻¹)</th>
<th>Outlet concentration (mg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>2.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>1.05</td>
<td>0</td>
</tr>
<tr>
<td>55</td>
<td>5.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td></td>
<td>4.61</td>
<td>1.19</td>
</tr>
<tr>
<td>85</td>
<td>5.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>110</td>
<td></td>
<td>4.76</td>
<td>3.87</td>
</tr>
<tr>
<td>120</td>
<td>5.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td></td>
<td>4.72</td>
<td>4.95</td>
</tr>
<tr>
<td>150</td>
<td>5.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>170</td>
<td></td>
<td>4.82</td>
<td>5.00</td>
</tr>
<tr>
<td>190</td>
<td>5.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td></td>
<td>4.92</td>
<td>4.96</td>
</tr>
<tr>
<td>225</td>
<td>5.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>230</td>
<td></td>
<td>4.46</td>
<td>4.93</td>
</tr>
<tr>
<td>260</td>
<td>5.15</td>
<td>5.05</td>
<td>4.97</td>
</tr>
<tr>
<td>290</td>
<td></td>
<td>4.64</td>
<td>5.22</td>
</tr>
<tr>
<td>320</td>
<td></td>
<td>4.54</td>
<td>5.30</td>
</tr>
<tr>
<td>350</td>
<td></td>
<td>4.47</td>
<td>4.59</td>
</tr>
<tr>
<td>360</td>
<td>5.45</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experimental conditions:

- Micropollutant - p-chlorophenol
- Column diameter - 100 mm
- Bed depth - 12.0 cm
- Flow rate - 10 l min⁻¹
Appendix 2 - Sample Calculations

A) Calculating the Richardson-Zaki model for an inverted fluidised bed

The Richardson-Zaki model is commonly used for correlating the expansion behaviour of beds of particles fluidised by a liquid medium. Karamanev and Nikolov successfully adapted this model for inverted fluidised beds to show that they also obey Richardson and Zaki. In an attempt to characterise the hydrodynamic behaviour of a fluidised bed of stabilised bubbles, this author used the Richardson and Zaki model to explain the expansion behaviour. This was achieved by comparing the expansion data with the predicted results of the correlation. This section of Appendix 2 shows how the correlation was calculated.

The Richardson-Zaki model is based on the physical parameters of the system, which were found by dimensional analysis to be the liquid velocity, $U$ (ms$^{-1}$), the particle Reynolds number ($Re_t$) and the wall effects of the column, represented by the ratio of the particle diameter, $d$ (m) to the column diameter, $D$ (m). In this example, the Richardson-Zaki model will predict the voidage, due to the liquid velocity, of an inverted bed of particles of diameter 1 mm in a column of internal diameter 50 mm. The first thing to know is the physical properties of the system, which in this case are shown below:-

\begin{align*}
\text{Bubble diameter, } d &= 0.001 \text{ m} \\
\text{Column internal diameter, } D &= 0.05 \text{ m} \\
\text{Liquid (water) density, } \rho_l &= 1000 \text{ kgm}^{-3} \\
\text{Particle density, } \rho_p &= 1 \text{ kgm}^{-3} \\
\end{align*}

(Note: The "particle" in this case is obviously an air bubble surrounded by a layer of activated carbon. It has been assumed that the density of the stabilised bubble is close to that of air)

\begin{align*}
\text{Liquid (water) viscosity, } \mu &= 0.001 \text{ kgm}^{-1}\text{s}^{-1} \\
\text{Acceleration due to gravity, } g &= 9.81 \text{ ms}^{-2} \\
\end{align*}
Appendix 2 - Sample Calculations

Particle/Column diameter ratio, \( \frac{d}{D} = 0.02 \)

The most important parameter to calculate is the Reynolds number, \( Re_b \), as this determines the values of the bubble rising velocity, \( U_t \) and the exponent, \( n \). In order to calculate \( Re_b \), the Archimedes number, \( Ar \) must be calculated.

From Eq. 3.8b,

\[
Ar = \rho_i \left( \frac{\rho_i - \rho_p}{\mu^2} \right) gd^3
\]

(A)

Hence,

\[
Ar = 1000 \left( \frac{1000 - 1}{(0.001)^2} \right) \times 9.81 \times (0.001)^3
\]

\[= 9800.2 \text{ kgm}^{-1}\text{s}^{-1}\]

Also, from Eq. 3.8b, the Best number, \( N_D \), is calculated,

\[
N_D = 4/3 \times 9800.2
\]

\[= 13066.9 \text{ km}^{-1}\text{s}^{-1}\]

In order to calculate \( Re_b \), the logarithmic value of \( N_D \) must be known,

\[
\log(N_D) = \log(13066.9) = 4.12
\]

This value is then substituted into Eq. 3.7, to get \( \log(Re_t) \),

\[
\log(Re_t) = -1.814 + 1.347 \times 4.12 - 0.1243 \times (4.12)^2 + 0.00634 \times (4.12)^3 = 2.07
\]

\[Re_t = 117.2\]
Eq. 3.7 is based upon the standard drag curve and so is only valid in the range, 12.2 > \text{Re}_t > 130. If this value is outside the specified range, then the modified drag curve (i.e. \( C_D = 0.95 \)) is used and \( \text{Re}_t \) is calculated from Eq. 3.9, i.e.

\[
\text{Re}_t = \sqrt{\frac{N_D}{0.95}} \tag{3.9}
\]

However, on this occasion, Eq. 3.7 suffices. The bubble rise velocity is then calculated using \( \text{Re}_t \),

\[
U_t = \left( \frac{\text{Re}_t \mu}{\rho_i d} \right) \tag{B}
\]

\[
U_t = \left( \frac{117.2 \times 0.001}{1000 \times 0.001} \right) = 0.117 \text{ms}^{-1}
\]

Alternatively, Eq. 3.3 can be used. Eq. 3.1 then allows calculation of the superficial fluidising velocity, \( U_i \),

\[
\log(U_i) = \log(U_t) - \frac{d}{D} \tag{3.1}
\]

\[
\log(U_i) = \log(0.117) - 0.02
\]

\[\therefore U_i = 0.11 \text{ms}^{-1}\]

The exponent, \( n \), is calculated from Eq. 3.4, for the range 1 < \( \text{Re}_t < 200 \),

\[
n = [4.4 + (18 \times 0.02)] \times (117.2)^{-0.1}
\]

\[n = 2.95\]

Therefore, for this particular system, the Richardson-Zaki equation is,

\[
\frac{U}{0.11} = e^{2.95} \tag{C}
\]
Appendix 2 - Sample Calculations

By inserting values of $U$ into eq. C, a prediction of the voidage with the fluidising velocity is possible. The hydrodynamic behaviour for a bed of stabilised bubbles, of size 1.0 mm in diameter in a column of diameter 50 mm, is predicted to be:

<table>
<thead>
<tr>
<th>Liquid Fluidising Velocity $U$ (ms$^{-1}$)</th>
<th>Voidage $e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.44</td>
</tr>
<tr>
<td>0.02</td>
<td>0.56</td>
</tr>
<tr>
<td>0.03</td>
<td>0.64</td>
</tr>
<tr>
<td>0.04</td>
<td>0.71</td>
</tr>
<tr>
<td>0.05</td>
<td>0.76</td>
</tr>
<tr>
<td>0.06</td>
<td>0.81</td>
</tr>
<tr>
<td>0.07</td>
<td>0.85</td>
</tr>
<tr>
<td>0.08</td>
<td>0.89</td>
</tr>
<tr>
<td>0.09</td>
<td>0.93</td>
</tr>
<tr>
<td>0.10</td>
<td>0.96</td>
</tr>
</tbody>
</table>

If this data is plotted on a log-log graph, the Richardson-Zaki model looks as follows,

Figure A2.1 - Predictive data for the expansion of an inverted fluidised bed of stabilised bubbles, of size 1.0mm in diameter, in a column of 50mm diameter

This procedure is repeated for fluidised beds of various bubble sizes and gradually, the expansion behaviour of different beds can be plotted on the same graph. The time to
complete this procedure is reduced if a spreadsheet is used. The actual experimental
data is then compared with the data predicted by Richardson and Zaki.

It is worth bearing in mind that the most crucial equations are those representing the
exponent, n (Eqs. 3.4, 3.5 and 3.6) and those used to calculate Re_t (Eqs. 3.7 and 3.9).
These equations are defined by Re_t and care should be taken to ensure the right equations
are used.

**B) Changing the experimental data into a useful form for comparison with the
Richardson-Zaki model**

The table below is typical of the format of results obtained from an expansion
experiment.

<table>
<thead>
<tr>
<th>Liquid Flow rate</th>
<th>Bed depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>(lmin⁻¹)</td>
<td>(cm)</td>
</tr>
<tr>
<td>3.00</td>
<td>13.0</td>
</tr>
<tr>
<td>3.25</td>
<td>14.0</td>
</tr>
<tr>
<td>3.75</td>
<td>14.9</td>
</tr>
<tr>
<td>4.10</td>
<td>16.8</td>
</tr>
<tr>
<td>4.50</td>
<td>19.2</td>
</tr>
<tr>
<td>5.00</td>
<td>22.2</td>
</tr>
<tr>
<td>5.50</td>
<td>26.8</td>
</tr>
<tr>
<td>6.00</td>
<td>32.0</td>
</tr>
<tr>
<td>6.50</td>
<td>36.9</td>
</tr>
<tr>
<td>7.00</td>
<td>44.8</td>
</tr>
</tbody>
</table>

These results, for a bed of initial depth 13.0 cm in a column 50 mm in diameter, must be
converted into the form liquid velocity, U vs. bed voidage, e, i.e. in the form of the
Richardson-Zaki equation. To convert the bed depth to voidage, an assumption must be
made. As explained in Chapter 3, the assumption is that at the minimum flow rate (in
this case 3.0 lmin⁻¹) the voidage of the bed, e₀, is 0.40. Using this assumption and Eq.
3.12, the various bed voidages can be calculated,
Appendix 2 - Sample Calculations

\[ e_1 = 1 - \frac{h_o}{h_1} (1 - e_o) \quad \text{(3.12)} \]

To calculate the bed voidage, \( e_1 \), at a bed depth of \( h_1 = 14.0 \) cm,

\[ e_1 = 1 - \frac{13.0}{14.0} (1 - 0.4) \]

\[ \therefore e_1 = 0.44 \]

By substituting values of \( h_1 \) into Eq. 3.12, the various values of \( e_1 \) can be calculated. The velocity of the liquid is calculated simply using the traditional equation,

\[ Q = U A \]

where \( Q = \) is the flow rate (\( m^3 s^{-1} \))

and \( A = \) the cross-sectional area of the column (\( m^2 \))

Taking a flow rate of 3.0 \( l \text{min}^{-1} \), this must first be converted into \( m^3 s^{-1} \),

\[ Q = \frac{3.0}{60 \times 1000} m^3 s^{-1} \]

The velocity, \( U \), is then calculated by dividing \( Q \) by \( A \),

\[ U = \frac{\frac{3.0}{60 \times 1000}}{\frac{\pi (0.05)^2}{4}} \]

\[ \therefore U = 0.025 \text{ ms}^{-1} \]

The process is continued for each flow rate until a table of data is produced which can be added to the graph of \( \log(e) \) vs. \( \log(U) \).
Appendix 2 - Sample Calculations

<table>
<thead>
<tr>
<th>Liquid Velocity, $U$ (ms$^{-1}$)</th>
<th>Bed Voidage, $e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>0.40</td>
</tr>
<tr>
<td>0.027</td>
<td>0.44</td>
</tr>
<tr>
<td>0.031</td>
<td>0.48</td>
</tr>
<tr>
<td>0.034</td>
<td>0.54</td>
</tr>
<tr>
<td>0.037</td>
<td>0.59</td>
</tr>
<tr>
<td>0.041</td>
<td>0.65</td>
</tr>
<tr>
<td>0.045</td>
<td>0.71</td>
</tr>
<tr>
<td>0.049</td>
<td>0.76</td>
</tr>
<tr>
<td>0.053</td>
<td>0.79</td>
</tr>
<tr>
<td>0.058</td>
<td>0.83</td>
</tr>
</tbody>
</table>

This data is then plotted and compared to the prediction of the Richardson-Zaki model as shown below.

![Figure A2.2](image)

Figure A2.2 - The converted data is plotted onto a log-log graph of $e$ vs. $U$ and compared to the model prediction.
Appendix 2 - Sample Calculations

Appendix 2 - C) Batch Trials - how to calculate the Freundlich isotherm

The object of performing a batch trial is to produce a data point for plotting on a graph of \( q_e \), the amount of sorbate adsorbed per gram of carbon (mg g\(^{-1}\)), against \( C_e \), the equilibrium concentration of the bulk solution (mg l\(^{-1}\)). Several batch experiments have to be performed to collect enough data to produce an adsorption isotherm. The data can then be fitted by an appropriate equation, in this case, the Freundlich equation.

After analysing the sample to find the value of \( C_e \), typically the researcher will know the amount of carbon used in the experiment, the initial concentration and the equilibrium concentration, e.g. for phenol in the absence of any spreading agent,

<table>
<thead>
<tr>
<th>Mass of carbon in batch (mg)</th>
<th>Initial concentration (mg l(^{-1}))</th>
<th>Equilibrium concentration, ( C_e ) (mg l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.3</td>
<td>19.97</td>
<td>7.01</td>
</tr>
</tbody>
</table>

The amount of phenol adsorbed by the carbon is then calculated,

\[
19.97 - 7.01 = 12.96 \text{ mg l}^{-1}
\]

After removing a sample to measure the initial concentration, the amount of solution remaining in the flask was 490 ml. The above value therefore has to be adjusted to discover how much actual phenol was adsorbed,

\[
12.96 \times \frac{490}{1000}
\]

To calculate the value of \( q_e \), the above value was divided by the amount of carbon used in grams,

\[
12.96 \times \frac{490}{1000} \times \frac{1000}{100.3} = 63.31 \text{ mg / g}
\]
Appendix 2 - Sample Calculations

In this manner, data can be produced as below,

<table>
<thead>
<tr>
<th>Equilibrium concentration $(mg , l^{-1})$</th>
<th>$q_e$ (mg phenol per gram of carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.31</td>
<td>25.29</td>
</tr>
<tr>
<td>0.50</td>
<td>32.25</td>
</tr>
<tr>
<td>2.15</td>
<td>44.09</td>
</tr>
<tr>
<td>7.01</td>
<td>63.31</td>
</tr>
<tr>
<td>12.17</td>
<td>77.25</td>
</tr>
</tbody>
</table>

The Freundlich isotherm is of the form,

$$q_e = K \, C_e^{1/n}$$

To find the values of $K$ and $1/n$, this equation must be modified to the log form,

$$\log(q_e) = \log(K) + \frac{1}{n} \log(C_e)$$

If log values of $q_e$ and $C_e$ are calculated and plotted on a graph of $\log(q_e)$ against $\log(C_e)$, the result is,

![Figure A2.3 - A log-log plot of the data for phenol in the absence of any surfactant](image)

2-9
To find the values of \(\log(K)\) and \(1/n\), a regression must be performed to find the line of best fit for the experimental data. Many software packages have regression techniques for such a task. For these results, the regression tool in the spreadsheet package, Quattro Pro, was used. Performing a regression on the data, the result is produced as follows:

Regression Output:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>1.565354</td>
</tr>
<tr>
<td>Std. Err of Y Est</td>
<td>0.022737</td>
</tr>
<tr>
<td>R Squared</td>
<td>0.990341</td>
</tr>
<tr>
<td>No. of Observations</td>
<td>5</td>
</tr>
<tr>
<td>Degrees of Freedom</td>
<td>3</td>
</tr>
<tr>
<td>X Coefficient(s)</td>
<td>0.28725</td>
</tr>
<tr>
<td>Std. Err of Coef.</td>
<td>0.016379</td>
</tr>
</tbody>
</table>

The important information from these results is the value of the Constant, which corresponds to a value of \(\log(K)\), and X Coefficient, which represents \(1/n\). From this the Freundlich equation is as follows:

\[
q_e = 36.76C_e^{0.287}
\]

This can then be plotted on the \(q_e\) vs \(C_e\) graph, to represent the line of best fit.
Appendix 2 - D) Calculating the diffusion data for Fig. 5.1

Fig. 5.1 shows how thin shelled adsorbents attain equilibrium faster than conventional spherical homogeneous particles. The calculations are performed using Eq. 5.16, which was derived from the general diffusion equation for spherical particles with boundary conditions suitable to shell particles. Eq. 5.16 is:

\[
\frac{Q}{Q_\infty} = 1 - \left[ \frac{6(1+q)^2}{(3+3q+q^2)} \sum_{n=1}^{\infty} \frac{\beta_n^2 + q^2}{\beta_n^2 (q + q^2 + \beta_n^2)} \exp\left[ -\beta_n^2 \frac{Dt}{(a-b)^2} \right] \right]
\]

where \(Q\) is the amount of adsorbate retained by unit amount of adsorbate after it has been in contact for time, \(t\), \(Q_\infty\) is the amount adsorbed after infinite time, \(q\) is the dimensionless shell thickness with relation to the core radius, \(b\), i.e. \(q = (a-b)/b\), where \(a\) is the shell radius, \(D\) is the solute diffusion coefficient and \(\beta_n\) are the roots of the equation \(\beta \cot \beta + q = 0\).

Consider a thin shelled particle, described by \(q = 0.5\), i.e. \((a-b)/b = 0.5\). It is possible, using the above equation, to plot \(Q/Q_\infty\) against \(Dt/(a-b)^2\), the dimensionless time. This will show how long it will take for the shell adsorbent to reach \(Q/Q_\infty = 1\), i.e. reach saturation. In order to calculate this, the roots \(\beta_n\) are required for \(q = 0.5\). From Carslaw and Jaeger (1959), these are:

\[
\begin{align*}
\beta_1 & = 1.8366 \\
\beta_2 & = 4.8158 \\
\beta_3 & = 7.9171 \\
\beta_4 & = 11.0409 \\
\beta_5 & = 14.1724 \\
\beta_6 & = 17.3076
\end{align*}
\]

Consider \(Dt/(a-b)^2 = 0.1\). To calculate the \(Q/Q_\infty\) value at this (dimensionless) time, the summation term in Eq. 5.16 must first be calculated for each of the \(\beta_n\) roots.
Appendix 2 - Sample Calculations

For $\beta_1$, this is:

$$
\sum_1^\infty \frac{(1.8366^2 + 0.5^2)}{1.8366^2 (0.5 + 0.5^2 + 1.8366^2)} \exp[-1.8366^2 (0.1)] = 0.186
$$

In a similar manner, the values for the other roots are obtained, and the summation of these values equals 0.1901.

Next, the value of the constant has to be calculated. This is,

$$
\frac{6(1+0.5)^2}{3+3(0.5)+(0.5)^2} = 2.842
$$

Hence, the $Q/Q_\infty$ value can be calculated:

$$
\frac{Q}{Q_\infty} = 1 - (2.842 \times 0.1901)
$$

This method is then repeated for various values of $Dt/(a-b)^2$, so that a plot can be obtained. However, if various shell thicknesses are to be compared, the plot must be for shell adsorbents of the same particle size and hence, the plot must be $Q/Q_\infty$ against $Dt/a^2$, as $a$ represents the external particle radius. Hence, all values of $q$ and $Dt/(a-b)^2$ must be converted.

For $q$ to be converted, one says:

$$
\frac{a-b}{b} = 0.5
$$

$$
\therefore a-b = 0.5 \cdot b
$$

$$
\therefore a = 1.5 \cdot b
$$

Substituting this back, we obtain:
Appendix 2 - Sample Calculations

\[
\frac{a - b}{a} = 0.5
\]

\[
\therefore q' = 0.33
\]

To convert to \( \frac{D_t}{a^2} \), we say:

\[
a - b = 0.33 \ a
\]

\[
(a - b)^2 = (0.33 \ a)^2 = 0.1089a^2
\]

\[
\therefore \frac{D_t}{a^2} = 0.1089 \frac{D_t}{(a - b)^2}
\]

Hence, Fig. 5.1 is a plot of \( \frac{Q}{Q_{oo}} \) against \( \frac{D_t}{a^2} \), for various \( q' \) values, using the conversion measures shown. In order to compare the effectiveness of shell adsorbents, the results are compared with that of a completely homogeneous particle. This particular result is obtained from Eq. 5.11. Fig 5.2 plots \( \frac{D_t}{a^2} \) against \( \frac{(a-b)}{a} \) using the data obtained from Eq. 5.16.