Preparation and properties of granular ferric hydroxide as an adsorbent in potable water treatment

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Preparation and properties of granular ferric hydroxide as an adsorbent in potable water treatment

by

Nichola Newton

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of

Doctor of Philosophy

of

Loughborough University

10 September, 2002

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Abstract

Three iron oxide materials have been studied for uptake of three anions (arsenate, phosphate and fluoride) and a cation (cadmium) from aqueous solutions. Two of the materials were produced using original procedures developed at Loughborough University. The former material was conditioned by a controlled freeze-thaw procedure to enhance granularity and the latter was air-dried at room temperature. Their capacities were compared with a commercially available material supplied by GEH Wasserchemie, Germany.

Pore size distributions and specific surface area values were determined by N$_2$ analysis at 77 K. All samples possessed a reasonable specific surface area, in the range 200–300 m$^2$/g and were mesoporous. Samples produced at Loughborough University also contained some macropores, evidence of a more amorphous structure or lack of pH control during production.

X-ray diffraction indicated that all samples had some $\beta$-FeOOH present and that the chloride content and production pH affected the material crystallinity. Crystallinity increased with increasing chloride content and a higher production pH resulted in the presence of more than one phase.

Chemical characterisation was also completed on all three samples. The point of zero net proton charge and isoelectric point for each material was obtained by potentiometric batch titrations and zeta potential measurements respectively. The difference in these values increased with a higher chloride content and all samples studied possessed a positive surface at low pH and negative surface at high pH. These parameters were not greatly affected by the background electrolyte concentration, implying that the background electrolyte is not specifically adsorbed. However, arsenate and phosphate appeared to be specifically adsorbed as the isoelectric point decreased.

The uptake capacities for arsenate, phosphate, fluoride and cadmium of all three samples were obtained by measuring batch isotherms at 25 °C. The pH range was 4–9, using various initial concentrations up to a maximum of approximately 30 𝜇M.
For all anionic species studied, the capacity decreased with increasing pH, and the reverse trend was noted for cadmium. The Langmuir model provided a good fit for the anionic isotherms and the Freundlich model for the cationic isotherms. The materials studied possessed a markedly higher capacity for fluoride than arsenate and phosphate, with an intermediate capacity for cadmium. This indicates that fluoride is attached to the surface via monodentate (single) bonds, whilst both arsenate and phosphate are primarily attached to the surface via bidentate (two) bonds. Cadmium is probably bound by both these mechanisms.

The effect of competing anions on arsenic uptake capacity was determined using mini-column experiments of binary (arsenate-fluoride, arsenate-phosphate and phosphate-fluoride) and ternary (arsenate-fluoride-phosphate) mixtures. Arsenate removal was strongly affected by the presence of phosphate, but was only slightly lower in the presence of fluoride. Phosphate-fluoride produced a marginally higher separation, indicating that the selectivity sequence for the iron oxide materials studied was $P\sim As\gg F$. Uptake increased with increasing chloride content and the column pH was reduced. The columns were successfully eluted with 0.1 M sodium hydroxide.

**Keywords:** Adsorption, granular ferric hydroxide, mini-columns, potable water, pollutants.
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## Nomenclature

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<td>Constants from Langmuir equation</td>
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<td>Heterogeneity constant</td>
</tr>
<tr>
<td>\gamma</td>
<td>Surface tension</td>
</tr>
<tr>
<td>\Gamma</td>
<td>Adsorption density</td>
</tr>
<tr>
<td>\epsilon</td>
<td>Permittivity</td>
</tr>
<tr>
<td>\zeta</td>
<td>Zeta potential</td>
</tr>
<tr>
<td>\eta</td>
<td>Solute viscosity</td>
</tr>
<tr>
<td>\theta</td>
<td>Bragg angle</td>
</tr>
<tr>
<td>1/\kappa</td>
<td>Debye-Hückel parameter</td>
</tr>
<tr>
<td>\lambda</td>
<td>Wavelength</td>
</tr>
<tr>
<td>\sigma</td>
<td>Surface charge density</td>
</tr>
<tr>
<td>\Psi</td>
<td>Electric potential</td>
</tr>
</tbody>
</table>
Chapter 1

General Introduction

Water is ubiquitous and used in many aspects of life. It is necessary for sustaining human, animal and plant life. Drinking water contains many trace contaminants, both cationic (positively charged) and anionic (negatively charged). The sources for such contamination of the aqueous environment are twofold: directly from factory effluent and waste treatment plants or indirectly from the soil by agricultural or industrial runoff. There are European Union standards for drinking water that cover thousands of pollutants, e.g. inorganic materials (Table 1.1) [1, 2, 3].

1.1 Health effects of some anionic pollutants

There are toxicological effects associated with several drinking water contaminants. Chlorination by-products cause bladder and colon cancer [4]. An elevated quantity of nitrate in potable water may cause a blood disorder commonly referred to as “blue baby” [5]. Studies in Spain and the UK have also shown a link between high nitrate levels in water and stomach cancer [6]. Above an optimum level of fluoride concentration teeth, particularly among children, become mottled. Exposure to high levels of arsenic in drinking water results in hyperpigmentation, gangrene and gastrointestinal cancer [7]. Selenium is an element essential to humans and animals; however chronic exposure results in dermatitis and problems with the central nervous system [7].
Table 1.1: EU standards for drinking water levels of various inorganic contaminants

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Maximum permitted value (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>200</td>
</tr>
<tr>
<td>Arsenic</td>
<td>10</td>
</tr>
<tr>
<td>Cadmium</td>
<td>5</td>
</tr>
<tr>
<td>Chlorine</td>
<td>40 000</td>
</tr>
<tr>
<td>Chromium</td>
<td>50</td>
</tr>
<tr>
<td>Fluorine</td>
<td>1500</td>
</tr>
<tr>
<td>Iron</td>
<td>200</td>
</tr>
<tr>
<td>Lead</td>
<td>10</td>
</tr>
<tr>
<td>Mercury</td>
<td>1</td>
</tr>
<tr>
<td>Nitrate</td>
<td>50 000</td>
</tr>
<tr>
<td>Phosphorus (as P₂O₅)</td>
<td>5000</td>
</tr>
<tr>
<td>Selenium</td>
<td>10</td>
</tr>
<tr>
<td>Sulphate</td>
<td>250 000</td>
</tr>
</tbody>
</table>

1.2 Removal technologies

The primary use of ion exchange technology has been for water softening, a cationic exchange process. In addition the need to remove radionuclides has increased the use of ion exchange resins. The majority of radioactive substances are present in water as cationic species. There are relatively few options for removal of anionic species.

The most effective method of removing nitrate and chromate is by a specific ion exchange resin [8, 9]. Fluoride can also be removed by ion exchange material or activated alumina [5, 10]. Conventional iron or aluminium sulphate (alum) precipitation can remove more than 90 % As (V) at pH < 7 and lime softening removes all As (V) present at pH > 10.6. Arsenate can also be removed by either activated alumina or bone char [7]. Selenium is effectively removed (> 90 %) by reverse osmosis, ion exchange [7] and activated alumina [11].

More recently, chitosan has been used to reduce the concentration of both cations and anions from solution. For example, copper, chromium [12], platinum [13] and vanadium [14], have successfully been removed. Arsenate sorption has also been achieved with molybdate impregnated chitosan beads [15].
Chapter 1. General Introduction

1.2.1 Inorganic ion exchange removal

Inorganic ion exchangers have been overshadowed by their organic counterparts. The earliest examples of ion exchange reactions are in soils. Ammonia was added to a soil sample and an equivalent quantity of calcium was released [16]. There are three types of inorganic exchangers, namely clay materials, zeolites (both natural and synthetic), and other oxide materials. Exchange with clay materials is not stoichiometric, but depends on the degree of isomorphous substitution [17]. Zeolites were first used as water softeners [9] and have been used as molecular sieves to separate polar and non-polar compounds, in addition to acting as ionic sieves and achieving chromatographic separations [17].

Hydrous oxides are amphoteric i.e. are able to remove both cations and anions, depending on solution pH. Quadrivalent oxides, e.g. titanium dioxide and zirconium oxide are able to remove bromide and nitrate ions from solution. Trivalent oxides are able to remove alkaline earth metals; aluminium hydroxide has removed anionic isotopes of F, Mo, Tc, I and Te [17], and inorganic anionic species of molybdate, chromate, sulfate and selenate [18]. Activated red mud, which contains both aluminium and iron, has been used to remove chromium [19] and phosphate [20]. The selectivity series of alumina for anions is as follows [17]:

\[
\text{Fe(CN)}_6^{4-} > \text{HPO}_4^{2-} > \text{CrO}_4^{2-} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- \quad (1.1)
\]

Recently, there have been concerns over the use of aluminium-containing compounds in the water treatment industry. The use of activated alumina and alum salts for co-precipitation often leads to a higher aluminium concentration in the treated water than in the raw water [21]. There is a possibility that this high level in drinking water, in addition to elevated concentrations in food and drink, could lead to a higher risk of Alzheimer’s disease and dementia [22]. The link between aluminium and Alzheimer’s was first suggested after haemodialysis patients were given aluminium orally and an increase in the symptoms of dementia was noted [6].
Chapter 1. General Introduction

Iron oxide is chemically similar to aluminium, i.e. iron is a trivalent oxide and an amphoteric material. Depending on the solution pH, both cations, e.g. Co, Ni [23], Zn [24], Cd [25], Pb [26], Cu [27] and anions, F [28], P [29], As [30], Cr (VI) [31], V [32], SeO\textsubscript{3}\textsuperscript{2-} [33] can be removed by iron oxide materials.

1.2.2 Adsorption

Adsorption of a substance involves its accumulation at the interface between two phases, solid and liquid. The accumulated substance is known as the adsorbate and the solid onto which it accumulates is the adsorbent. Several forces can contribute to the adsorbate being held at the surface, such as hydrogen bonds, dipole-dipole interactions and van der Waals forces. The adsorption of a substance onto the surface of a material can be characterised by an adsorption isotherm [34].

1.3 Adsorbents used

The adsorbents used in this study were iron hydroxides. One material was produced in the laboratory by contacting hydrous ferric chloride and iron oxide in stoichiometric quantities. The precipitate produced was aged, washed, filtered and then conditioned using a freeze-thaw methodology which resulted in a granular sample. Another iron oxide was produced in the laboratory by V Strelko Jr., again using iron oxide and sodium hydroxide, but there was no conditioning of the material. These adsorbents were compared with a commercially available material obtained from GEH Wasscherchemie, Germany.

1.4 Thesis aim

The aim of this thesis is to study the adsorbents mentioned in the previous section for their physical and chemical characteristics, and to determine the uptake capacity for certain anions and cations in both batch and column modes. Possible uptake mechanisms and types of bonding will be postulated from these results.
All three adsorbents were characterised physically by scanning electron microscopy (SEM) and X-ray diffraction (XRD), and chemically by chloride content, pH titration and zeta potential measurements. The samples were challenged batch-wise with three anionic species, namely arsenate, phosphate and fluoride. Cadmium, Cd$^{2+}$ uptake capacity was also studied, as the surface of iron is amphoteric. Mini-column experiments were carried out to determine the competitive interactions between the anionic species studied.
References


REFERENCES


REFERENCES


Chapter 2

Literature survey

In the previous chapter, several anionic contaminants and removal technologies were described. The course of this study focused primarily on arsenic. The other anions studied, namely phosphorus and fluorine are ubiquitous in the aqueous environment and can themselves pose ecological and health concerns. A cationic species was also used in the adsorption experiments. Cadmium is known to cause certain health risks, particularly through accumulation in the kidneys. The legislation, sources, health effects and chemistry concerning all adsorbates are outlined below.

2.1 Background to the arsenic problem

2.1.1 Legislation

There has been growing concern over the potential cancer and other health risks associated with a high level of arsenic in natural waters. Incidences of high arsenic levels have been identified in many parts of the world. Probably the worst case is within the Ganges Delta region, covering India and Bangladesh.

Consequently, in 1993, the World Health Organisation (WHO) reduced the maximum permitted level of arsenic in potable water from 50 ppb (μg/L) to 10 ppb [1]. Following this threshold reduction, several countries followed
suit; the USEPA considered a limit between 2–20 μg/L [2]. The proposed new standard of 10 μg/L was delayed in Jan 2001 but was finally agreed to come into force in Jan 2006 [3]. The European Union issued a directive reducing the limit to 10 μg/L [4] and Australia set a new level of just 7 μg/L [5].

2.1.2 Arsenic levels in Bangladesh

Millions of people in Bangladesh and neighbouring India are at risk from contaminated groundwater. Arsenic poisoning has reached epidemic proportions in this area. Water from the tubewells, dug since the 1970’s, contain dangerously high levels of arsenic. In Bangladesh the level of arsenic in groundwater in some areas was over 80 times the present limit in the United States of 50 μg/L [6]. Within West Bengal alone, it is estimated that there are 16–20,000 wells with an arsenic concentration in excess of 50 ppb [7].

The primary reason for the increase in arsenic poisoning within the Bengal Delta is due to the increased consumption of groundwater extracted from wells. The suggested mechanism for the mobility of arsenic in the groundwater is that coagulation and precipitation occur in the aerobic surface waters; the precipitates sink and are deposited on the sediments. As the deeper groundwater is anaerobic, the iron precipitate is reduced and redissolves, liberating arsenic [8]. The rate of dissolution is driven by the microbial metabolism of organic matter found in anaerobic groundwater. Hence the distribution of organic matter determines the quantity of arsenic released [9].

2.1.3 Arsenic levels worldwide

There are many others areas of the world where there are elevated levels of arsenic in the aquatic environment, primarily due to natural geochemistry. In the US, approximately 5% of the national drinking water will require treatment to meet the new requirement [10]. Other countries with naturally elevated levels of arsenic include Argentina [11], Chile [6], China [12, 13], India [14, 15], Mexico [16], Taiwan [17, 18] and Vietnam [19]. There are other areas that have a high arsenic concentration from anthropogenic sources, namely Devon and Cornwall in the UK [20], Greece [21] and Ghana [22].
2.1.4 Arsenic levels in the UK

The European Union has issued a directive to reduce the arsenic threshold from 50 µg/L to 10 µg/L [4]. At present, specific water treatment to remove arsenic is not required to meet the existing standard. However, the new limit has generated research in the UK, as 30 treatment works will be required to take some measures to reduce the level down to 10 µg/L [23].

2.2 Arsenic in the environment

Arsenic occurs naturally in aquatic systems from chemical interactions of arsenic-rich sediment and from industrial sources. The chemistry of arsenic in the environment is dependent on other anionic species present, the nature of the sediment, natural organic matter and bacteria.

2.2.1 Sources of arsenic

The majority of arsenic in natural waters results from the leaching of geological material [24]. The most important ores of arsenic are arsenic pyrites or mispickel (FeAsS), realgar (As₄S₄) and orpiment (As₂S₃) [25]. Arsenic forms stable bonds with sulphur and carbon. In the presence of sulphides, precipitation of realgar or orpiment can remove As (III) and have considerable control over arsenic concentrations. To some degree, the quantity and speciation of arsenic depends on the local geology and soil type. An important group of compounds is the methylarsines. Trimethylarsine is formed by some microorganisms from inorganic compounds of arsenic. However, organic species are rarely present at concentrations above 1 µg/L and are not considered of greatest importance when considering water treatment [8].

There are several industrial sources that elevate naturally occurring levels. One source is smelting ores that contain arsenic trioxide, which is the raw material for industrial arsenic materials. The oxidised forms are converted back to sulphides by anaerobic processes on land and in water [26]. Coal fired power stations are another source of pollution for heavy metals such as
arsenic, selenium and chromium [27]. Arsenic and its compounds have also been used extensively as herbicides and insecticides, hence runoff from treated fields contribute to higher arsenic levels.

### 2.2.2 Arsenic chemistry

Iron and manganese have a considerable effect on the arsenic concentration in the environment. FeAsS, arsenopyrite and Mn$_3$(AsO$_4$) affect arsenic solubility [28] through co-precipitation-adsorption of arsenic on iron and manganese oxides [11]. Hence, arsenic content can be correlated to Mn (II) and Fe (II) concentrations. It has also been noted that aluminium hydroxide and clays adsorb arsenate in the environment [12]. Hence studies were carried out by Prasad [29] to determine the removal of arsenic by naturally occurring geological material, namely hematite and feldspar.

Some plants have been shown to possess bioaccumulation properties. *Hydrilla verticillata* Casp. is able to remove arsenic from the surrounding soil [30]. More recently, brake fern was observed to adsorb arsenic to such an extent that it comprised 2% of its entire weight [31]. These plants could be used to remediate land previously spoilt by mine tailings.

Occurrence of arsenic in natural waters depends on the geology and pH of the aquatic environment. The chemicals present in the sediment and their interactions will control the retention and liberation of arsenic. Redox conditions are also important in determining the mobility of arsenic. Figure 2.1 highlights the complexities of arsenic in the environment, both at surface and groundwater levels.

**Oxidation/reduction of arsenic species**

The most prevalent species of arsenic depends on the pH and the redox potential. As a general rule, arsenite, As (III), is more likely to be found in anaerobic ground water, whilst arsenate, As (V), is found in aerobic surface water. Dissolution from the solid phase results in arsenolite (As$_2$O$_5$), arsenic hydride (As$_2$O$_5$) and realgar [33].
# Chapter 2. Literature survey

## Groundwater Key reactions

- Oxidation of As(III) to As(V)
- Sorption-co-precipitation of As to oxides
- Exchange of phosphate for sorbed As(V)

### Aerobic

- \( \text{Mn}^{2+} \rightarrow \text{MnO}_2 \cdot \text{H}_2\text{AsO}_4 \)  
- \( \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \rightarrow \text{Fe(OH)}_3 \cdot \text{H}_2\text{AsO}_4 \)
- \( \text{HAsO}_2 \rightarrow \text{HAsO}_4^{2-} \)

![Figure 2.1: Arsenic reactions within the aquatic environment. After Edwards [32]](image)

### Anaerobic

- No \( \text{H}_2\text{S} \)

- \( \text{HAsO}_4^{2-} \rightarrow \text{HAsO}_2 \)
- \( \text{Fe(OH)}_3 \cdot \text{H}_2\text{AsO}_4 \rightarrow \text{Fe}^{2+} + \text{HAsO}_2 \)
- \( \text{MnO}_2 \cdot \text{H}_2\text{AsO}_4 \rightarrow \text{Mn}^{2+} + \text{HAsO}_2 \)

- Reduction of As(V) to As(III)
- Reduction of Fe/Mn oxides
- Release of soluble As

### Anaerobic

- \( \text{HAsO}_2 + \text{HS}^- \rightarrow \text{As}_2\text{S}_3 \) or AsS
- \( \text{Fe}^{2+} \rightarrow \text{FeS} \cdot \text{HAsO}_2 \)

- Precipitation of soluble As(III) as realgar or orpiment, or co-precipitation with FeS

Arsenate is more readily removed from water than arsenite, as it is an ionic species in the pH range typically found in aquatic systems. Arsenite does not readily oxidise to arsenate if the pH is < 10 without the presence of additional oxidisers [34]. Conventionally, chloride or potassium permanganate are used in a pre-oxidation stage to remove any As (III) present. However, recent studies have shown that the rate of this oxidation step, which is thermodynamically favoured, can be greatly increased by photochemical oxidation. i.e. the addition of acid to a solution exposed to UV light in the presence of iron. This has the added benefit of removing dissolved iron present. This can occur in minutes, rather than hours or even days, under natural oxic conditions [35]. Rapid oxidation can also occur in the presence of ozone [36]. Using FT-IR and XANES
(X-ray Absorption Near Edge Structure). Sun and Doner [37] found that some arsenite present in solution oxidised on the surface of goethite. Arsenates can be reduced, but only in very acidic conditions [38].

Cullen and Reimer [8] reported that certain bacteria converted arsenate to the more toxic methylarsenate species. Johnson [39] also found that arsenate was reduced to arsenite in sea waters. The reverse is also possible, with arsenite being oxidised by iron-rich sediment [40] and abiotic bacteria [41].

2.2.3 Arsenic health effects

Arsenic levels in groundwater have been examined recently in the light of new research regarding cancer risks [1], and studies carried out in Taiwan during the 1960's [42].

Some organic forms have been used for medical purposes, although there is insufficient data as to whether arsenic is an essential element for humans. Arsenic is believed to be carcinogenic; although there is some disagreement about the carcinogenic nature of arsenic, and there have been no positive examples in animal tests [43]. Humans are exposed to arsenic from air, food and water. The arsenic concentration in the air is extremely small, a few ng As/m³ [44]. A higher concentration of arsenic is found in foods, particularly fish (0.5–3 ppm) and crustaceans (3–100 ppm) [11]. A lower concentration can be found in meat and freshwater fish [45]. In drinking water, the concentration of arsenic can reach a maximum of 2 ppm [42].

Tseng et al. [42] studied the effect of arsenic exposure in drinking water in a small area of Taiwan. The length of exposure was estimated as 45 years. The long-term health effects of exposure to inorganic arsenic species are skin lesions, cancers of the skin, kidneys, lungs and liver, diabetes, pulmonary disease and hypertension [46]. There is a latency period in the symptoms of arsenic poisoning, hyperpigmentation takes 6 months to 3 years [42], skin cancer 20 years [46] and bladder cancer 20–35 years [47] to develop.

The lifetime risk of developing skin cancer by drinking 2 μg/L of water is 1x10^-5, the level at which the USEPA would consider the substance to be a carcinogenic risk [2]. At the new threshold level of 10 μg/L, the risk increases
Valberg [48] has calculated that drinking 2 litres of water a day at 50 µg/L results in a lifetime skin cancer risk of 2.5x10^{-3}.

Arsenic can occur in four oxidation states in water, although it is usually found in the trivalent (arsenite) and pentavalent (arsenate) forms. The toxicity of arsenic compounds is as follows [49]:

\[
\text{arsine} > \text{arsenite} > \text{arsenate} > \text{alkyl arsenic}
\]

Ingested arsenic is methylated in the liver, hence this is the organ primarily affected by arsenic exposure. As (III) is considered to be more toxic as it is more easily methylated than As (V) and the latter is usually reduced before undergoing any methylation process. As (III) is a potential enzyme inhibitor through reacting with the sulphhydryl groups [50], and has a high affinity for cell protein [51].

Despite the growing number of case studies to determine the effect of ingested arsenic on human health, opinion is still divided. A report issued by the National Academy of Sciences, USA published in 2001, calls for more clarification on the dose response of arsenic [47].

**Estimated costs and benefits from reducing arsenic in drinking water**

The cost of compliance with the proposed new regulations in the United States (a reduction from 50 ppb to 10 ppb) has been estimated by the US Environmental Agency [52]. The total treatment cost was estimated in 1999 as $164.9-194.8 M, the total bladder and lung cancer health savings as being in the region of $137 M. Hence the net cost to reduce the maximum allowable arsenic level to 10 ppb is $27.9-57.8 M. Within the UK, the Department of the Environment, Transport and the Regions has estimated that the cost of compliance to the EEC directive 98/83/EC to be £490 M up to March 2005 (non-recurring costs) and £22 M per annum recurring costs. The minimum expected savings are £724 M for total health benefits and £124 M for non-health benefits. These costs include meeting the new lead standard [53].
2.3 Arsenic removal

There are several available methods for the removal of arsenic, the choice of which depends on the throughput, degree of maintenance and expertise required and final water quality. The removal technologies can be split into three categories; precipitation, membrane and adsorption processes. A summary of these processes is given in Table 2.1.

2.3.1 Precipitation processes

The most common technique currently used for arsenic removal is coagulation followed by filtration. This can be split into several further categories: conventional coagulation, lime softening, advanced colloid flotation and combined ferrous/manganese precipitation. Co-precipitation is the incorporation of soluble arsenic species into a hydroxide phase and adsorption is the formation of surface complexes between soluble arsenic and the solid surface. Dissolved inorganics may be removed by adsorption, occlusion and solid-solid formation. Coagulation is the primary mechanism at high coagulant doses [55].

The main disadvantage of this method is the large volume of sludge produced. Merrill et al. [27] used pressure filtration to dewater the sludge cake from 6–8 % to 40 % solids content after approximately 8 hours. Another suggested method for disposal, landfill, can itself be a source of groundwater pollution if the waste solids are not sufficiently stable. However, Merrill et al. [27] and Pal [56] have carried out leaching tests and the extractant concentration was lower than the required limit. Crystalline forms of iron oxide have a lower solubility than their amorphous counterparts under most leaching conditions [57].

Coagulation

The primary coagulants used in the water industry are ferric salts, namely ferric chloride and ferric sulphate, and aluminium sulphate (alum). Several investigators have compared the effectiveness of these coagulants.
Table 2.1: Arsenic removal technologies (after Clifford et al. [54])

<table>
<thead>
<tr>
<th>Technologies</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Co-precipitation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alum coagulation</td>
<td>Relatively low capital cost</td>
<td>Produces toxic sludge</td>
</tr>
<tr>
<td>Iron coagulation</td>
<td>Relatively simple operation</td>
<td>Low removal of As (III)</td>
</tr>
<tr>
<td>Lime softening</td>
<td>Common chemicals available</td>
<td>Pre-oxidation may be required</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pH adjustment required</td>
</tr>
<tr>
<td><strong>Sorption techniques</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated alumina</td>
<td>Relatively well-known and commercially available</td>
<td>Produces toxic solid waste</td>
</tr>
<tr>
<td>Iron coated sand</td>
<td>Well-defined technique</td>
<td>Replacement / regeneration required</td>
</tr>
<tr>
<td>Ion exchange resin</td>
<td>Plenty of possibilities and scope of development</td>
<td>High-tech operation and maintenance</td>
</tr>
<tr>
<td>Other sorbents</td>
<td>Copes with a change in inlet flowrate</td>
<td>Relatively high cost</td>
</tr>
<tr>
<td><strong>Membrane techniques</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>Well-defined and high removal efficiency</td>
<td>Very high capital and running cost</td>
</tr>
<tr>
<td>Electrodialysis</td>
<td>No toxic solid waste produced</td>
<td>High-tech operation and maintenance</td>
</tr>
<tr>
<td></td>
<td>Capable of removing other contaminants</td>
<td>Toxic wastewater produced</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fouling</td>
</tr>
</tbody>
</table>
Gulledge and O'Connor [58] and Shen [59] both found that ferric salts had a greater removal capacity than alum at a pH < 7. Edwards [32] also found that the removal efficiency, using ferric salts at pH 7-7.5 for a 0.06 mM coagulant dose, was 87 % versus 67 % for alum. Iron coagulants perform better than alum since they are more insoluble over a wider pH range than aluminium hydroxide and form a heavier, denser floc. Amorphous ferric hydroxide Fe(OH)$_3$ is formed by ferric chloride in water in the pH range 6-10. Below pH 6, cationic monomers such as Fe$^{3+}$ and Fe(OH)$_2^+$ are formed, hence anionic arsenate species which are formed in water are electrostatically attracted to the iron coagulants.

Tokunaga et al. [60] compared iron and alum salts with lanthanum salts. All were able to remove arsenite and arsenate. Lanthanum salts could be used over a wider pH range, 5-9 for effective arsenic removal.

The speciation of arsenic in the water affects its removal. Gulledge and O'Connor [58] found that without prior oxidation, ferric sulphate removed 40-60 % of As (III) and alum only removed 5-15 % from an initial concentration of 0.3 mg/L. However, on oxidation with 2 mg/L chlorine, 95 % removal was achieved. This is comparable to As (V) removal. Shen [59] also found that chlorine was a better oxidising agent than potassium permanganate. Aeration alone was also not sufficient to oxidise the water [61].

The effect of source water variations were more pronounced for As (III) than As (V). Under acidic condition, sulphate did not appear to have a detrimental effect on As (V) removal. Below neutral pH, As (III) was greatly affected by the presence of sulphate [62]. Natural organic matter (NOM) drastically reduced the removal of As (III) and As (V) by co-precipitation, but arsenate removal by adsorption at pH 6 was not affected [55]. The presence of positively charged ions, such as calcium appeared to aid removal at pH 9 [62].

Much of the earlier work [58, 59] was aimed at achieving a residual concentration of 50 µg/L. In addition, the initial concentrations used were higher. Shen [59] found that 50 mg/L ferric chloride was sufficient with an initial arsenic concentration of 0.8 mg/L, although, this increased to 77 mg/L in field tests. There were, however, indications that a lower residual level could be reached. For example, 100 mg/L ferric sulphate reduced an effluent concentration from an initial level of 1.5 mg/L to 10 µg/L [58].
More recently, Cheng [63] noted a level of 10 μg/L could be reached with a dose of ferric salts less than 10 mg/L and initial concentration of 20 μg/L arsenic. Scott et al. [64] reported that 90 % removal can be achieved with a coagulant dose greater than 6.5 mg/L, i.e. an effluent concentration of 2 μg/L. This method can effectively reduce the effluent concentration to below 10 μg/L, provided that the influent is pre-oxidised with chlorine and has a pH < 7.

Lime softening

Lime softening removes hardness but can also remove arsenic at pH > 10.5 [65]. McNeill and Edwards [66] found a maximum removal of 95 % with magnesium hydroxide and calcite at full scale, from an initial concentration of 5 μg/L if the pH was adjusted to above pH 10.5. The water may not require pre-oxidation, depending on the initial concentration, as As (III) removal was relatively high.

Combined Fe/Mn precipitation

Fe (II) and Mn (II) form insoluble hydroxide precipitates on oxidation. Co-precipitation and adsorption onto the hydroxide surface removes soluble arsenic species. 1 mg/L Fe (II) removed 88 % of a 22 μg/L influent concentration [32]. At full scale, McNeill and Edwards [66] noted that up to 90 % can be removed with 100 μg/L of arsenic in the influent. pH played an important role in arsenic removal; this method was most effective at pH 5.

Adsorbing Colloid Flotation

A floc-forming compound, usually ferric chloride or alum, was added to collect the dissolved heavy metals by adsorption and/or co-precipitation. Hydroxides are formed by the addition of base. The flocs were then removed by flotation in a column using a surfactant [67]. High arsenate removal was achieved with 75–100 mg/L alum and 30 mg/L surfactant from an initial concentration of 5 mg/L. The optimum pH for removal was pH 5–6, and increasing the ionic strength decreased the removal efficiency [61].
2.3.2 Membrane processes

Reverse Osmosis

There are two types of reverse osmosis, nanofiltration and hyperfiltration. The former is a relatively low pressure process and rejects material with a molecular weight > 1000 Daltons through a semi-permeable membrane. It is also known as membrane softening, as it is able to remove calcium and magnesium that cause hardness. It is also able to remove sulphate and to a lesser degree monovalent substances such as chloride. Hyperfiltration operates at much higher pressures and provides a greater rejection all of dissolved solids (molecular weight > 150–200 Daltons).

The rejection of co-ions such as arsenate will be greater for a solution brought into contact with a slightly negatively-charged membrane. Reverse osmosis is more effective at removing As (V) than As (III). The latter removal efficiencies are 40–80%. The removal efficiency of both As (III) and As (V) increase with increasing pH, the former being affected more strongly [68]. However, up to 97% removal of pentavalent arsenic has been reported [65]. Generally, a smaller quantity of particulate arsenic was found in groundwaters than surface waters.

As (III) maximum rejection was below 90%, which decreased with increasing specific flux (gallons/foot²/day). As (V) removal was unaffected by flux, and gave a rejection of 98% for an initial concentration of between 15 and 30 μg/L. The rejection of arsenic decreased in the presence of ions that are rejected more easily. In particular, phosphate lowered the arsenic removal. However, the presence of cadmium did not effect removal [69]. Brandhuber and Amy [70] found that arsenic was rejected to a greater extent in high levels of dissolved organic carbon (DOC). Hence, humic substances may enhance rejection.

Oxidising agents such as chlorine were harmful to the membrane. However, depending on the initial concentration and speciation of the water, oxidation may not be necessary [71]. The method was too effective at removing total dissolved solids (TDS), 250 mg/L reduced to 10 mg/L [65]. Hence post treatment, such as aeration and chlorination would be required [72]. The wastewater was 10% of the feed water and there was no sludge resulting from this process.
Electrodialysis

An electric current is applied to draw the ions through the membrane, leaving the effluent water behind. The membranes are made up of both cation and anion exchange resin. The quantity of wastewater is around 10% of the feed and up to 95% removal has been reported [65].

Membrane processes are effective for the removal of arsenic if the pH is > 10. The disadvantages of this removal technology are that the capacity is dependent on the presence of competing anions and also the high cost [73].

2.3.3 Adsorption

The removal of substances through physical or chemical bonding on a surface is known as adsorption. There are several types of adsorbent—activated alumina, activated carbon, zeolites, activated bauxite, ferric hydroxide, and other composite materials. The advantages of adsorption are the ability to use a column and that the solid can often be regenerated. This produces less solid waste than precipitation, although regeneration results in a more concentrated liquid effluent. If regeneration is not possible, the spent adsorbent could be sent to landfill.

Activated alumina

Bellack [74] first discovered the affinity of activated alumina (AA) for arsenic when studying the removal of fluoride. AA has the following selectivity sequence, hence the expected affinity for As (V) is even greater than for fluoride.

\[
\text{OH}^- > \text{H}_2\text{AsO}_4^- > \text{Si(OH)}_3^- > \text{F}^- > \text{HSeO}_3^- > \text{SO}_4^{2-} > \text{CrO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{Br}^- > \text{I}^- \tag{2.2}
\]

Bellack [74] found that by reducing the pH to near neutral conditions with an initial concentration of 60 ppm, the residual concentration was 3 ppb after 14 bed volumes (BV). For well water with 0.1 mg/L initial arsenic concentration.
at neutral pH, the level was reduced to below the detectable limit of 2 µg/L. Hathaway and Rubel [75] noted that the AA was exhausted after only 800 BV without pH adjustment, with a raw pH of 9 and an influent concentration of 0.09 mg/L. With pH adjustment, the effluent concentration remained below the detectable limit for approximately 9000 BV.

Gupta and Chen [76] investigated AA, activated bauxite and granular activated carbon (GAC) and found that AA produced consistently high removal and the fastest adsorption rates (50% of the total arsenic removed within ten minutes). Rates of As (III) removal were much lower, about 6% and 2% for AA and GAC respectively. The rate of adsorption decreased with increasing salinity. As (III) removal decreased sharply above pH 9 and As (V) adsorption decreased above pH 7. Anion adsorption should have a point of inflection at the pKa values for arsenic and arsenious acid, i.e. pH 7 and 9, respectively. Despite the recent concerns over the possibility of a link between AA and Alzheimer’s, other investigators have noted the efficacy of AA for arsenic removal [77, 78].

At high pH the surface charge of AA was either neutral or negative. The adsorption appeared to be independent of pH if the pH was less than the pH of the point of zero charge (pHpzc), but decreased with increasing pH. At pH > pHpzc, adsorption must compete with coulombic repulsion forces. Hence, there was chemical adsorption to the AA surface [76, 79, 80].

Sulphate, carbonate, silicate, and phosphate had a detrimental effect on the removal of arsenic [81, 82, 83]. Silicate had a drastic effect, with a maximum adsorption at pH 9, decreasing with decreasing pH. Calcium may enhance the adsorption, by making the surface more positive and even by forming complexes with the arsenate. In general, As (V) was more affected by chemical composition than As (III) [76].

When all the adsorption sites are exhausted, AA can be regenerated with caustic soda, then neutralised with a sulphuric acid rinse. To aid regeneration, Bellack [74] used 1% caustic soda and every fifth cycle a stronger solution of caustic soda was used to reduce the loss of AA. Driehaus et al. [84] estimated that the regeneration efficiency was only 90% since AA has such a high affinity for arsenic.
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Activated carbon

Gupta and Chen [76] used 3 g/L GAC and noted that it was one twelfth as effective as AA. Huang and Fu [85] found that powdered activated carbons were effective for arsenic removal with 84% removal from an initial concentration of $5 \times 10^{-5}$ M As (V) (3.75 ppm) using 1 g/L activated carbon at pH 4.5.

Huang and Vane [86] developed a ferrous treated activated carbon to increase the surface charge and 90% of arsenite was removed at pH 3.5–4 for an influent concentration of $5 \times 10^{-5}$ M As (III). The most effective regenerant was ferrous ammonium sulphate [85, 86]. Reed et al. impregnated activated carbon with a ferric oxide, which increased both As (III) and As (V) uptake by one or two orders of magnitude [87]. Manju et al. [88] produced GAC impregnated with copper. The maximum uptake of As (III) was at pH 12 with 88% removal for an initial concentration of 50 mg/L. The arsenite at this high pH was anionic, hence removal was increased.

Activated bauxite

Gupta and Chen [76] compared AA, activated bauxite and GAC. It was only 50% as effective as AA and there are no further reports of this adsorbent in the literature.

Granular ferric hydroxide

The arsenic removal method selected in this work was using a packed column with granular ferric hydroxide. Driehaus et al. [84] developed a granular product similar to akaganeite, to be applied in a similar way to AA or GAC. The granular ferric hydroxide developed appeared to have a greater affinity for arsenic than AA. Pierce and Moore found that amorphous ferric hydroxide possessed 5–10 times greater capacity for arsenic than AA [89]. For an influent concentration of 21 µg/L, 30 000–40 000 BV were passed before an effluent concentration of 10 µg/L was reached. This method does not require much maintenance or manpower. There is no pre-treatment required other than chlorination, which is usually present at an existing water treatment plant.
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The resulting arsenic-loaded ferric hydroxide is usually sent to landfill. As explained previously in Section 2.3.1, researchers have found that spent iron oxide material is sufficiently stable, with a leachate concentration lower than the required limit [27, 56]. However the material could be eluted with a strong base, *e.g.* sodium hydroxide, and reused. A further issue would arise as to disposal of the concentrated eluent

**Composite adsorbents**

Shigetomi *et al.* [90] used polyacrylamide as a binder for hydrous ferric oxide. This adsorbent removed more than 95 % As over a pH range of 5–6 for an initial arsenic concentration of 1.33 mM. Iron coated sand has been used to treat metal bearing waste [91]. Also, zirconium oxide [92, 93], aluminium-loaded shirasu zeolites [94], lanthanum impregnated silica gel [95], molybdate-impregnated chitosan beads [96], clinoptilolite-containing rocks [97] and yttrium carbonate [98] have been used to effectively remove arsenic.

**Ion exchange**

A strong base anion exchange resin is usually loaded with chloride ions and the arsenic and other anions are exchanged for the chloride ions. The resin is eventually exhausted and requires regenerating. The pH should be greater than 7.5 and the feed pre-oxidised for optimum conditions. This is to oxidise any As (III) that is present. Ion exchange resin are susceptible to oxidising agents, hence this process may have a detrimental effect on the resin.

Ramana and Sengupta [99] loaded a chelating ion exchange resin Dow 2N with Cu (II) to act as an anion exchanger. At pH 7–8.5 the equilibrium uptake of As (V) reached a maximum of 35 mg As/mg resin at an influent concentration of 5 mg/L. Ghyre *et al.* [100] used a sulphate specific resin to remove both nitrate and arsenic simultaneously. The maximum throughput at pH 7–8 was 900 BV with an inlet concentration of 14 µg/L. Shen [59] used a weak base resin and achieved 26 % removal of As (V) and 21 % of As (III) from a synthetic solution containing 1 mg/L arsenic. Only a small quantity of raw water can be passed through columns before the resins become exhausted.
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The selectivity sequence [65] of strong base anions is estimated as:

\[
\text{SO}_4^{2-} > \text{HAsO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{HCO}_3^- > \text{H}_2\text{AsO}_4^- \quad (2.3)
\]

Hence, in the presence of sulphate, chloride and nitrate, the amount of arsenate removed is quite small, and is further reduced if weak base resins are employed. Hathaway and Rubel [75] concluded that ion exchange can be an effective method of arsenic removal, although it is sensitive to source water composition. It is more suited to small scale removal as only a small quantity of water can be passed through before exhaustion.

2.3.4 Novel methods

There have been a number of simple methods developed for arsenic removal, primarily with the crisis of Bangladesh in mind. The simplest is passive sedimentation i.e. the arsenic precipitates with the naturally elevated level of iron and settles overnight. The top portion of the water is decanted and then used [101]. Another method also uses the ferrous ion present in the water. On the addition of citric acid and allowing photo-oxidation to occur, the arsenic concentration is reduced by 80–90 % from an initial concentration of 500 µg/L [102]. The third is a small-scale co-precipitation and adsorption process with either ferric or alum salts [103]. A bucket treatment unit using 100 mg/L ferric chloride and 1.4 mg/L potassium permanganate was used to reduce levels to 20–40 ppb from an initial concentration in the range 375–640 ppb [101]. A final method for removing arsenic has been developed using iron filings [10, 104]. Highly contaminated waters, 2000 µg/L can be made safe with 93 % removal of arsenic. The arsenic was strongly bound and the filings could be reused at least 100 times [104].
2.4 Background information on other species studied

2.4.1 Phosphate

Legislation

Phosphorus is required for the growth, health and reproduction of all living beings. Phosphate itself does not have notable adverse health effects. However, its release to surface water in agricultural runoff and wastewater has led to legislation such as the European Union Urban Wastewater directive [105]. This states that the maximum allowable phosphorus for 10 000–100 000 p.e.\(^1\) should be 2 mg/L. For drinking water, the European Union set a maximum admissible level of 5 ppm P\(_2\)O\(_5\) [106].

Chemistry

Phosphorus is present in igneous and sedimentary rocks. The primary source of phosphorus used in industry is fluorapatite, Ca\(_5\)F(PO\(_4\))\(_3\) [107]. At present, 75 % of phosphate production worldwide is from phosphorus minerals. Arsenate is chemically similar to phosphate and may be substituted in apatite minerals [108].

Phosphorus in the environment

Phosphorus is the eleventh-most abundant mineral in the earth’s crust. Natural inorganic phosphorus deposits occur primarily as phosphate in the mineral apatite. When released into the environment, orthophosphate will be the primary species, according to the pH of the surrounding soil. Currently, there is on average 0.1 ppm phosphorus in sea water due to weathering of rocks [109].

Phosphorus is a primary ingredient in fertilisers used in agriculture to increase productivity. It is also found in detergents and pesticides [108]. All these

\(^1\) p.e. (population equivalent) means the organic biodegradable load having a five day biochemical oxygen demand (BOD\(_5\)) of 60 g of oxygen per day.
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sources increase phosphorus concentrations in the aqueous environment and lead to the production of algal bloom. This is caused by phosphorus enriched conditions, allowing greater nitrogen uptake and results in an increase of algae.

Removal technologies

Concerns regarding eutrophication lead to the development of technologies for phosphorus removal in the 1950s. Removal was initially achieved by chemical precipitation [110], which in addition to biological methods is the usual method used to remove phosphorus at full-scale [111].

The usual metals used in the precipitation process are iron and aluminium, added as either chloride or sulphate. Salt addition can achieve 80–95 % total phosphorus removal. This results in the phosphorus reacting and precipitating with the metal salt and its disposal as sludge, to be potentially reused in the agricultural industry. Seida and Nakano [111] have developed double layered hydroxides containing iron. The release of the cations in the iron compounds in addition to any hydroxide ions released act as coagulants to remove phosphorus. More recently biological phosphorus removal, crystallisation technology and technologies extending chemical precipitation to assist nutrient removal are also considered to be viable technologies [112].

Adsorbents have also been investigated for their ability to remove phosphorus from water. The primary advantages are that unlike chemical precipitation, no additional sludge is produced, and no reagents are required to adjust the pH. Adsorbents such as AA [113], activated red mud [114] and iron oxide coated filter medium [115] have been investigated.

2.4.2 Fluoride

Legislation

The current acceptable level of fluorine in drinking water is 1.5 ppm within the European Union [4] and WHO [1]. There have been cases of endemic fluorosis in both Mexico [116] and India [117]. The natural levels of fluorine in tap water were in the range 1.54–4.7 ppm. In non-fluoridated water, the level of fluorine
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is often less than 1 ppm, after fluoridation the fluoride concentration is in the range 0.6–1.7 ppm [118]. Fluoride is often added to vitamin supplements and pharmaceutical products, primarily toothpaste [119].

Chemistry

The fluoride ores of most importance are fluorspar (the primary industrial source for fluorine), CaF₂, fluorapatite and cryolite, Na₃AIF₆ [120]. Recovery of fluorine from fluorapatite used in phosphorus production, with an average fluorine content of 3.5 %, has both economic and environmental benefits.

Fluorine in the environment

The primary routes of fluoride into the environment are natural and anthropogenic. Fluoride is present in many naturally occurring minerals. Erosion results in an increase in fluoride surface species. Fluoride is also extensively used in the semiconductor, nuclear [121], glass and electroplating industries [122].

Health effects

Low levels of fluorine are beneficial, particularly for babies and young children. Skeletal and dental problems are reduced with an intake of approximately 1 ppm. However, if fluoride levels exceed 1.5–2 ppm, abnormal bone growth and teeth discoloration can occur [121].

Removal technologies

Many methods have been used on a laboratory scale to remove fluoride from aqueous systems; most are based on column operations. AA [113, 123], GAC [124, 125], bone char [122] and fly ash [126] have all been used successfully to remove fluoride. The most frequently employed large-scale fluoride treatment is ion exchange by either GAC, bone char or tricalcium phosphate [125].
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Fluoride has also been removed by precipitation with lime and aluminium sulphate [125], calcium hydroxide [127] and calcium phosphate [128]. Sinha et al. [129] have used a phytoremediation route, namely *Hydrilla verticillata* (l.f.) royle to some degree of success in fluoride removal.

2.4.3 Cadmium

Legislation

The current threshold for cadmium in potable water is 5 µg/L within the European Union [4]. WHO have also set a limit of 5 µg/L for cadmium [1]. Generally, the concentration of cadmium in drinking water is < 1 µg/L [130]. However the discharge limit for industry has a maximum permissible level of 0.2 mg/L [131].

Chemistry

The only ore of cadmium is greenockite, CdS, which is very rare. This has been used extensively in the pigment industry. Zinc ores and other heavy metal ores also contain cadmium as an impurity. Hence this is the primary source of cadmium in the environment [132].

Cadmium in the environment

The amount of this toxic heavy metal in the environment has increased as a result of human activities. Industrial wastes of long-life batteries and colour pigments containing cadmium, electroplating, mine tailings and the impact of contaminated phosphate fertilisers, oil, and coal burning have all contributed to its wider presence in the environment [133]. Cadmium is also present naturally from volcanic activity and in rocks in concentrations in the order of 1.0 mg/kg [134].

Cadmium plays no essential part in plant biology, but there are several types of algae that exhibit bioaccumulation. Some fruit and vegetables, depending on the local soil conditions also possess high levels of cadmium [130].
Health effects

Cadmium is not regarded as essential to human life [130]. Humans normally absorb cadmium into the body either by ingestion or smoking. For example, certain crops (e.g. sunflowers) and shellfish contain naturally accumulated levels of cadmium [135]. Food accounts for almost 20% of cadmium uptake. Smoking and drinking contribute equally to the daily uptake, i.e. 1–2% [130]. Uptake through the skin (dermal exposure) is not generally considered to be of significance.

Cadmium is known to accumulate in the human kidney for a relatively long time, from 20–30 years. At high doses, it is also known to produce health effects on the respiratory system and has been associated with bone disease [136]. Cadmium is not thought to be cytogenetic or produce hypertension, however, there has been a higher incidence rate of prostate cancer after prolonged exposure [135].

Removal technologies

Cadmium is present primarily as a cation in the aquatic environment. Typically, in industrial wastewater treatment, cadmium and other heavy metals are removed by lime precipitation [137]. More selective removal can be achieved by carbon [138], chelating [139] or iminodiacetic acid ion exchange resins [137]. The latter type of resin cannot be used in some countries to treat water, hence interest is developing in weakly basic ion exchange resins which possess similar properties, and are permitted in food and water treatment [137].

Biosorbents have also been studied to determine cadmium removal capacities. Both flotation [140], algae [141], seaweeds [142] and waste brewery biomass [143] have been used. In addition, Gao et al. [144] have developed a hybrid sorbent containing both ferrihydrite and akermanite to effectively remove cadmium. Hydrous oxides of aluminium, iron and manganese have also been used as sorbents for divalent metal ions [145, 146].
References


REFERENCES


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Chapter 3

Production of iron oxide material

This chapter reviews literature covering the formation and conditioning of iron oxide material, and experimental procedures used for all iron oxide samples.

The ultimate aim of this work is to generate an iron oxide material of sufficient size and mechanical strength to be used in a column. The physical and chemical characteristics of the material produced that meet these criteria can then be compared to other iron oxide samples.

3.1 Literature survey

The formation of iron hydroxides, the factors that control the nucleation and growth of iron oxide particles are examined and methods of maximising the final granule size are considered. The effect of the anions used as reagents (particularly chloride) on the form and stability of the final product is also examined.

The formation of akaganeite is highlighted which is the commercial sample of iron hydroxide supplied by GEH Wasserchemie. The subsequent conditioning of the precipitate (i.e. washing and freeze-thaw treatment) is outlined.
3.1.1 Iron chemistry

Ferric hydrous oxides occur naturally as minerals such as goethite, hematite and ferrihydrite. Akaganeite is found in marine, chloride-containing environments as a corrosion product of iron [1].

Iron oxides are produced by the precipitation of ferric salts. Although the products vary in chemical structure, composition, and physical characteristics. Preparative techniques alter the surface area, morphology and colour of the final product. A diagram illustrating the complexities of iron chemistry is given in Figure 3.1 and Table 3.1 lists the oxides with their respective formulae.

Figure 3.1: Summary of iron chemistry [2]
The basic structure of all iron oxides is octahedral with a central Fe ion surrounded by O or OH ions. The $\alpha$-phase of a mineral is more stable than the $\gamma$-phase and has hexagonally close packed layers of O and OH ions: the latter type has cubic close-packed layers. The Fe octahedra can be linked by edge-sharing or corner-sharing which results in the many types of iron oxide. The FeOOH oxides all possess double band edge-sharing Fe$_3$O$_3$(OH)$_3$ octahedra. Only half of the octahedral interstices are filled with Fe$^{3+}$ [3].

Goethite forms tunnels through octahedra sharing vertices, akaganeite consists of double chains of multiple octahedra joined lengthwise by sharing corners to make channels, and lepidocrocite forms corrugated layers of distorted edge-sharing octahedra [2, 4]. A diagram illustrating the structure of some iron oxides is given in Figure 3.2.

The Fe$_6$ octahedra in hematite are linked by edge and corner-sharing to form sheets [3]. These sheets are stacked between two layers of oxygen. Two thirds of the interstices are filled with Fe$^{3+}$. Magnetite has a cubic structure, with divalent Fe (II) tetrahedrally co-ordinated and trivalent Fe (III) octahedrally co-ordinated with oxygen. The iron octahedra are layered between close-packed sheets of oxygen [4].

Ferrihydrite has a low degree of crystallinity, but has a similar structure to hematite, hexagonally close-packed planes with Fe$^{3+}$ ions in the octahedral interstices. Not all the interstices are filled with Fe, but are replaced by H$_2$O and OH, hence the formula of ferrihydrite has not been fully established. There are several types of ferrihydrite that exist, the most common being 2-line and 6-line...
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Figure 3.2: Structures of iron oxides [3]

ferrihydrite, named after the number of peaks on an X-ray diffraction output. These materials are often precursors to other iron oxide phases e.g. goethite and hematite, the former occurring through dissolution and reprecipitation and the latter by dehydration and internal rearrangement [5].

Hydrolysis

Fe$^{3+}$ exists as a hexa-aqua ion [Fe(H$_2$O)$_6$]$^{3+}$ at pH < 1. Protons are eliminated successively in the process of hydrolysation. A precipitate will form if the final product possesses no charge. A typical reaction sequence is shown below [6]:

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Chapter 3. Production of iron oxide material

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O} & \rightarrow \text{Fe(OH)}^{2+} + \text{H}^+ \\
\text{Fe(OH)}^{2+} + \text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3^+ + \text{H}^+ \\
\text{Fe(OH)}_3^+ + \text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_4^+ + \text{H}^+ \\
2\text{Fe}^{3+} + 2\text{H}_2\text{O} & \rightarrow \text{Fe}_2\text{(OH)}_4^+ + 2\text{H}^+ \\
3\text{Fe}^{3+} + 4\text{H}_2\text{O} & \rightarrow \text{Fe}_3\text{(OH)}_4^+ + 4\text{H}^+
\end{align*}
\]

(3.1) (3.2) (3.3) (3.4) (3.5) (3.6)

The process of hydrolysation occurs by adding a base or heating a ferric salt. The solution pH is lowered at the onset of hydrolysation, particularly if heated. If pH drops too low no further hydrolysis occurs, reducing the final yield.

Ferric chloride dissolves in water to form a hydrated ferric ion. At low pH, 0.5–2, the hydrated ferric ion hydrolysates to form a mixture of loosely bound water molecules and tightly bound hydroxide ions. The hydroxide ions can then ‘bridge’ using oxygen atoms to form complexes with ferric atoms [7]. The formation of Fe-OH-Fe oxide bridges is known as olation:

\[
-\text{Fe} - \text{OH} - \text{Fe} - \text{OH}_2 \rightarrow -\text{Fe} - \text{OH} - \text{Fe} - +\text{H}_2\text{O}
\]

(3.7)

Oxolation involves the formation of oxobridges i.e.

\[
-\text{Fe} - \text{OH} + \text{OH} - \text{Fe} - \rightarrow -\text{Fe} - \text{O} - \text{Fe} - +\text{H}_2\text{O}
\]

(3.8)

An oxobridge results from the dehydration of two hydroxide ligands. This process is very pH dependent as the reactants are hydrolysed species. Generally both olation and oxolation occur before a heterogeneous (two phase) system is generated [8].

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3.1.2 Nucleation and growth

The distribution of crystals in a solution depends on the relative rates of crystal growth and nucleation. The driving force is the difference in free energy between the solute in the supersaturated fluid and the bulk solid. The first step during nucleation is the formation of very small clusters. The surface area is high compared to the volume, hence the free energy is higher on the surface than in the bulk. The driving force must be large to overcome this 'activation' energy. Nucleation may be increased by increasing the temperature and inducing collisions by ultrasonics [9].

Growth kinetics

The rate of growth depends on [10]:

1. The quantity of material available.
2. The viscosity, which influences diffusion to the particle surface.
3. The ability for the material to be incorporated into the lattice.
4. Impurities adsorbing onto the surface of the material, which retard the growth.
5. Particle-particle aggregation.

The growth rate of the crystal also depends on the precursor. This rate may be increased by stirring, i.e. by transfer of solute from the bulk to the surface. The rate of hydrolysis is determined primarily by the rate at which a base is added [11]. Localised pH differences are partially overcome by rapidly mixing the reagents [12]. Impurities can slow this process by being adsorbed onto the surface instead of the solute.

The kinetics of ageing depend on the solubility of the precipitate. Chemical ageing may occur with amorphous precipitates through transformation to another stable monohydrate. Hydrous ferric oxides are initially amorphous, becoming more crystalline with time [5].
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Aggregation and size distribution

A long nucleation period causes nuclei to form at different rates and leads to a polydisperse sol. Slow addition of the precursor can compensate for the growth of nuclei. The kinetics of crystal growth are dependent on the initial size. For akaganeite particles, growth occurs through aggregation of small single crystals. This may be caused by the formation of a large number of small nuclei [13].

The greatest influence on the ageing process is the difference in solubility between the larger and smaller particles. If the precipitate is polydisperse, the larger nuclei will grow at the expense of the smaller. Hence the particle number decreases with time, but the average particle size increases, a process known as Ostwald ripening [14].

3.1.3 Effects of anions used on iron oxide product

A simple assumption is that the only complexing ligands involved in the precipitation process are OH\(^-\), H\(_2\)O and O\(^2-\). Only a few anions are considered inert in this procedure (namely nitrate and perchlorate) and even these affect the final particle morphology [8].

The effect of the presence of different anions used as reagents on the precipitate was first recognised by Weiser and Milligan [15] and Dasgupta and Mackay [16]. Acidic solutions of ferric chloride produced beta ferric hydroxide on ageing [17, 18]. Ferric fluoride also produced the beta form, although the structure was more irregular [19]. Matijević and Scheiner [20] found that hematite was the primary product in ferric nitrate precipitation (determined by X-ray analysis), with a small amount of goethite. Hematite was also produced by precipitation with ferric perchlorate, although crystal shape varies with ferric salt concentration. Lepidocrocite was formed through the addition of base to ferrous salts [3]. Table 3.2 summarises the effect of the anion used on the final form of iron oxide produced.
Table 3.2: Anions used in iron oxide formation

<table>
<thead>
<tr>
<th>Iron salt</th>
<th>Type of iron oxide produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric nitrate</td>
<td>Hematite, goethite</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>Akaganeite</td>
</tr>
<tr>
<td>Ferric perchlorate</td>
<td>Hematite</td>
</tr>
<tr>
<td>Ferrous chloride</td>
<td>Lepidocrocite</td>
</tr>
</tbody>
</table>

Anions affect the morphology of the final product. The influence may be exhibited in three ways:

1. The anions can be incorporated to form hydrated salts rather than hydrous oxides. For example, ageing ferric salts containing phosphates result in the formation of hydroxophosphates [21].

2. The structure of the particle may be determined by the presence of an anion. One particular case is the formation of akaganeite in the presence of chloride ions [22].

3. The size and morphology of the oxide is strongly dependent on the nature and concentration of anions present in solution [6].

3.1.4 Formation of akaganeite

Nambu was the first to name the material akaganeite after the locality in which it was found, i.e. Akagane, Japan [23]. The structure of beta ferric hydroxide is similar to hollandite. A summary of the numerous methods of akaganeite production is given in Table 3.3.

Akaganeite can be produced by the hydrolysis of ferric chloride or fluoride at 60–100 °C for approximately 6 hours. The slow hydrolysis of ferric chloride always produces akaganeite [24]. It can also be precipitated from 0.5 M ferric chloride at 75 °C by adding 3.5 M $K_2CO_3$ [26]. Ammonium carbonate has also been used as a precipitating agent [19]. The dry oxidation of $3Fe(OH)_2 \cdot FeCl_2$ with an intermediate product of $Fe_2(OH)_3 \cdot Cl$ transforms to akaganeite [23]. Akaganeite can also be formed by the damp oxidation of $FeCl_2 \cdot H_2O$ [1].

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Table 3.3: Methods of akaganeite production

<table>
<thead>
<tr>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis</td>
<td></td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>[24, 25]</td>
</tr>
<tr>
<td>Addition of K$_2$CO$_3$ to ferric chloride</td>
<td>[26]</td>
</tr>
<tr>
<td>Addition of ((NH$_4$)$_2$CO$_3$) to ferric chloride</td>
<td>[19]</td>
</tr>
<tr>
<td>Addition of urea ((NH$_2$)$_2$CO) to ferric chloride</td>
<td>[27, 28, 29]</td>
</tr>
<tr>
<td>Addition of NaOH to ferric chloride</td>
<td>[3, 30]</td>
</tr>
<tr>
<td>Addition of urea ((NH$_2$)$_2$CO) to ferric fluoride</td>
<td>[29]</td>
</tr>
<tr>
<td>Addition of NaCl to ferric nitrate</td>
<td>[31]</td>
</tr>
<tr>
<td>Oxidation</td>
<td></td>
</tr>
<tr>
<td>Dry oxidation</td>
<td>[23]</td>
</tr>
<tr>
<td>Damp oxidation</td>
<td>[1]</td>
</tr>
</tbody>
</table>

The hydrolysis of urea can be used as a source of OH$^-$. Nightingale and Benck [27] produced akaganeite by direct precipitation of an iron (III) solution acidified with dihydroxyethylglycine. Kanungo and Mahapatra [28] also used urea to hydrolyse ferric chloride under reflux. More recently, Cai et al. [29] used microwaves to heat a solution containing ferric chloride and urea, adjusting the solution pH by ammonia addition. The required heating time was greatly reduced (90 minutes from 6.5 hours) and crystallinity of the final product increased with microwave heating rather than using a conventional water bath.


Role of chloride in akaganeite formation

Akaganeite is formed in ferric chloride solutions due to the interaction of the chloride ions with the surface of the hydrous ion [23, 25, 32]. Murphy et al. [33] have shown that there was little effect on the final product if chloride ions were added after a certain period of ageing. Anions were possibly acting as bridging ligands, similar to olation (see Equation 3.7) and intermediate polynuclear chains were produced [34].
In a freshly prepared akaganeite sample, chloride was present up to a ratio of 1:5 Cl:Fe [24]. The chloride trapped in the sample pores can be partially removed by prolonged washing with distilled water [23], ammonia [24], displacing the chloride ions with either nitrate or fluoride ions [18], and by dialysis [19]. However approximately 2% of the chloride remains [18, 23]. Extensive washing with a base leads to transformation to goethite [1, 35]. The presence of chloride therefore affects the stability of the compound. The chloride (or fluoride) ions are sufficiently small to diffuse into the elongated pores and stabilise the structure [6].

The beta form on prolonged ageing oxidises to hematite [16, 36]. This transformation is an example of the Stranski rule, where the least stable form (i.e. akaganeite) will nucleate first, as interfacial requirements are more easily met [20]. At pH > 5, akaganeite is not formed, as OH\(^-\) competes with chloride ions, hence hematite is formed even if chloride salts are used [29]. Similarly, akaganeite oxidises to hematite when suspended in water and heated [36]. Transformation to hematite occurs at around 200 °C when heated in air, although this figure was lower with lower amounts of chloride present in the compound.

### 3.1.5 Freeze-thaw process

After the material has been aged to increase the particle size, the precipitate is washed and dried at room temperature to increase the solids content. The iron oxide material produced cannot be heated to reduce the moisture content, as akaganeite is transformed to hematite [23]. Conventional freeze-drying results in a powdery material, unsuitable for a column application. However the material can be dewatered further using freeze/thaw technology. The degree to which it is dried before freezing alters the effectiveness of this process.

### Types of water

Water exists in four types within a sludge material, e.g. precipitate (see Figure 3.3).
Chapter 3. Production of iron oxide material

Figure 3.3: Types of water in sludge material [37]

1. Water unassociated with the solid material is free. This does not move within the solid.

2. Water held by capillary forces or held within the precipitate is known as interstitial water. If the aggregates break up, this water is now free water. Some, if not all of this type can be removed by mechanical dewatering.

3. Surface water is that held by surface forces and cannot be removed by mechanical means.

4. Chemically bound water can only be removed by thermochemical destruction.

Historically, water in precipitates and sludge material has been defined as either bulk water or bound water. Heukelekian and Weinburg defined bound water as that which does not freeze at $-20\, ^\circ\text{C}$ [38]. However, Vesilind and Hsu [39] determined that unfrozen water is present from several categories: all the water of hydration, surface water and some interstitial water. Even at $-30\, ^\circ\text{C}$, some water remained unfrozen. The quantity of unfrozen water decreased rapidly between $0\, ^\circ\text{C}$ and $-2\, ^\circ\text{C}$.

Much of the research carried out on freeze-thaw technology has been with iron and alum sludges from the water and waste water industries. Freeze-thaw has also been used to dewater activated sludge, although this was found to be less effective due to the high salt content and dissolved organic matter [40].
Foote and Saxton [41] noted that a high proportion of water could be removed from colloidal precipitates by freezing. Vol’khin and Zolotavin [42] first suggested a mechanism for the freeze-thaw process. Provided that the temperature of freezing was sufficiently low to account for the presence of dissolved impurities, the ferric hydroxide sludge could be successfully dewatered. Dewatering occurs through dehydration of solid particles, rather than a squeezing mechanism of ice crystals as first thought [43].

**Direct and indirect methods of freezing**

Direct methods used immiscible gases with lower boiling points than the freezing point of water. Butane was used as the heat transfer was more efficient, despite its boiling point being only slightly lower than 0 °C. Randall et al. [44] noticed that cake concentrations increased with increasing exposure to butane. However, this method did not change the appearance of the material as in indirect freezing; the latter produced a more granular material. Direct methods often formed a foam on the surface, which was physically removed, and after which there appeared to be no real improvement in dewaterability [45].

Freeze-thaw has been carried out using indirect methods, e.g. using heat transfer between a refrigerant and sludge. Wilhelm and Silverblatt [46] used circulation of chilled brine or glycol through alum sludge. The costs were higher for indirect methods, as a higher temperature difference was required for heat transfer.

The usual industrial freeze-thaw method uses a naturally cold climate to freeze sludge in large open beds [37]. Most of the experimental work studying the effects of freeze-thaw technology employs some form of anti-freeze bath controlling the rate at which the samples are lowered into the bath [47, 48, 49]. A conventional freezer has been used by some researchers without the use of controlled freezing [37, 40, 50].

**Ice front progression**

Ice crystals grow incorporating water, rejecting dissolved impurities and solid particles to the boundary of the ice front, where they are compressed or de-
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hydrated. This is known as gross migration [51]. This process requires a slow rate of freezing to allow for the diffusion of water to occur [40]. Water moves from within the material to the surface to be incorporated into the ice crystal, effectively dehydrating the particle.

Halde [52] has shown that smaller particles benefit from this conditioning process, as smaller colloidal particles are pushed together to form aggregates [37] (see Figure 3.4).

![Figure 3.4: Ideal ice front progression [51]](image)

Once the free water is frozen, water molecules inside the solid are extracted, making the material more solid. Larger particles, greater than 100 μm, are trapped without moving, forming large flocs [48], a process known as micromigration (Figure 3.5). Micromigration dewater the sludge to a certain degree, but does not enhance the strength of the material.

**Effect of salt concentration**

Dissolved ions affect the freezing point of the water and slow the rejection of the particle from the ice-water layer. The presence of impurities such as sodium chloride make the ice front progress in an uneven way [40] and lower the freezing point of the ice front (Figure 3.6). This in turn reduces the material movement which affects the material morphology [48].
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Jean and Lee [53] found that the type of electrolyte present as an impurity did not greatly alter the efficiency of the freeze-thaw process. Salts with both a higher and lower freezing point than the experimental temperature exhibited a similar effect on the filterability of the final product. However, no reference was made to the effect on the sample morphology or strength of floc produced.

Effect of freezing rate

Fast freeze methods have been investigated and the resulting product was weakly-linked aggregated material [54]. Hung et al. [47] and Chen et al. [55] found that that the filterability of activated sludge was improved, but the particle morphology was generally unaffected by a high freezing speed. Instant freezing was not sufficient to dewater the material [51].

Effect of time and temperature of freezing

Many researchers [37, 49, 53] have noted that an increased freezing time increases the effect on the final product morphology. Logsdon and Edgerley [51] found that leaving sludge frozen for a period of time rather than immediate thawing increased the dewaterability. Vesilind and Martell [37] determined
Figure 3.6: Ice front progression, in the presence of dissolved salt [51]

that a lower freezing temperature resulted in better filterability of the sludge for a similar freezing time.

3.2 Experimental method

A summary of the experimental methods of iron oxide materials used for adsorption experiments (designated GEH, NN and VL) is given in the following section. Details of the freeze-thaw rig used to condition sample NN with optimum experimental parameters are outlined. The three samples were compared physically (by scanning electron microscopy and X-ray diffraction) to a synthetic akaganeite. An experimental procedure for this material is also provided.

3.2.1 Chemicals used

The NN and synthetic akaganeite were prepared from FeCl₃·6H₂O, and VL from anhydrous FeCl₃ in addition to NaOH pellets, all purchased from Fisher, UK.
3.2.2 Sample GEH production

The exact production method for GEH is unknown. However some information has been provided by the manufacturer. Sodium hydroxide and ferric chloride were contacted at 40 °C. The resulting precipitate was washed, passed through a membrane then stored in plastic tubs. The tubs were conditioned in situ with a solids content as low as 15 %, then left to naturally dewater until the volume was reduced by 75 %. The equilibrium pH of the product was 7.

3.2.3 Akaganeite production

A pure sample of the mineral akaganeite was produced using the partial neutralisation of ferric chloride, outlined by Schwertmann and Cornell [3]. 26.9 g FeCl₃ · 6H₂O was dissolved in 100 ml deionised water, i.e. a 1 molar solution was prepared. 75 ml 1 M NaOH was added to partially neutralise the solution. A temporary brown precipitate formed which redissolved on shaking to give a dark brown solution. The vessel was left for two days, after which 20 ml 10 M NaOH was added to the vessel and the mixture heated at 70 °C in an oven for one week.

The resulting precipitate was washed with deionised distilled water and filtered using a Buchner funnel. The filter cake was frozen at −20.5 °C and then placed in a freeze-drier for 17 hours. The sample was then refrozen at the same temperature for a further 24 hours.

3.2.4 Sample NN production

1 litre each of 0.1 M hydrated ferric chloride and 0.3 M sodium hydroxide (following stoichiometric quantities) were added simultaneously to a plastic beaker, using a double-headed positive displacement pump. The contents of the beaker were held at 40 °C using a water bath. A schematic diagram of the experimental set up is given in Figure 3.7. The flowrate of both the reagents was approximately 30 ml/min. The pH of the reaction was maintained at 4.2 ± 0.1, by slight adjustment to the flow of sodium hydroxide.
Throughout the reaction the material was vigourously stirred and the temperature was maintained at 40 °C. The contents of the beaker were stirred further for one hour to allow the reaction to reach equilibrium, i.e. there was no change noted in the pH. The vessel was removed from the water bath, covered and left for four days at room temperature (approximately 18 °C). From previous experimental work this has been shown to be the optimum ageing time for the material (see Table 3.5). The final pH of the material was approximately 4 ± 0.05.

After the ageing period, the supernatant was removed and the remaining material was washed by decantation with 16 bed volumes of tap water. Decantation was carried out four times, i.e. four bed volumes of tap water were used each time to wash the sample. After washing, the sample was allowed to settle, the excess water removed by decantation and the precipitate immediately filtered using a Buchner funnel and a Whatman 3 filter. The filter cake was removed and left on a warm surface (approximately 25 °C) until the solids content was in the range 25-30 %.
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Previous experimental work has shown that the freeze/thaw process is effective with a solids content greater than 20% (see Table 3.5). The solids content was determined by weighing approximately 0.5 g of the moist sample, transferring to a ceramic crucible and heating at 105 °C in an oven. After 30 minutes, the crucible was removed from the oven, placed in a dessicator to cool and reweighed. The crucible was again placed in the oven for a further 15 minutes, after which a similar procedure was used to reweigh the sample. If no change was observed in the sample weight, this value was used to calculate the solids content. This was found by dividing the final weight by the initial weight.

Impact of variables on granule size

Several different variables were studied for their effect on the final particle size of the material. The parameters studied can be found in Table 3.4.

Table 3.4: Variables studied for their effect on final particle size

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
<th>Default value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent used</td>
<td>Hydrated or anhydrous ferric chloride</td>
<td>Anhydrous ferric chloride</td>
</tr>
<tr>
<td>Flowrate of reagents</td>
<td>15, 30, 60 ml/min</td>
<td>60 ml/min</td>
</tr>
<tr>
<td>Washing method</td>
<td>None, decantation, Buchner funnel</td>
<td>Decantation</td>
</tr>
<tr>
<td>Solids content</td>
<td>25–35 %</td>
<td>25 %</td>
</tr>
<tr>
<td>Freezing method</td>
<td>Controlled, uncontrolled, graduated</td>
<td>Controlled</td>
</tr>
<tr>
<td></td>
<td>and supernatant removed and placed in freezer</td>
<td></td>
</tr>
<tr>
<td>Freezing rate</td>
<td>1, 2 °/hr</td>
<td>1 °/hr</td>
</tr>
</tbody>
</table>

It was found that controlled thawing did not increase the final particle size. However the parameters that have caused an appreciable increase in granule size are the solids content of the material, the flowrate of the reagents, the type of reagents used and controlling the freezing process. From the data collected, the optimum conditions are outlined in Table 3.5. Prior to use in adsorption experiments the material was crushed in an agate mortar and pestle, sieved and the size fraction 150–300 μm used.
Chapter 3. Production of iron oxide material

Table 3.5: Optimum conditions for the production of NN

<table>
<thead>
<tr>
<th>Variable</th>
<th>Optimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids content</td>
<td>25–30%</td>
</tr>
<tr>
<td>Flowrate of reagents</td>
<td>30 ml/min</td>
</tr>
<tr>
<td>Type of ferric chloride</td>
<td>FeCl₃·6H₂O</td>
</tr>
<tr>
<td>Method of freezing</td>
<td>Controlled freezing at 1 °/hr</td>
</tr>
<tr>
<td>Method of thawing</td>
<td>Left overnight in the fridge at 7 °C</td>
</tr>
</tbody>
</table>

Freeze-thaw method

Much of the freeze-thaw literature involves the slow lowering of samples into anti-freeze baths [47, 51, 52]. A rig was developed to control the rate of freezing (Figure 3.8), although there was no restriction on the direction of the ice front progression. Figures 3.9 and 3.10 give the dimensions of the rig.

![Freeze-thaw rig diagram](image)

**Figure 3.8: Freeze-thaw rig**

On reaching the desired solids content, the sample (approximately 3 g) was placed in a plastic cup and loaded into an aluminium chamber placed within an industrial freezer. The setpoint of the West 6100 controller was set to 0 °C.
and left to stabilise for 3 hours. This ensured that all the samples were frozen starting from the same temperature. After the controller had stabilised, the ramp rate was set to $-1 \, ^\circ C/hour$, the smallest available ramp rate available on the controller. The final freezing temperature was $-20 \, ^\circ C$ at which the rig was held for 24 hours. The material was then removed from the rig at this final freezing temperature and placed overnight in a fridge at $7 \, ^\circ C$. The sample (granule size 1–3 mm) was finally placed into a glass vial, flooded with deionised water and sealed.

![Freeze-thaw rig lid dimensions](image)

**Figure 3.9: Freeze-thaw rig lid dimensions**
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Figure 3.10: Freeze-thaw rig body dimensions
3.2.5 Sample VL production

Another iron oxide sample (VL) was generated by V Strelko, based on a larger scale production. 25 L 0.9 M NaOH was added at 150–270 ml/min to 25 L 0.3 M FeCl₃ held in a glass reactor at 40–50 °C by a steam heat exchanger. Continuous mixing of reagents was maintained by a stainless steel stirrer. The reaction was terminated when pH 5.5 was reached (after 1.5–3 hours), but stirring continued for another hour. After 30 litres of wash water was added, the settled volume of the precipitate was 19 litres.

The slurry was initially dewatered by a ceramic cross-flow microfilter (0.14 µm cut-off), reducing the precipitate volume to 10–12 litres. After which the material was left as a thick cake to air dry for 3–5 days on perforated sheets, rather than employing a freeze-thaw method. Moisture content of the final material (determined by the method described in section 3.2.4) was 20 %. Hence the total amount of material produced was over 3 kg. The resulting dry material formed large chunks which were washed, crushed and sieved before being used for adsorption experiments.
References


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REFERENCES


REFERENCES


REFERENCES


Chapter 4

Physical characterisation

Two samples produced in the laboratory (NN and VL), and a commercial sample (GEH) were compared by measuring their specific surface area and pore size distribution. These parameters are important for adsorption, as a large surface area and pore size increases the number of active sites available for adsorption. In addition, scanning electron micrographs (SEM) and X-ray diffraction (XRD) were completed. SEM provides visual information on the morphology of the samples. XRD analysis characterises the material by its crystal structure. The chemistry of iron is complicated, as illustrated in the previous chapter, and small changes in reaction conditions can greatly effect the final product. Therefore XRD can be used as a form of quality control to identify the phases present in the final iron oxide material.

4.1 XRD theory

The crystal structure of each material is unique and depends on how its atoms are ordered in planes and axes. The intercept of these planes with the symmetry axis determines their position within the crystal lattice. The atoms interact with the electromagnetic properties of the X-rays causing them to scatter. The majority of the waves are made extinct through destructive interference; however, some are enhanced by constructive interference. The direction of these latter waves is related to the distance between the atomic planes, known as d-values, and the Bragg angle \( \theta \) (Figure 4.1). \( \theta \) is the angle at which the waves
hit the crystal producing the maximum interference. The Bragg equation links this angle of scattering to the d-values as follows [1]:

\[
n\lambda = 2d \sin \theta
\]  

(4.1)

where \( \lambda = \) wavelength used (nm)  
\( n = \) order of reflection

The output is the observed intensity plotted against Bragg angle, from which the d-values are calculated. The type of radiation usually used for iron samples is either CoK\(\alpha\) or FeK\(\alpha\). If CuK\(\alpha\) is used, the observed intensity is much lower, as iron absorbs much of the radiation.

### 4.1.1 d-values of common iron oxides

Each crystalline product has characteristic d-values that can be found on reference cards in the Joint Committee on Powder Diffraction Standards (JCPDS) mineral powder diffraction file. A compound can be identified by comparing
the calculated d-values against the JCPDS diffraction file of iron oxides, summarised in Table 4.1. The values are in order of intensity; the greatest is listed first.

Table 4.1: d-values of iron oxides, adapted from Schwertmann and Cornell [1]

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Most intense d-values (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>2.70, 3.68, 2.52</td>
</tr>
<tr>
<td>Magnetite</td>
<td>2.53, 1.49, 2.97</td>
</tr>
<tr>
<td>Goethite</td>
<td>4.18, 2.45, 2.69</td>
</tr>
<tr>
<td>Akaganeite</td>
<td>3.33, 2.55, 7.47</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>6.26, 3.29, 2.47, 1.94</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>2.54, 2.24, 1.97, 1.73, 1.47</td>
</tr>
<tr>
<td>Ferroxyhyte</td>
<td>2.54, 2.22, 1.69, 1.47</td>
</tr>
</tbody>
</table>

4.2 Specific surface area and pore size analysis

The specific surface area is a key functional parameter for an adsorbent. The analysis of various ferric compounds, namely NN, GEH and VL, were completed using nitrogen adsorption.

Summaries of adsorption theory, Langmuir and BET equations are given. The resulting isotherms from nitrogen adsorption can be classified and a pore size distribution extracted from the data. The types of isotherms and hysteresis loops are outlined, in addition to the various methods used for pore size distribution determination.

4.2.1 Adsorption theory

When a disperse solid is exposed to a gas in an enclosed space at a known pressure, the solid will adsorb the gas. After a period of time, the pressure will become constant. The extent of gas adsorption on a porous solid depends on the temperature, pressure and the molecular size of the gas, and available
Chapter 4. Physical characterisation

surface area. The amount of gas adsorbed can be calculated from the change in pressure, if the volume of the vessel and solid are known.

Hence for a known gas held at a specified temperature, the amount of gas adsorbed is solely dependent on the pressure and therefore an adsorption isotherm can be constructed (volume adsorbed vs. relative pressure, (pressure/saturated vapour pressure, $p/p^o$)). The surface free energy is reduced by adsorption, hence entropy is reduced. It is an exothermic process, with the heat of physical adsorption being similar in magnitude to the heat of condensation [2].

**Langmuir equation**

Langmuir [3] was the first to present a kinetic approach to adsorption. This was based on a flat surface with zero accumulation on the surface, i.e. the rate of adsorption is equal to the rate of desorption. It is assumed that the energy of adsorption is constant, implying that the surface is uniform and monolayer coverage is reached at saturation.

**BET equation**

The BET equation (Equation 4.2) is based on kinetics and is a modified version of the Langmuir isotherm with multilayer, rather than monolayer adsorption [4]. The previously adsorbed layer serves as adsorption sites for the next layer and so on. Generalising the Langmuir equation maintains the disadvantage of the assumption that the surface is energetically uniform, i.e. all adsorption sites are equivalent and that there is no interaction between adsorbed molecules. It is also assumed that at saturated pressure the number of layers are infinite.

The BET equation is restricted in its validity to a relative pressure ($p/p^o$) in the range 0.05-0.35 [5]. The lower limit is set so as not to include the heat of adsorption for the first layer of molecules, which is much greater than subsequent layers. The BET equation breaks down at relative pressures $> 0.35$ and over-predicts adsorption by computing a high entropy value [6].
\[ \frac{p}{x(p^o - p)} = \frac{1}{x_m c} + \frac{c - 1}{x_m c} \cdot \frac{p}{p^o} \]  \hspace{1cm} (4.2)

where  
- \( x \) = adsorption capacity (mmol/g)
- \( x_m \) = monolayer adsorption capacity (mmol/g)
- \( p \) = pressure (Pa)
- \( p^o \) = saturation pressure (Pa)
- \( c \) = BET constant

The specific surface can be calculated if the 'knee' (point B in Figure 4.2) on the isotherm is well defined. This would be characterised by a high value of the BET constant \( c \). \( x_m \) represents the monolayer adsorption capacity and is calculated from the BET equation (Equation 4.2), assuming one molecule of nitrogen occupies 16.2 Å².

### 4.2.2 Isotherm classification

The isotherm produced from nitrogen adsorption can usually be identified as one of five classes proposed by Brunauer, Deming, Deming and Teller (BDDT) [7] in addition to a stepwise isotherm (see Figure 4.2). Table 4.2 provides a summary of the characteristics of each isotherm, degree of porosity and an example system.

The Type IV isotherm which describes the adsorption for ferric hydroxide can be used to calculate the specific surface of the material and the pore size distribution [7]. Type IV is characteristic of a material possessing a pore size distribution in the range of up to hundreds of angstroms. The definition of pore size as recommended by IUPAC is an arbitrary classification, developed using nitrogen as an adsorbent at its normal boiling point [8]. Pores widths less than 20 Å are given the term micropores, between 20 and 500 Å are mesopores and greater than 500 Å are macropores. Each classification has a particular significance in terms of the adsorption isotherm (see Table 4.2).
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Figure 4.2: Classification of BDDT adsorption isotherm [7]

Table 4.2: Types of isotherms, characteristics and examples

<table>
<thead>
<tr>
<th>Type</th>
<th>Characteristics</th>
<th>Example system</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Microporous with small internal surface</td>
<td>Oxygen on activated carbon</td>
<td>[7]</td>
</tr>
<tr>
<td>II</td>
<td>Reversible non-porous or macroporous</td>
<td>Nitrogen on iron catalyst</td>
<td>[5]</td>
</tr>
<tr>
<td>III</td>
<td>Adsorbent-adsorbate interaction is weak</td>
<td>Water vapour on non-porous carbon</td>
<td>[9]</td>
</tr>
<tr>
<td>IV</td>
<td>Hysteresis loop with a plateau, mesoporous</td>
<td>Benzene on iron oxide gel</td>
<td>[5]</td>
</tr>
<tr>
<td>V</td>
<td>Adsorbent-adsorbate interaction is weak, porous</td>
<td>Water on charcoal</td>
<td>[7]</td>
</tr>
<tr>
<td>VI</td>
<td>Stepwise multi-layer, non-porous</td>
<td>Argon on graphitised carbon black</td>
<td>[8]</td>
</tr>
</tbody>
</table>
Chapter 4. Physical characterisation

During the adsorption process, the adsorbate diffuses through the pores of the solid. Initially this is through the smallest, or micropores. These sites have the most energy and have greatest polarity. As the pressure increases, the adsorbate molecules diffuse to larger and therefore less energetic pores. In monolayer coverage, all the molecules are in contact with the surface. For multilayer adsorption, only the lowest layer is in contact with the surface [8].

Hysteresis loop

Capillary condensation of the adsorbate is evident in the hysteresis loop (see Figure 4.2). There are several types of hysteresis loop (Figure 4.3) ranging from near-vertical parallel branches (H1) to near-horizontal parallel adsorption/desorption branches (H4).

![Hysteresis loop diagram](image)

Figure 4.3: Types of hysteresis loop [9]
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H1 hysteresis loop is common for agglomerated material with uniform spheres and a narrow size distribution. Inorganic oxides produce H2 loops, indicative of poorly defined pore size and shape. H3 and H4 are associated with material possessing slit-shaped pores; the former is typical of aggregates and the latter of microporous materials. Common to all hysteresis loops is the steep closure point in the desorption section, characterised by the nature of the adsorbate used. For nitrogen at its boiling point, this occurs at $p/p^o \sim 0.42$ [8].

At a low equilibrium pressure, a monolayer of the adsorbate develops on the adsorbent surface. Subsequent layers are built up, the thickness increasing with increasing pressure until the pores are filled with the adsorbate, illustrated by the lower line of the hysteresis loop. Thereafter the adsorption is restricted to the exterior of the material.

On desorption the adsorbate forms a meniscus across the pore and evaporates when the pressure of the system drops below a critical value [6]. This critical value is determined by the pore radius from the Kelvin equation [9]:

$$\frac{1}{r_1} + \frac{1}{r_2} = -\left(\frac{RT}{\gamma v^1}\right) \ln\left(\frac{p}{p^o}\right)$$

(4.3)

where $p^o$ = saturation vapour pressure (Pa)
$p$ = critical pressure (Pa)
$\gamma$ = surface tension of liquid condensate (N m$^{-1}$)
$v^1$ = molar volume of the liquid condensate (cm$^3$ mol$^{-1}$)
$r_{1,2}$ = principle pore radii of curvature in the liquid meniscus (Å)
$R$ = universal gas constant (J mol$^{-1}$ K$^{-1}$)
$T$ = temperature (K)

Hence the critical pressure is less for smaller pores than for larger ones. The difference in methods for adsorption and desorption are evidence for the existence of a hysteresis loop. However, there are two relative pressures with corresponding radii values, the desorption pressure always the lower and more likely to represent the true equilibrium value [10], this value is used in calcu-
Chapter 4. Physical characterisation

lating the pore size. Below a certain pressure pores do not undergo capillary condensation, but fill continuously with increasing pressure. Hence, at lower relative pressure values the adsorption and desorption values are coincident.

Equation 4.3 can be used if it is assumed that the pore size and shape control the meniscus curvature. Below 20 Å the Kelvin equation is not reliable, due to solid-fluid interactions being ignored [11]. Adsorption forces increase with decreasing pore size [12] and hence its accuracy decreases. This leads to pore size underestimation by overestimation of the thickness correction of the adsorbed film.

4.2.3 Pore size distribution

There are several methods for determining the pore size distribution (PSD) from isotherm data. Some have a mechanistic basis (e.g. Barrett, Joyner and Halenda (BJH) and Dubinin-Stoeckli (D-S)), Horvarth-Kawazoe (H-K) uses a quasi-thermodynamic approach and the density functional theory (DFT) is generated by statistical thermodynamics. The advantages and disadvantages of these different methods are outlined below.

Mesopore determination

PSD based on the Kelvin equation, such as the BJH method [13] assume there are no micropores and that the material exhibits a regular pore structure [8]. The BJH method is only suitable for mesoporous size analysis and is incompatible with the H-K, D-S and t-plot methods [14].

Micropore determination

Much of the work in this area of determining micropore volume was completed by Dubinin and his co-workers [15, 16]. Other methods include the t-plot modification and the H-K method [17]. However there has been some doubt as to their ability to describe micropore adsorption realistically [18].
More recently interest has developed in a model using a density functional theory (DFT) to calculate model isotherms. From this data a pore size distribution can be generated using a deconvolution technique. A slit-like or cylindrical shape pore geometry is assumed [19]. This has enabled a method to describe the entire pore size range, rather than that limited by the Kelvin equation (Equation 4.3). For more details regarding the DFT approach see [20].

There is a characteristic drop in the PSD using DFT model between 8–10 Å due to the packing effect of adsorbate molecules in the pores. Initially a monolayer is formed in the narrowest pores, a process known as volume filling. After a critical pore value, a second layer is required to fill the pore. This leads to an abrupt increase in adsorbate uptake, indicating the onset of multilayer formation [19].

This model does not take into account the heterogeneity of the pore walls, namely geometric and energetic differences [21]. In addition, electrostatic interactions are not considered in the DFT model, which assumes spherical adsorbate molecules and interaction solely by van der Waals forces [18]. This leads to an underestimation of the PSD.

### 4.3 Experimental procedure

An outline of the experimental methods used for specific surface area and pore size determination, scanning electron microscopy (SEM) micrographs and X-ray diffraction (XRD) analysis is given below.

#### 4.3.1 SEM

Scanning electron micrographs were taken on a Cambridge Instrument stereo scan 360 microscope at room temperature. The normal second electron mode (i.e. not back scattering) was used and the accelerating voltage was set to 10 kV. Prior to analysis, the iron oxide material was dried in a vacuum oven at room temperature, then mounted using PVA glue on an aluminium platform and gold coated.
4.3.2 XRD

For all the samples a Philips PW1050 goniometer with a copper X-ray tube was used. A graphite monochromator with a 1 ° divergence slit, 1 ° scatter slit and a 0.2 mm receiving slit was added. A Hilton Brooks nucleonics and automation system was also used.

Prior to analysis all samples were dried in a vacuum oven at room temperature. An agate mortar and pestle was used to crush the material before pressing into an aluminium holder. XRD scans were carried out in the range 10–80 ° at 0.05 ° step size and 0.2 °/min.

4.3.3 Surface area and pore size analysis

A similar method was adopted for each sample, using a Micromeritics ASAP 2010 analyser. All samples were dried in a vacuum oven at room temperature before sampling. The glass tubes used in the analysis were degassed for approximately one hour, until the vacuum was below 50 mmHg, back filled with nitrogen then removed and weighed. A quantity of iron oxide was then measured on a Sartorius BP210D balance, accuracy ±0.0005 g, and transferred to the sample tube. The sample was degassed to remove volatile compounds (e.g. carbon dioxide and oxygen) attached to the material surface. The sample mass was then determined by reweighing the glassware. The tube was degassed again until the vacuum fell below 50 mmHg. The stability of the vacuum was established by backfilling and comparing the pressure in the tube.

The actual analysis for specific surface area used liquid nitrogen at its boiling point, 77 K. The sample tube was degassed after insertion in a liquid nitrogen bath. The tube free space was then measured using helium (as helium does not adsorb onto the solid surface) at room temperature and at 77 K. To enable the sample to be analysed, nitrogen was added until the first equilibrium point was reached.
4.4 Results

4.4.1 SEM

A description of the results found from SEM micrographs for all samples are given below. They are compared to a synthetic akaganeite, also prepared in the laboratory.

4.4.2 Akaganeite

A pure sample of the mineral akaganeite was produced using the partial neutralisation of ferric chloride, as described in Section 3.2.3.

![SEM image of synthetic akaganeite](image)

**Figure 4.4: SEM image of synthetic akaganeite**

The product appears to have a crystalline structure (shown in Figure 4.4). The average particle size is quite large, 500–650 μm. The crystal structure is also
longer and thinner, unlike the other samples, which are more spherical. There appear to be impurities on the surface, which could be sodium chloride, a by-product of the reaction procedure. The surface is smooth, with no aggregate material.

4.4.3 Sample NN

This sample was produced in the laboratory at Loughborough University (see Section 3.2.4 for method). The structure (shown in Figure 4.5) appears to be robust and without aggregated material. On the surface there is some fine material. There is no visual evidence of any pore structure at the resolution used.

![Figure 4.5: SEM image of sample NN](image)
4.4.4 Sample GEH

The information regarding the production of sample GEH is given in Section 3.2.2. The SEM's for the sample GEH are similar to NN (Figure 4.6), although the surface appears rougher and has more surface fines.

![SEM image of sample GEH](image_url)

Figure 4.6: SEM image of sample GEH

4.4.5 Sample VL

The last sample, VL was also produced in the laboratory at Loughborough University (see Section 3.2.5 for method). The material is granular in appearance with some fines on the surface (Figure 4.7).
Figure 4.7: SEM image of sample VL

4.4.6 XRD

Akaganeite

A sample of pure akaganeite was produced according to a method of partial neutralisation of ferric chloride, as described by Schwertmann and Cornell [1]. The details of the peaks from XRD analysis are given in Figure 4.8. The XRD scan was used as a comparison for the other iron oxide materials.

Other iron oxide samples

The XRD output for sample NN (Figure 4.8) shows that it is amorphous, i.e. that there is no evidence of strong distinct peaks, which would be expected from a more crystalline material. Conversely both the commercial
Chapter 4. Physical characterisation

Figure 4.8: XRD data for all samples compared to synthetic akaganeite

Sample GEH and the other laboratory produced sample, VL, exhibit a higher degree of crystallinity, comparable to that of synthetic akaganeite (see Figure 4.8). Both the latter samples are not pure, as there is a peak associated with hematite (33°), VL showing a stronger intensity implying a greater quantity of the impurity is present.

Cai et al. found that reaction pH affected the crystallinity of the final iron oxide product. Nucleation and growth occurred most rapidly at pH < 1.5 (Figure 4.9). At low pH the peaks are narrow and distinct, at higher pH there are two wide peaks for the diffraction pattern at pH 4 (the production pH for sample NN), similar to Figure 4.8. At pH > 6, the iron oxide produced was a mixture of goethite (G) or hematite (H) [22].

Therefore, the reaction pH does affect the final nature of the iron oxide material. Sample VL was not prepared at a constant pH, but NaOH was added to ferric chloride until the pH was 5.5. Hence akaganeite may have formed initially whilst the pH < 5, after which hematite began to form as hydroxide
is more competitive for structural sites than chloride [1]. Chloride (or fluoride) is essential for the formation of akaganeite as it brings stability to the tunnel structure [23].

The time of ageing the precipitate can also be a contributing factor to increased crystallinity. The longer a material is left the more crystalline it becomes. Further details regarding the time of ageing or reaction pH are not supplied for sample GEH, but the XRD outputs are very similar. It may be assumed that these variables are comparable to those used for VL.

Ellis et al. [24] state that the quantity of chloride present in the final product affects the XRD output, a lower chloride content causes peak broadening. Section 5.3.3 indicates that VL possesses the highest quantity of chloride, followed by GEH and NN chloride content is significantly lower than the former samples. Chloride content of the samples would be affected by the degree of washing. This trend is reflected in the degree of crystallinity.

A final factor that could affect the nature of the product formed is the temperature of reaction. However all samples were prepared at 40 °C, therefore it is not a contributing parameter.
4.4.7 Specific surface area and pore size analysis

The BET surface area and average pore size values are given in Table 4.3. All samples have a reasonable specific surface area, 200–300 m$^2$/g and the average pore size implies that the material is primarily mesoporous. A high c constant indicates a strong energy of adsorption.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$/g)</th>
<th>c value</th>
<th>Average pore size BET (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NN</td>
<td>240</td>
<td>206.8</td>
<td>40</td>
</tr>
<tr>
<td>GEH</td>
<td>310</td>
<td>89.7</td>
<td>29</td>
</tr>
<tr>
<td>VL</td>
<td>204</td>
<td>116.92</td>
<td>53</td>
</tr>
</tbody>
</table>

All three samples had a comparable specific surface area to that of Deli et al. [10] who produced akaganeite material at room temperature with a specific surface area of 330 m$^2$/g. However, this material was nanocrystalline which could account for the high specific surface area. González-Calbet and Alario-Franco determined a BET surface area of 70 m$^2$/g with N$_2$ as an adsorbent for akaganeite produced at 70 °C [25]. Crosby et al. [26] determined the BET surface area of a number of ferric oxide materials, all were in the range 160–230 m$^2$/g and were identified as an amorphous material, am-FeOOH. Generally, the higher degree of crystallinity, the lower the specific surface area.

Nitrogen adsorption isotherms

All three samples (Figures 4.10–4.12) show a Type IV isotherm (see Figure 4.2), with hysteresis in the desorption curve. This is a characteristic of mesoporous substances, where capillary condensation occurs. A bottleneck effect between micropores and mesopores causes adsorbate condensation to occur.
Figure 4.10: Adsorption isotherm of sample NN

Figure 4.11: Adsorption isotherm of sample GEH
Chapter 4. Physical characterisation

Figure 4.12: Adsorption isotherm of sample VL

Figure 4.13: Adsorption isotherm for akaganeite produced at 298 K [10]
A small pressure difference is required when nitrogen is adsorbed onto the surface. On desorption, however, a higher pressure difference is required to enable the nitrogen to desorb back into the micropores.

The shape of the hysteresis loops differ for the samples. The adsorption isotherm for sample NN does not have a well-defined loop (Figure 4.10), indicating a small amount of mesoporosity and presence of slit-shaped pores [27]. GEH and VL on the other hand have a more defined desorption loop and therefore greater mesoporosity. The desorption branch closure is not very steep which indicates that the diameters of the pores are not particularly uniform [28]. The nitrogen adsorption isotherms for these latter samples concur with that produced by Deli et al. [10]. The shape and magnitude of the hysteresis loops are similar, although there is no evidence of macropores at a higher relative pressure (Figure 4.13).

The initial steep gradient to the ‘knee’ of the isotherm reveals that there are some micropores present in all iron oxide samples. Figure 4.11 indicates that GEH has the greater number of micropores, as it has the highest quantity of adsorbed nitrogen in the initial portion of the isotherm. Sample NN has a comparable number of micropores (Figure 4.10) while VL possesses the lowest amount (Figure 4.12). This trend in micropore content is mirrored in the trend of specific surface area (Table 4.3).

The quantity of micropores could be related to the pH control during production. The pH of both samples GEH and NN were controlled to a constant value throughout the reaction procedure. Conversely VL was produced by adding NaOH to ferric chloride until the pH > 5.5. This lack of control could lead to a more heterogeneous material with less micropores.

At higher relative pressures, there is an abrupt increase in nitrogen adsorption which indicates the presence of macropores [28]. Both NN and VL possess a higher degree of macroporosity, particularly NN as more than half of the total nitrogen adsorbed occurs at high relative pressure. A greater number of macropores would decrease the specific surface area (Table 4.3), as these contribute only 1–10 % to the overall figure [13].
Pore size distribution

The pore size distributions (PSD) generated by the DFT model (Figure 4.14) for samples GEH and VL have comparable shape and magnitude, and hence similar quantities of mesopores. Deli et al. produced a material which had a similar nitrogen adsorption isotherm to samples GEH and VL. However, Figure 4.15 illustrates that this material possesses a much narrower PSD [10], due to the nanocrystalline nature of the material produced.

Sample NN appears to have fewer mesopores which correlates with the slight hysteresis seen in Figure 4.10. Moreover Figure 4.16 shows that samples VL and NN have a reasonable degree of macroporosity. This again concurs with the adsorption isotherm shape, i.e. a rapid increase in nitrogen adsorption at very high relative pressures (Figures 4.10–4.12). It would be expected for an amorphous material (NN) to have a high degree of macroporosity, evidence of a poorly crystalline material. The presence of larger pores in sample VL could be due to poor pH control, increasing the surface heterogeneity.

![Figure 4.14: Lower range DFT pore size distribution of all samples](image)

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Figure 4.15: Desorption pore size distribution [10]

Figure 4.16: Higher range DFT pore size distribution of all samples
Chapter 4. Physical characterisation

The disparity between the average pore size (given in Table 4.3) which indicates all samples are mesoporous and the data found in Figure 4.16, implying a high degree of macroporosity for samples NN and VL can be explained as follows. The BET method for pore size determination relies on the Kelvin equation (Equation 4.3), which does not take into account solid-fluid interactions. Hence, the equation is only reliable in the pore size range $20 \ \text{Å} < x < 250 \ \text{Å}$. At lower pore radii the pore size is underestimated, as the adsorption forces are underestimated [12]. At higher values it becomes increasingly difficult experimentally to obtain the pressure differences necessary to calculate pore size; a relative pressure of $p/p^0 = 0.95$ corresponds to a radius of 200 Å [7]. DFT does not use the Kelvin equation, but models gas adsorption using statistical thermodynamics and hence is able to determine much larger pore size ranges [18].

4.5 Conclusions

SEM identifies that all the materials studied are robust and granular, not aggregated, and that samples VL and GEH appear to have fine material on the surface. All three samples have a more powdery surface than the synthetic akaganeite, which appears to have some surface material, probably NaCl, a by-product of the reaction.

Nucleation and growth for akaganeite formation occur most rapidly at pH 1.5. As the pH of the reaction solution increased, the peaks from X-ray diffraction (XRD) analysis become broader, indicating a decrease in crystallinity. There is a similarity between the GEH and VL samples and the pure sample of akaganeite. The XRD output signal for GEH and VL is stronger with more distinct peaks, implying a higher degree of crystallinity. The peaks do not exactly match up, indicating that there are probably two phases present in the sample.

The quantity of chloride in the final product also affects the width of XRD peaks. VL contains the most chloride and has the strongest output and most distinct peaks, followed by GEH with intermediate crystallinity and chloride content and NN possesses the lowest chloride content and produces wide XRD peaks, indicating that it is amorphous.
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The presence of other phases, particularly in the VL sample could be due to the change in pH throughout the reaction procedure. The pH was not controlled, but approached a value of 5.5. Hence initially akaganeite was formed, and at pH > 5, hematite began to form, as hydroxide ions compete more effectively with chloride ions for surface sites.

The BET surface area analysis shows that all samples have a reasonable specific surface area in the range 200–300 m²/g and are mesoporous. Sample GEH has the largest, followed by NN and VL. This trend is also reflected in the degree of microporosity. The difference in the amount of porosity could also be due to the lack of pH control during VL production, resulting in a wider pore size distribution.

Sample NN has the greatest quantity of macropores, owing to its poor crystallinity. VL also possesses a number of macropores, but has a similar amount of mesopores as GEH. The latter samples GEH and VL are comparable to a synthetic akaganeite material.

Good agreement was found between the experimental nitrogen adsorption isotherms and the pore size distributions generated by the DFT model. This highlighted the number of macropores present in samples NN and VL which was not seen in the average pore size calculated using the BET method. The limitation of the method was due to the restrictions of the Kelvin equation.

From the physical characterisation data alone, GEH appears to be the best adsorbent, with the greatest surface area, highest amount of micropores and a reasonable degree of crystallinity.
References


REFERENCES


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Chapter 5

Surface chemical characterisation

5.1 Introduction

The mechanisms and models that describe the development of surface charge are examined. The regions within the electric double layer (EDL) and definition of zeta potential is given. Understanding surface charge phenomena and determining the point of zero net proton charge and isoelectric point of the materials studied are important for adsorption studies. These parameters determine a suitable pH range for removal of anionic species. The effect of the presence of anions (arsenate, phosphate and fluoride) on the zeta potential measurements for sample NN are determined. Chloride content of each iron oxide material are also calculated. Experimental methods for pH titration, zeta potential measurements and chloride determination are outlined.

5.1.1 Development of surface charge

Most materials acquire a surface charge when brought into contact with a polar material, e.g. water. This charge arises from ionisation, ion adsorption or ion dissolution. An EDL forms because ions of opposite charge (counter-ions) are attracted to and ions of similar charge (co-ions) are rejected from the material
Chapter 5. Surface chemical characterisation

surface [1]. One part of the EDL consists of the charged surface and the other a diffuse cloud of predominantly counter-ions in addition to co-ions.

Surface charge arises from ionisation of surface groups, i.e. hydroxide on the iron oxide surface. This process and hence the net charge of the surface is pH dependent. Surface charge can also be affected by the adsorption of oppositely charged ions. The surface of a material is usually negatively charged as cations maintain the water of hydration, whereas anions which have a smaller ionic radius are more likely to become specifically adsorbed (i.e. lose their water of hydration). Dissolution of oppositely charged ions is a third mechanism for development of surface charge. These ions are known as potential determining ions, i.e. for iron oxide, H$^+$ and OH$^-$ concentrations determine the electrical potential at the surface [2]. The characteristic equations are as follows:

\[ \equiv \text{FeOH} + H^+ \rightarrow \equiv \text{FeOH}_2^+ \]  \hspace{1cm} (5.1)

\[ \equiv \text{FeOH} + \text{OH}^- \rightarrow \text{FeO}^- + H_2O \]  \hspace{1cm} (5.2)

where \( \equiv \) represents a surface species.

Diffuse double layer

The electrical double layer consists of two regions; the first closest to the surface contains any adsorbed ions and the second is a diffuse layer where ions are less tightly bound, their positions determined by thermal motion and the effect of electrical forces.

The most straightforward representation of the double layer was suggested by Gouy and Chapman (G-C), however the magnitude of the ionic radii were ignored, causing the model to break down near the surface and at high electric potential values. One method to overcome these problems, suggested first by Stern, is to subdivide the region nearest the surface [3].

A plane known as the Stern plane separates the two sections of the inner region, and is located approximately one hydrated ionic radius from the surface. The
Chapter 5. Surface chemical characterisation

values of $\epsilon_1$ and $\epsilon_2$ are assumed to be constant, hence there is a linear decay in the potential across the two regions. The potential at this surface is denoted by $\psi_d$, beyond the Stern plane, the G-C treatment of the diffuse layer can be used, substituting $\psi_0$ with $\psi_d$ [2].

The introduction of the inner and outer Helmholtz planes (IHP and OHP respectively) further divide the inner region (Figure 5.1). The ions closest to the metal surface that are specifically adsorbed are dehydrated and indistinguishable from the surface [5]. Ions held by van der Waals forces are also assumed to be directly associated with the surface, namely hydrogen and hydroxide ions. These are located in the 0 plane and experience a potential $\psi_0$ and contribute $\sigma_0$ to the surface charge [6].

The centres of the dehydrated ions adsorbed specifically and by electrostatic forces are located in the IHP, possessing a potential $\psi_\beta$ and surface charge density $\sigma_\beta$. The third type of ion maintains its water of hydration and has its

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure51.png}
\caption{Schematic representation of electric double layer with two inner regions [4]}
\end{figure}
centre at the OHP [3]. These solvated ions are at a potential \( \psi_d \) and surface charge \( \sigma_d \). Finally, the diffuse layer which is situated outside the shear plane consists of loosely bound counter-ions and has a permittivity \( \varepsilon_{\text{bulk}} \). Similarly there is an inner compact layer permittivity \( \varepsilon_1 \) with capacitance \( C_1 \), an outer layer permittivity \( \varepsilon_2 \) and capacitance \( C_2 \) [5].

5.1.2 Zeta potential

The potential at the shear plane separating the bulk solution from the charged surface is known as the zeta potential. This can be determined by measuring electrophoretic mobility in an induced potential gradient. Electrophoresis is the movement of a charged surface relative to a static fluid. The Smoluchowski equation relates the electrophoretic mobility to the zeta potential thus [7]:

\[
    u_E = \frac{v_E}{E} = \frac{\zeta \varepsilon}{\eta}
\]  

(5.3)

where \( u_E \) = electrophoretic mobility (ms\(^{-1}\)V\(^{-1}\))
\( v_E \) = electrophoretic velocity (ms\(^{-1}\))
\( E \) = electric field (Vm\(^{-1}\))
\( \zeta \) = zeta potential (mV)
\( \varepsilon \) = permittivity (Fm\(^{-1}\))
\( \eta \) = solute viscosity (kgm\(^{-3}\))

The assumptions are [7, 8, 9]:

1. The permittivity \( \varepsilon \) and viscosity \( \eta \) are constant across the entire mobile region.
2. The thickness of the double layer is very thin compared to the particle radius (\( \kappa a >> 1 \)).
3. The particles are non-conductive and rigid.
4. The zeta potential is uniform across the particle surface.
**Isoelectric point**

The zeta (ζ) potential is effected by the pH of solution. The pH at which the ζ potential is zero at the shear plane is known as the isoelectric point (IEP). pH causes protonation/deprotonation of surface hydroxide groups, resulting in a negative surface charge at pH > IEP and positive surface charge at pH < IEP.

The zeta potential decreases with increasing distance from the surface, eventually falling to zero in the bulk solution. The rate of decrease depends on the electrical properties of the interface region and the effect of the background electrolyte (Figure 5.2). The Debye-Hückel parameter (1/κ) decreases with increasing concentration of the background electrolyte as the Stern layer becomes more compact.

![Figure 5.2: Schematic representation of an ion cloud surrounding a negatively charged particle in water](image-url)

Figure 5.2: Schematic representation of an ion cloud surrounding a negatively charged particle in water [10]
5.1.3 pH titration

The surface characteristics are important factors for adsorbents. pH titration can be used to determine the acid/base nature of the material [11]. The capacity of the material for anionic and cationic exchange can be inferred from the net amount of $H^+$ ($OH^-$) released.

Determination of the point of zero net proton charge

If $H^+$ is adsorbed in excess of $OH^-$ ions on the addition of acid, the surface of the iron oxide will have a net positive charge, i.e. the pH after 48 hours with sample present (equilibrium pH) will be higher than the pH without the sample present (blank). $H^+$ adsorption is balanced by the adsorption of negative counter-ions from solution in the OHP or the diffuse layer [12].

Similarly, if $OH^-$ is adsorbed in excess of $H^+$, the surface possesses a net negative charge and the equilibrium pH is lower than the blank. At known pH values the relationship to determine the adsorption of ions onto the surface is given by Equation 5.4. This can be used to plot a differential pH-titration (proton binding) curve with ions released vs. pH.

\[
IR = \frac{C(V_0 - V_1)}{m} \tag{5.4}
\]

\[
IR = 0 \quad \text{at the point of zero net proton charge, then} \tag{5.5}
\]

\[
V_0 = V_1 \tag{5.6}
\]

where
- $IR$ = ions released (mmol/g)
- $V_1$ = volume of titrated alkali (acid) solution corresponding to the equilibrium pH (ml)
- $V_0$ = volume of titrated alkali (acid) solution at a given pH in the blank solution (ml)
- $C$ = concentration of the titrant (mol/L)
- $m$ = mass of the sorbent used (g)
At a specific pH value, the surface possesses no net charge, as sufficient H⁻ and OH⁻ are adsorbed, hence there is no adsorption of counter-ions from solution. According to the nomenclature of Sposito [13] the pH value at which $\sigma_H = 0$ is known as the point of zero net proton charge (PZNPC). Hence on the acid side of the PZNPC, the material has a mixture of acid and neutral sites, conversely at alkaline values, the surface is a combination of negative and neutral sites (see Figure 5.3).

![Surface interactions with non specific adsorption on an iron oxide surface](image)

**Figure 5.3: Surface interactions with non specific adsorption on an iron oxide surface** [14]

**Effect of specific adsorption on surface characteristics**

The IEP and PZNPC are equal if there is no specific adsorption of ions. If the zeta potential curves are repeated for different salt concentrations and cross at the same pH value, it is assumed that the salt is not specifically adsorbed. This value is termed the point of zero salt effect [15]. An ion is specifically adsorbed onto the surface of the oxide material if there is a change in the isoelectric point, provided the conditions are otherwise kept constant [16].

On specific adsorption the pH values of PZNPC and IEP shift in opposite directions, which can be explained as follows. If an anionic species is specifically adsorbed whilst the cationic counter-ion is loosely adsorbed, the former ions-
are at a higher concentration near the surface. The adsorption balance between H\(^+\) and OH\(^-\) is affected, i.e. H\(^+\) adsorption increases and OH\(^-\) decreases by the presence of an anion at the surface. For the condition of PZNPC i.e. adsorption of H\(^+\) = OH\(^-\), the OH\(^-\) concentration of the system must be increased by increasing the pH. Conversely the IEP measurement includes both the surface charge and Stern layer charge up to the shear plane. The \(\zeta\) potential would become more negative on specific adsorption of negative ions. Hence to maintain the IEP, more H\(^+\) must be adsorbed, i.e. the pH must be decreased [16].

**Specific adsorption of fully dissociated ions**

Ions that are fully dissociated are only adsorbed on the acidic side of the PZNPC. An equivalent amount of non-specifically charged anion is displaced from the OHP, hence the ratio of hydroxyl-hydroxide ions and the charge on the surface is not altered; effectively ligand exchange occurs with water at the surface. The effect of the exchange process on the surface is to neutralise positively charged sites until a new point of zero net proton charge is achieved, i.e. no further adsorption of the added ion occurs (see Figure 5.1).

![Figure 5.4: Surface interactions with specific adsorption of fully dissociated species on an iron oxide surface](image-url)

Figure 5.4: Surface interactions with specific adsorption of fully dissociated species on an iron oxide surface [14]
Specific adsorption of not fully dissociated ions

For ions that are not completely dissociated, specific adsorption can occur on both the acidic and alkaline sides of the PZNPC (Figure 5.5) and is primarily dependent on chemical and electrostatic forces. The undissociated acid is able to adsorb on the negative surface if, on adsorption, the species is dissociated and donates a proton to the surface to form water which can then be replaced with the anion [17].

Phosphate is used as an example below, arsenate would be expected to behave in a similar fashion, as the pKa values are comparable (≡ represents a surface species).

\[
\begin{align*}
\equiv \text{FeOH}_2^+ + \text{H}_2\text{PO}_4^- &\leftrightarrow \equiv \text{FeOPO}_3\text{H}_3^+ + \text{OH}^- \\
\equiv \text{FeOH}_2^+ + \text{H}_2\text{PO}_4^- &\leftrightarrow \equiv \text{FeOPO}_3\text{H}_2 + \text{H}_2\text{O} \\
\equiv \text{FeOH}^- + \text{H}_2\text{PO}_4^- &\leftrightarrow \equiv \text{FeOPO}_3\text{H}^- + \text{H}_2\text{O} \\
\equiv \text{FeOH}_2^+ + \text{HPO}_4^{2-} &\leftrightarrow \equiv \text{FeOPO}_3\text{H}_2 + \text{OH}^- \\
\equiv \text{FeOH}^- + \text{HPO}_4^{2-} &\leftrightarrow \equiv \text{FeOPO}_3\text{H}^- + \text{OH}^- \\
\equiv \text{FeO}^- + \text{H}_2\text{PO}_4^- &\leftrightarrow \equiv \text{FeOPO}_3\text{H}^- + \text{OH}^- 
\end{align*}
\]

(5.7) \quad (5.8) \quad (5.9) \quad (5.10) \quad (5.11) \quad (5.12)

Hence the hydroxyl:hydroxide ratio increases as dissociation of water would increase the negative charge on the surface. H\(^+\) can also be liberated from the surface due to the adsorption of anions capable of protonation (Equations 5.13 and 5.14) [17]. When the average charge added to the surface is equivalent to the average charge of the dissociated ion in solution, a new PZNPC is achieved. If the extra surface charge exceeds or falls below that in solution a release or uptake of OH\(^-\) occurs [14].
5.2 Experimental procedure

The procedures for batch pH titration and zeta potential experiments are given below. The effect of the presence of anionic species, (arsenate, phosphate and fluoride) on the zeta potential for sample NN is also noted. For each iron oxide sample the chloride content is determined.
5.2.1 Chemicals used

Aldrich supplied titrated acid and base solutions, namely HNO₃ and NaOH, used for the potentiometric titrations. Sodium nitrate used as a background electrolyte was supplied by Fisher. Arsenate and fluoride solutions were prepared using Na₂AsO₄·7H₂O and KF respectively and were supplied by Fisons. Phosphate solutions were prepared using Na₂H₂PO₄ (Sigma). Chloride content determination by digestion was carried out using oxalic acid (May and Baker, Dagenham).

5.2.2 pH titration

A batch method of potentiometric pH titration was carried out. A number of samples were prepared by measuring and transferring 10 ml 0.1 M sodium nitrate to several 25 ml Erlenmeyer flasks. An electrolyte was added to maintain a high background concentration [18]. Nitrate was used as an electrolyte as Fe (III) complexes are less likely to form [19]. Aliquots of 0.0972 M HNO₃, and 0.1033 M NaOH (usually between 0.025 ml and 0.7 ml) were added to produce solutions across a range of pH. A total batch volume of 15 ml was maintained by the addition of deionised distilled water, to ensure the sorbent weight to solution volume ratio was kept constant [11].

The pH of the solution prior to the addition of the iron oxide sorbent was measured using a Mettler-Toledo 340 digital pH meter calibrated at pH 4 and pH 10. The iron oxide samples were crushed in an agate mortar and pestle and the fine fraction (< 45 μm) used. 25 mg of sample NN was measured on a Sartorius BP210D balance, accuracy ±0.0005 g and transferred into the Erlenmeyer flasks. The equilibrium pH was measured after agitation at 25 °C ± 1 °C for 48 hours.

This procedure was repeated using 0.01 M and 0.001 M sodium nitrate background electrolyte concentrations and for samples GEH and VL. A range of concentrations was used to determine the effect of the background electrolyte on the PZNPC.
5.2.3 Zeta potential

Zeta potential measurements in absence of additional anions

The zeta potential of the iron oxide material was determined using the same samples that were prepared for pH titration. The zeta potential of each solution was measured after the equilibrium pH had been determined. The measurements all took place at 25 °C using a Malvern Zetasizer 3000Ha. 5 ml of the supernatant material was drawn off using a plastic Luer syringe, which resulted in an optimum count rate of 4000 counts/sec. The suspension was injected into a quartz cell in an electrophoresis chamber.

The calculations are determined by the frequency of laser light scattered by the suspended particles using a photon counting detector and a digital correlator. The electrophoretic mobilities are measured as a function of pH hence the zeta potential can be calculated. The average over three readings was taken for each sample (NN, GEH and VL).

Zeta potential measurements in the presence of additional ions

10 ml 0.1 M NaNO₃ was added to a series of 25 ml Erlenmeyer flasks. 3 ml 21.8 mmol/L arsenic (prepared by dissolving Na₂H₃AsO₄·7H₂O) was then added. This concentration of arsenic was used to maintain the same ratio of sorbent mass:solution concentration used in the adsorption experiments (i.e. 2000 ppb) As and 5 mg material in 490 ml. Various quantities of 0.1 M HNO₃ and NaOH were added to produce a range of solution pH. A constant volume of 15 ml was maintained by the addition of deionised water. After being left at 25 °C for 48 hours the pH of each solution was measured using a Mettler Toledo 340 pH meter, calibrated at pH 4 and pH 10, prior to the addition of 25 mg of sample (sieved at <45 μm).

A similar procedure, using the same molar concentration, was used to determine the effect of the presence of phosphate and fluoride ions on the isoelectric point.
5.2.4 Chloride content determination

Each iron oxide sample underwent digestion to quantify the chloride content. Approximately 0.5 g of iron oxide sample was weighed on a Sartorius BP210D balance, accuracy ±0.0005 g and transferred into a 100 ml Erlenmeyer flask. 50 ml 0.5 M oxalic acid was then pipetted into the flask and the flask sealed with Parafilm. This procedure was repeated for each sample and the flasks left for 72 hours in an orbital shaker at 25 °C. The resulting liquid was analysed for chloride content using a Dionex ion chromatograph. An average of two readings was taken and a five point calibration curve for chloride was constructed.

5.3 Results

5.3.1 pH titration

A plot of the pH prior to (blank) and after the addition of sorbent (at equilibrium) against the volume of acid or alkali added is given in Figure 5.6.

The point of zero net proton charge (PZNPC) was found to be in the range 4.6.8 for all pH titration experiments. At pH > PZNPC a negative charge results from deprotonation of surface hydroxide groups (Equation 5.2). The degree of deprotonation gives an indication of the anion exchange capacity of the material as a function of pH. Likewise, protonation of the surface produces a positive charge at pH < PZNPC (Equation 5.1), indicating the cation exchange capacity [20].

Effect of background electrolyte

Three concentrations of NaNO₃ were used to establish if the background electrolyte concentration had any effect on the PZNPC. The net adsorption of ions increases with increasing ionic strength (Figures 5.7–5.9). The non-specific adsorption (the formation of outer sphere complexes in the outer Helmholtz plane (OHP) or diffuse layer) of negative nitrate ions onto the iron oxide surface
at pH < PZNPC increases with increasing background electrolyte concentration. This would result in a decrease in the surface electrical charge, attracting hydrogen ions.

Similarly, at pH > PZNPC, the non-specific adsorption of sodium ions could increase the surface positive charge, causing hydroxide ions to adsorb onto the surface. Non-specific or outer-sphere complexes affect the thickness of the Stern layer, but does not affect the PZNPC [17]. Figures 5.7-5.9 show the positive values become less positive and negative values less negative that with an increasing concentration of background electrolyte.

VL and GEH samples showed the most drift of 1 pH unit. This could be due to the methodology of production of the iron oxide. Changes in pH, temperature of reaction, drying and washing conditions will affect the surface characteristics of the final material [21]. Parks [21] noted that for a material containing chloride as an integral part of the structure, the PZNPC shifts to a
Figure 5.7: Proton binding curve for sample NN, at different concentrations of background electrolyte

Figure 5.8: Proton binding curve for sample GEH, at different concentrations of background electrolyte
Chapter 5. Surface chemical characterisation

Figure 5.9: Proton binding curve for sample VL, at different concentrations of background electrolyte

more acidic pH. The chloride content of each material is determined in Section 5.3.3, and follows the same trend as the PZNPC, i.e. the higher the chloride content the lower the PZNPC. This will be discussed further in Section 5.3.3.

However, sample NN gave a common intersection of 6.4 ± 0.2, which is an indication that no specific adsorption of the background electrolyte occurred and that H⁺ and OH⁻ are potential determining ions [22].

Kanungo calculated a PZNPC for amorphous FeOOH of 7.15 and for akaganeite of 7.2, in the presence of potassium nitrate, using rapid titration [23]. This titration method may not allow sufficient time for equilibrium to be reached. Production and treatment methods could be another reason for the difference between these values and those determined in the experiments outlined. Both materials analysed by Kanungo were extensively washed for several days by decantation to remove chloride, hence could account for a higher PZNPC value. Breeuwsma and De Bruyn indicated that drying and other pre-treatments affect the surface characteristics [24]. Parks and De Bruyn [12] found that for other iron oxides materials the PZNPC ranged from 4–8.5.
As both OH\(^-\) and H\(^+\) are potential determining ions for the material studied, a possible adsorption mechanism for the presence of a charged surface is given below [25]:

\[
\begin{align*}
\equiv \text{FeOH} + H^+ + NO_3^- &\rightarrow \equiv \text{FeOH}_2^+ + NO_3^- \\
\equiv \text{FeOH} + OH^- + Na^+ &\rightarrow \equiv \text{Fe(OH)}_2^- + Na^+
\end{align*}
\]  

(5.15)  
(5.16)

where \equiv is a surface species.

Thus, in acidic conditions, the surface is positive, and in alkali conditions the material possesses a negative surface charge. Another possibility is that hydrogen ions either protonate or deprotonate the surface thus:

\[
\equiv \text{FeOH} + OH^- + Na^+ \rightarrow \equiv \text{FeO}^- + H_2O + Na^+
\]  

(5.17)

Parks and De Bruyn [12] suggest that this second mechanism (Equation 5.17) is more likely, as the adsorption of a hydroxide ion would increase the coordination number to 7 (cf Equations 5.1 and 5.2).

### 5.3.2 Zeta potential

The values for the IEP and PZNPC for each material are given in Table 5.1. The zeta potential results show the amphoteric nature of the material, with an approximately equal amount of positive and negative surface charge across the pH range (Figures 5.10–5.12). The IEP of the material occurs between pH 7–8. At pH > IEP the iron surface will attract cations from the surface, conversely at pH < IEP it will attract anions.
Table 5.1: Comparison of point of zero net proton charge and iso-electric point values (*where P-I is PZNPC-IEP)

<table>
<thead>
<tr>
<th>Conc. NaNO₃ (mol/L)</th>
<th>NN</th>
<th>GEH</th>
<th>VL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>6.6</td>
<td>5.6</td>
<td>5.0</td>
</tr>
<tr>
<td>0.01</td>
<td>6.3</td>
<td>4.8</td>
<td>4.5</td>
</tr>
<tr>
<td>0.001</td>
<td>6.2</td>
<td>5.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Comparison of PZNPC and IEP values

The IEP, determined when the zeta potential of the material is zero, is an indication of external charge only. The PZNPC takes into account both the external and internal charges [26]. The PZNPC is approximately equal to the IEP for sample NN, which indicates that the surface charge distribution is even throughout the material and that there is no specific adsorption of the background electrolyte (Table 5.1).

The difference between the PZNPC and IEP for the other samples is always negative. This indicates that the external surface is more positively charged than the internal surfaces. The possible explanations for this phenomenon have been previously stated, in terms of production and washing methods. The residual chloride content in the material would also reduce the PZNPC. In addition, the surface area and pore structure could affect the balance of internal and external charges. Sample GEH possesses a high percentage of micropores inhibiting the diffusion of ions.

Effect of the presence of anionic species on the zeta potential

The zeta potential for sample NN was remeasured in the presence of arsenate, phosphate and fluoride. If the anions were not potential determining (adsorbed specifically onto the iron oxide surface), the effect on the electrical double layer would be the same as increasing the inert background electrolyte concentration, i.e. the double layer becomes compressed with increasing background electrolyte concentration. This phenomena is not seen for either arsenate or phosphate. As described in Equations 5.13-5.14 the adsorbed species may
Figure 5.10: Zeta potential measurements for sample NN at various background electrolyte concentrations

Figure 5.11: Zeta potential measurements for sample GEH at various background electrolyte concentrations
Figure 5.12: Zeta potential measurements for sample VL at various background electrolyte concentrations

Figure 5.13: Comparison of zeta potential of sample NN with 0.1 M NaNO₃, and 4.36 mmol/L arsenic, phosphorus and fluoride
themselves be protonated, leading to substantial changes in the reactivity of the material [27].

Fluoride does not appear to effect the IEP deduced from the zeta potential measurements carried out (Figure 5.13). Sigg and Stumm [28] found that with increasing concentration of fluoride, the PZNPC increased. Hingston et al. [29] also observed a reduction in the IEP on the addition of fluoride. Zeta potential values below the IEP would be similar to the blank (i.e. without additional anionic species) as fluoride cannot adsorb onto a negative surface.

Fluoride is fully dissociated therefore cannot donate a proton to the surface to enable ligand exchange between fluoride and water. At pH < IEP, especially near the pKa value (pH = 3.5) a proton would be available for dissociation to occur. All pH values used were greater than the pKa. Both Hingston et al. [29] and Sigg and Stumm [25] used a wider pH range, including pH values less than the pKa, hence highlighting the change of sign on the surface.

Arsenate and phosphate decrease the IEP, indicating qualitatively that specific adsorption occurs on the iron oxide surface [27] (see Figure 5.13). Specifically adsorbed arsenate lowers the isoelectric point [30] by as much as 4 pH units. A lowering of the IEP of iron oxide by arsenate was also noted by several researchers [17, 18, 31]. A similar effect was observed for aluminium oxide, another amphoteric material [32].

The opposite effect is seen for the PZNPC with is raised by an approximately equal amount [17]. Phosphate, which is chemically similar to arsenate also caused a reduction in IEP [17, 33]. Both these anions are able to adsorb, even when conditions are electrostatically unfavourable.

Modern spectroscopic methods (FT-IR and X-ray absorption near edge structure (XANES)) have also been used to distinguish between inner- and outer-sphere complexes. These methods rely on the interpretation of bond angles and bond lengths to infer the nature of surface bonding. Arsenate [31, 34, 35, 36], arsenite [37, 38], phosphate [39] and chromate [40] are some examples of surface species studied.
Table 5.2: Chloride content determination, with average values of PZNPC and IEP, and equilibrium pH values

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chloride content (mmol/g)</th>
<th>PZNPC</th>
<th>IEP</th>
<th>Equilibrium pH in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>NN</td>
<td>0.04</td>
<td>6.4</td>
<td>7</td>
<td>7.2</td>
</tr>
<tr>
<td>GEH</td>
<td>0.61</td>
<td>5.2</td>
<td>8</td>
<td>4.0</td>
</tr>
<tr>
<td>VL</td>
<td>1.15</td>
<td>4.5</td>
<td>6.8</td>
<td>3.5</td>
</tr>
</tbody>
</table>

5.3.3 Chloride content determination

All samples were produced by contacting ferric chloride with sodium hydroxide and washed after production. Chloride is known to be essential in the production of akaganeite [41], provided that the ratio of Cl⁻ : Fe > 0.3 akaganeite will be produced [42]. Fluoride salts can also be used [43] as both chloride and fluoride ions are sufficiently small to diffuse into the pores and stabilise the structure [44].

Quirk et al. [45] studied the effect of adding chloride ions at various stages of the nucleation process. It was found that Cl⁻ was essential in the early stages of polymer formation and if added after a period of time, produced no effect on the final product. Refait and Génin [46] found that chloride ions seem to replace hydroxide ions in the iron oxide samples.

The chloride content of freshly prepared akaganeite is in the region of 8 %, Fe : Cl 4.79 [47]. Indeed, Biedermann and Chow [48] determined the chemical formula for freshly precipitated akaganeite as Fe(OH)₂₇₀Cl₀₃₀. It was also reported by Flynn [44] that the Cl⁻/Fe ratio increases with ageing of the solution and may be additional evidence for chloride replacement in the crystal structure.

It can be seen from Table 5.2, that there is a marked difference between the chloride content of each material. There is a trend in PZNPC and chloride content of iron oxide material. the PZNPC decreases with increasing chloride content.
Chapter 5. Surface chemical characterisation

The effect of washing on chloride content

Samples GEH and VL may have a higher chloride content as the material was washed to a lesser degree, hence residual chloride from the reaction may still be bound within the structure. From Section 4.4.7, it is evident that the pore size of sample GEH was much lower than the other two materials, hence inhibiting chloride removal. The remaining chloride slowly leaches out from the material as HCl, hence the equilibrium pH of GEH and VL in water is approximately 3.5–4. Paterson and Rahman [49] noted that the equilibrium pH of akaganeite in water was 3.5. This value would increase with decreasing chloride content.

Chloride from sample NN was removed by decantation with 16 bed volumes of tap water. Sample VL was placed in a column and washed with 10 litres deionised distilled water. No information was provided for the degree of washing for sample GEH. Other methods for removing chloride are by contacting with ammonia, then centrifuge the samples [50], displacement with nitrate or fluoride ions [51], or by dialysis [52].

5.4 Conclusions

The surface chemical characteristics for all iron oxide samples have been examined. pH titrations have been carried out and the point of zero net proton charge (PZNPC) was determined. Three concentration of sodium nitrate were used to determine whether the background electrolyte was specifically adsorbed onto the iron oxide surface. All samples exhibited a slight drift in pH, VL having the largest.

It is unlikely that sodium ions from solution were specifically adsorbed, as cations do not tend to lose the water of hydration that is necessary to form close bonds with the surface. Post treatment of the iron oxide could effect the surface charge characteristics. Sample NN gave the highest value of 6.5 followed by GEH, 5.2 and VL, 4.2. The drop in PZNPC maybe due to the differences in the degree of washing of the latter two samples.

When placed in water, excess chloride on the surface and within the pores of GEH and VL slowly leach to form HCl. This reduces the PZNPC values, decreas-
ing with increasing chloride content. Zeta potential measurements were also carried out, and were in the range 7–8 for all samples. The difference between the PZNPC and isoelectric point (IEP) values indicate that the internal surface is more negatively charged than the external surface, due to the presence of excess chloride on the surface.

Zeta potential measurements were determined for sample NN in the presence of arsenate, phosphate and fluoride. Both arsenate and phosphate ions reduced the IEP, indicating specific adsorption. The reduction occurs because of a higher quantity of negative ions near the surface, hence H\(^+\) ions are adsorbed to balance the surface charge.

It is not clear from the data gathered whether fluoride is also specifically adsorbed. Measurements near the pKa value of fluoride were not carried out, where the change in zeta potential would be expected to occur. There could be several inflection points in the zeta potential measurements on dissociation, as a greater amount of H\(^+\) is available for ligand exchange. Fluoride also cannot be adsorbed below the IEP, as it is fully dissociated and protonation of the surface cannot occur. Therefore the zeta potential would be similar to a blank (no additional anions added) measurement.

Both pH titration and zeta potential measurements show that all samples are amphoteric. The values for PZNPC and IEP are useful in determining the pH at which the surface is positively charged and would attract anions and negatively charged to attract cations. Chloride content determination also explains the equilibrium pH of each material in water and accounts for the difference in PZNPC and IEP values.

From the surface chemical characterisation data, it would appear that sample NN is the best adsorbent, with a greater amount of anionic exchange capacity, determined from pH titration and the least amount of chloride present, minimising any change in pH in aqueous solutions.
References


REFERENCES


REFERENCES


Chapter 6

Adsorption studies

6.1 Introduction

Adsorption occurs if a species is taken up and chemically binds to a material surface (adsorbent). This can be described by several types of models: empirical and semi-empirical, such as Langmuir and Freundlich models, and by surface complexation models. The latter group include various interpretations of the electric double layer (i.e. the number of electrical layers and equations to describe the potential and surface charge across each layer) and type of complexation with the adsorbent. Multi component adsorption can also be fitted by extending the empirical models, or by the ideal adsorption solution theory (IAST), which uses thermodynamic relationships to describe equilibrium.This theory can be modified further to include isotherm descriptions by Freundlich or Dubinin-Radushkevich.

The normal industrial practice for adsorption is to use a fixed bed, enabling the concentration of trace contaminants in drinking and waste water to be reduced by forming bonds with the adsorbent. A mass transfer zone develops within the column, the rate of transfer between the solution and adsorbent depends on the physical size and aspect ratio of the bed, adsorbent particle size, flowrate and affinity of the adsorbent for the trace ion. The effluent concentration can be plotted on a characteristic curve of concentration vs. volume passed and an operating capacity determined.
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In addition to the physical set up of the column, breakthrough of ions in the effluent is affected by the presence of other competing ions, as one may be preferred over the other. The least preferred ion leaves the column first, and ions previously adsorbed are displaced by ions with a greater affinity for the adsorbent. This phenomenon can be described in terms of distribution coefficients to quantify the selectivity of the adsorbent within a multi component system.

Speciation is very important when considering both selectivity and ideal pH conditions for adsorption. Trends in uptake capacity can be explained more easily if the valence and relative concentration of species at a certain pH are known. Maximum uptake capacity will occur when the surface is most attracted to the ion in solution. Possible uptake mechanisms can also be described.

The experimental methods for both batch and column operations are described, in addition to the analytical methods employed to determine the species studied. Batch isotherms were completed in the pH range 4-9 up to a maximum concentration 28 ± 4 μmol/L. The three iron oxide materials previously characterised chemically and physically (NN, GEH and VL) were challenged with both anionic (arsenate, phosphate and fluoride) and cationic (cadmium) species and their respective uptake capacities determined.

The resulting isotherms were fitted with both the Langmuir and Freundlich models. Theoretical maximum capacities calculated by the Langmuir model for the anionic species studied were compared to experimental equilibrium values found at pH 4, 7 and 9. Trends in pH and material type and the effects of pH, total species concentration and material type on the nature of the surface complexes have been studied. This enabled surface reactions for each species to be defined.

Competitive effects were examined in column operation. The operating capacity of a single component arsenate run was compared to the relative capacities of phosphate and fluoride in binary and ternary experiments. Effects of pH and material were also postulated and binding mechanisms described. Distribution coefficients were calculated for each column run and a selectivity sequence for the iron oxide materials studied to be defined as As ~ P ≫ F.
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All pre-loaded iron oxide material was successfully eluted with sodium hydroxide, although the material was not further tested for adsorption capacity. This indicates that adsorbent regeneration is possible, however the elution process was not optimised. The iron oxide material was also tested for Fe (III) dissolution at pH 4, 7 and 9. Only sample VL redissolved slightly at high pH, well within the acceptable limit for iron in drinking water.

6.1.1 Adsorption theory

The term adsorption is used if a species is taken up from solution and is bound to the surface of an adsorbent.

There are several types of bonding which may be exhibited in adsorption. If physical adsorption or “physisorption” is exhibited, the adsorbate is held at the surface by weak van der Waals bonds. Chemical adsorption “chemisorption” is characterised by much stronger covalent or ionic bonds between the adsorbate and the adsorbent surface. Physisorption is also known as non-specific adsorption and chemisorption as specific adsorption.

The former non-specifically bound species form “outer-sphere” complexes as there is no ligand capable of electron transfer and the water of hydration is retained [1]. Conversely specifically bound species form “inner-sphere” complexes with the surface by losing some or all of the water of hydration in the adsorption process [2]. Figure 6.1 illustrates both inner- and outer-sphere bonding with silica.

There are several types of adsorbent—activated alumina, activated carbon, activated bauxite, zeolites, ferric hydroxide, and other composite materials. The advantage of adsorption is the ability to use a column and the solid can often be regenerated. This produces less solid waste than precipitation, although regeneration results in a more concentrated liquid effluent.

Adsorption is dependent on the specific surface area of the adsorbent, increasing with increasing specific surface area. The amount of adsorption is related to the degree of porosity and particle size [3].
Figure 6.1: Schematic representation of inner- and outer-sphere complexes [2]. The sodium atom is bonded to the surface oxygen as an outer-sphere complex, by retaining the water of hydration. The Fe atom loses part of the water of hydration to form an inner-sphere complex.

**Langmuir isotherm**

Adsorption may be expressed in terms of an adsorption isotherm. This is the distribution ratio between the solute on the solid and liquid phases. It is a function of solution concentration, the nature of the species used, competing ions and characteristics of the adsorbent used. The amount of solute on the solid \( q \) (mmol/g) increases with equilibrium concentration \( C_{eq} \) (mmol/L). There have been several models developed to relate \( q \) and \( C_{eq} \). Langmuir [4] was the first to present a kinetic approach to adsorption. This model assumes

- monolayer adsorption;
- adsorption is localised with no adsorbate-adsorbate interactions;
- the adsorbent has a homogeneous surface.
Chapter 6. Adsorption studies

The Langmuir isotherm for the solid/liquid interface can be described thus:

\[
q = \frac{a b C_{eq}}{1 + b C_{eq}}
\]  

(6.1)

where

- \( q \) = adsorption capacity (mmol/g)
- \( a \) = monolayer capacity (mmol/L)
- \( b \) = dimensioned constant (L/mmol)
- \( C_{eq} \) = adsorbate concentration at equilibrium (mmol/L)

\[
q + q b C_{eq} = a b C_{eq}
\]

(6.2)

\[
\frac{q}{b} + q C_{eq} = a C_{eq}
\]

(6.3)

\[
\frac{1}{b} + C_{eq} = \left(\frac{a C_{eq}}{q}\right)
\]

(6.4)

Linearising the equation in the form \( y = mx + c \)

\[
\frac{1}{a} + \left(\frac{1}{a b} \cdot \frac{1}{C_{eq}}\right) = \frac{1}{q}
\]

(6.5)

The linear transformation of the Langmuir plot can be described by the double reciprocal, or Lineweaver-Burk plot, i.e. \( 1/q \) vs. \( 1/C_{eq} \). Hence from the gradient \((1/ab)\) and intercept \((1/a)\) the Langmuir constants can be calculated. The constant \( a \) (mmol/g) is the maximum adsorption per unit mass and \( b \) (L/mmol) is a constant related to the energy of adsorption [3]:

\[
b \propto e^{-\Delta H/RT}
\]

(6.6)

where

- \(-\Delta H\) = heat of adsorption (J kg\(^{-1}\))
- \(R\) = ideal gas constant (J kg\(^{-1}\) K\(^{-1}\))
- \(T\) = temperature (K)
The Langmuir equation can be applied across a wide range of solute concentrations [2]. If adsorption data is able to be fitted using the Langmuir model, it has been assumed that this indicates a single type of surface site. Sposito however argues that the goodness of fit of solute data to Langmuir does not imply a single site adsorption or that the uptake mechanism is adsorption. It cannot be used to predict adsorption, but parameters for the Langmuir equation are specific to experimental conditions [5].

Freundlich isotherm

Conversely, Freundlich assumed that the surface energy is not distributed evenly, i.e. it is heterogeneous. The constant $b$ used in the Langmuir model (Equation 6.1) is now defined as a function of surface coverage ($q$), according to variation in the heat of adsorption (constant $1/n$). Hence if $1/n$ is unity, Equation 6.7 reduces to the Langmuir model. Sites that have the same energy are grouped together. These sites are assumed not to interact with each other, such that the Langmuir equation can be applied locally. The result of this multilayer model is found below:

$$q = kC_{eq}^{1/n}$$

(6.7)

After linearisation:

$$\ln(q) = \ln(k) + \frac{1}{n}\ln(C_{eq})$$

(6.8)

$k \ ((\text{mmol/g})(\text{L/mmol})^{1/n})$ and $n$ are constants that are temperature dependent. The larger the value of $n$, the greater the non-linearity. The model parameters can be found by taking logarithms and plotting $\ln(q)$ vs. $\ln(C_{eq})$. The intercept gives an indication of the adsorption capacity ($k$ is equivalent to $K_d$, the distribution ratio) and gradient of the adsorption intensity [3]. Both the Freundlich and Langmuir isotherms predict similar adsorption capacities over a moderate range of equilibrium concentrations. However, unlike the Langmuir model, it is not linear at low concentrations, nor does it plateau at high concentrations.
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The Freundlich isotherm is often used to describe adsorption to multi-site or heterogeneous solids across a wide range of adsorbate concentrations. It simulates the layering of adsorbate on the surface with decreasing adsorption energy. It is relatively insensitive, as logarithmic plots do not give all data points equal weighting and hence tends to fit data well [6].

Temkin isotherm

The Temkin model is based on the energy of adsorption being a linear function of surface coverage:

\[ q = a + b \ln(C_{eq}) \]  \hspace{1cm} (6.9)

\(a\) and \(b\) are parameters only valid over an intermediate concentration range.

Toth isotherm

The Toth model obeys Henry’s law at low concentration and reaches a maxima at higher concentration. If \(\beta = 1\), Equation 6.10 reduces to the Langmuir model (Equation 6.1).

\[ q = \frac{a b C_{eq}}{\left[1 + (b C_{eq})^\beta\right]^{1/\beta}} \]  \hspace{1cm} (6.10)

where
- \(a\) = monolayer coverage (mmol/g)
- \(b\) = constant, related to affinity
- \(\beta\) = heterogeneity constant

Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich (D-R) isotherm shape is a parabola that is most suitable for an intermediate concentration range, but in its basic form has unrealistic asymptotic behaviour [7]. This can be eliminated by a simple modification, giving a fit similar to the Toth isotherm. It is usually used for trace
contaminant modelling and is more general than the Langmuir model, not
requiring surface homogeneity or constant adsorption potential [8].

\[
\ln(q) = -\beta [\ln(b C_{eq})]^2 + \ln(a) 
\]  
(6.11)

**Shortfalls of empirical or semi-empirical models**

Constants used in both the Langmuir (Equation 6.1) and the Freundlich
(Equation 6.7) models are dependent on the nature of the adsorbent used
and the solution concentration [2]. Some models are also restricted to a spe-
cific concentration range i.e. Temkin and D-R. The models do not provide any
information regarding the structure of the adsorbed species or account for any
changes in the electrical charge on the material surface [9].

**Other theories**

There are a set of models that have been developed that specifically incorporate
a representation of the electrical double layer. These are known as surface
complexation models (SCM) and use thermodynamic relationships to describe
equilibrium. Intrinsic equilibrium constants are used, which are less system
dependent (they are unaffected by solution pH and concentration), and are a
function of the solid and the adsorbate [2].

All SCM's have some common assumptions, as follows:

1. The surface of the adsorbent is assumed to be flat containing hydroxyl
groups.

2. Reactions at the adsorbent surface can be described by the mass law
equations, i.e. that there is a state of local equilibrium.

3. Any change in the surface charge is only due to surface chemical reac-
tions.

4. The effect of the surface charge on measured equilibrium constants \(K^{eq}\)
can be calculated and the intrinsic constants inferred experimentally.
A diagram illustrating the different approaches of the SCM's to modelling the electrical double layer, i.e. the number of planes and allocation of ions to those electrostatic planes and surface reaction modelling [10], is given in Figure 6.2.

*Figure 6.2: Different SCM approaches to modelling the electrical double layer [11]*

The constant capacitance model has three principle assumptions. The first is that all ions are specifically adsorbed within a single electrostatic plane and hence experience equal potential. The second is that the background electrolyte is not explicitly accounted for, either as a specific complex or in the diffuse outer layer. Specific reactions are also stated for assumed surface sites, to determine model constants [12].
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The diffuse layer model is based on the Gouy-Chapman approach to the charge potential relationship, with a fixed number of surface sites. The capacitance is fixed theoretically and is not adjustable. All surface species are assumed to be specifically adsorbed and experience the same potential [11].

The triple layer model is distinct in that the outer layer has a low fixed charge of 0.2 F/m² and the position and presence of ion pairs [13]. The layer nearest the adsorbent surface only contains OH⁻ and H⁺ ions [11]. The inner capacitance, however, can be adjusted to values of 1–1.4 F/m² [14].

Disadvantages of using SCM

Despite the alternative approaches to the exact nature and positioning of surface complexes and the nature of the electric double layer, all SCM's are able to describe the data well and there is no definitive answer to the adsorption energy values at the oxide surface.

Multi component modelling

There are models that are used to describe multi component isotherms. The extended Langmuir requires batch isotherms with multi component parameters and is only consistent if the solution concentrations are equal. The ideal adsorbed solution theory (IAST) was extended to liquid-solid equilibria and applied by Radke and Prausnitz [15]. This theory is based on the thermodynamic equivalence of the spreading pressure of each solute at equilibrium. The spreading pressure of a solute π is defined as the difference between the interfacial tension of the pure solvent-solid interface and that of the solution-solid interface for that solute.

If the Freundlich equation describes single solute equilibria and the constants K and 1/n are known the IAST may be calculated [16]. Crittenden et al. extended the IAST for multi component adsorption in fixed beds [17]. One disadvantage to this method is that the equations are not explicit, but only give a relation between the adsorbed and solution phases [18].
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6.1.2 Column studies

Adsorption of species onto a material surface can be carried out in a batch system, resulting in a characteristic isotherm, that can be described by the models outlined in the previous section. The usual method employed industrially is a packed column. This enables the material to be continuously challenged with the pollutant until the column becomes saturated or reaches a designated loading, after which the material can either be regenerated or replaced.

If a column is loaded with ion exchange material in a certain form, \( \overline{RA} \), as the solution BY is added a dynamic equilibrium develops thus:

\[
\overline{RA} + BY \leftrightarrow \overline{RB} + AY
\]  

(6.12)

![Figure 6.3: Solution concentration profile in a packed column](19)
As the exchange front progresses down the column, $A$ is exchanged for $B$, with $BY$ concentration reducing to zero and $AY$ passing through the column into the effluent. This exchange zone moves further down the column as the initial part of the column becomes saturated with $B$. Below this zone, the material is in its original form (Figure 6.3).

After a period of time has elapsed, the exchange zone moves sufficiently far down the column as to cause the concentration of $B$ in the effluent to increase, eventually reaching $C_0$. A curve of the effluent history can be plotted ($C/C_0$ vs. volume passed) producing a breakthrough curve (Figure 6.4).

If equilibria favours $B$, any $A$ ions behind the boundary are replaced by $B$ and will soon catch up with the boundary. Likewise, any $B$ ions ahead of the boundary will be retained on the adsorbent until the boundary reaches that point. Hence, for preferred ions, the breakthrough curve is self-sharpening, i.e. maintains a steady shape irrespective of time and column depth.

Unfavourable equilibrium is characterised by a broadening of the breakthrough curve, as equilibrium rather than kinetics dominate, hence $B$ ions overtake $A$ ions. Hence the exchange zone is lengthened [19].
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The shape and operating capacity of the adsorbent is dependent on several factors (see Table 6.1). For multi component adsorption the shape of the curve is related to the feed solution concentration, the capacity of the adsorbent and the relative affinity for each ion in the influent [20].

Table 6.1: Factors affecting column performance with ideal values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Effect on the column performance</th>
<th>Ideal value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed depth</td>
<td>increases with increasing length</td>
<td>-</td>
<td>[21]</td>
</tr>
<tr>
<td>Aspect ratio ($L_c/d_c$)</td>
<td>increases with a higher value</td>
<td>3:1</td>
<td>[22]</td>
</tr>
<tr>
<td>Exchange characteristics</td>
<td>increases with capacity</td>
<td>-</td>
<td>[19]</td>
</tr>
<tr>
<td>Flowrate</td>
<td>increases with decreasing flowrate</td>
<td>$Q = 0.04a_x$ (eq. 6.13)</td>
<td>[23]</td>
</tr>
<tr>
<td>Particle size</td>
<td>increases with decreasing size</td>
<td>$d_c : d_p &gt; 20$</td>
<td>[24]</td>
</tr>
<tr>
<td>Selectivity</td>
<td>increases with increasing selectivity</td>
<td>-</td>
<td>[25]</td>
</tr>
<tr>
<td>Initial feed concentration</td>
<td>decreases with increasing feed conc.</td>
<td>-</td>
<td>[23]</td>
</tr>
</tbody>
</table>

Carberry [26] suggests that the effect of axial dispersion on column performance is minimised if bed length:$d_p > 150$. If the particle size is between 100–200 μm, the velocity distribution dominates and has a greater effect on the axial dispersion within the column, hence, channelling and packing irregularities occur [27]. LeVann and Vermeulen [28] noted that there were no noticeable wall effects if $d_c : d_p > 20$ and bed length:$d_p > 50$.

Using the method of Glueckauf [23], the optimum linear flowrate ($F$) can be determined, if $D_L$ is assumed to be $10^{-5}$ cm$^2$/s, $r$ is 300 μm.

$$F \sim \frac{6D_L}{r} \sim \frac{6 \times 10^{-5}}{300 \times 10^5}$$  \hspace{1cm} (6.13)

$$Q = Fa_x = 0.04a_x$$
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where

\[ F = \text{linear flowrate (cm/s)} \]
\[ D_L = \text{liquid diffusion constant (cm}^2/\text{s}) \]
\[ r = \text{particle radius (cm)} \]
\[ Q = \text{volumetric flowrate (ml/s)} \]
\[ a_x = \text{cross sectional area of column (cm}^2\) \]

Flowrate is often expressed as a function of the bed volume, to be independent of the size of the experiment. A bed volume is defined as the volume of adsorbent in a column measured as the backwashed, settled and drained volume.

For example, the bed volume of a 10 cm bed length \( (L) \) and 2 cm column diameter \( (d_c) \) is calculated thus:

\[ V = \frac{\pi (d_c)^2}{4} \times L = 31.4 \text{ cm}^3 \]

The bed volume consists of both the volume of the adsorbent and voids, typically 0.25–0.33. The flowrate is inversely proportional to the empty bed contact time \( (\text{EBCT}) \) [20]. EBCT is usually in the range 1.5–7 minutes and is expressed as:

\[ \text{EBCT} = \frac{V}{Q} \]

where \( V = \) adsorbent bed volume \( (\text{cm}^3) \)

Small scale columns

Crittenden et al. developed a method for using rapid small scale adsorption test to obtain equilibrium data to estimate large scale performance of granular activated carbon [29]. Initially a relationship between the small and large scale breakthrough curves was determined (subscripts \( SC \) and \( LC \) respectively). It was assumed that the internal diffusion coefficient was not a function of particle diameter \( (d) \), hence they found that:

\[ \frac{EBCT_{SC}}{EBCT_{LC}} = \frac{\left(\frac{d_{SC}}{d_{LC}}\right)^2}{t_{SC}} = \frac{t_{SC}}{t_{LC}} \]
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The fraction $t_{SC}/t_{LC}$ is the ratio between the operating time of the small and large columns. The equation holds for both pore and diffusion controlled adsorption.

Further studies by Crittenden et al. highlighted that the previous assumption regarding the internal diffusion coefficient was not always valid. Hence a new relationship that included a linear function of the internal diffusion coefficient and particle diameter was developed:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \frac{d_{SC}}{d_{LC}} = \frac{t_{SC}}{t_{LC}}$$  \hspace{1cm} (6.17)

Therefore, there is the potential for time saving in obtaining column performance data. However, the effect of a fluctuating influent concentration and establishing conditions under which this method can be reliably used needs to be considered [30].

6.1.3 Selectivity

Breakthrough of ions, i.e. when an influent species is present in the effluent, depends on kinetics (mass transfer) and equilibrium (selectivity) considerations. A breakthrough curve can be gradual, as the primary mechanism for determining the shape is the affinity of the ion. A sharp curve implies that the exchange isotherm is favourable. However, in a multi component system, the breakthrough is much more complicated.

The species leave the column in the reverse order of the selectivity sequence i.e. the most preferred species will leave last. Moieties with greater affinity towards the adsorbent increase column run time and result in a sharper breakthrough curve. Ions that are not preferred by the adsorbent will become concentrated in the column as they are displaced by the preferred ion and at some time will exceed the influent concentration, a process known as chromatographic elution. Hence the adsorbent should be chosen to have a high affinity for the toxic ion [20].
Describing Selectivity

Ion exchange equilibria can be considered in terms of an ion exchange isotherm, a graphical representation of uptake capacity as a function of equilibrium concentration at a constant temperature. In column operations however, adsorption equilibria can be described quantitatively by a distribution coefficient (K_d). This is a ratio of the amount of target ion adsorbed to the amount of target ion remaining in solution. K_d is independent of concentration only if the isotherm is linear. A higher value indicates a higher affinity for removal of the target ion [31]:

\[ K_d = \frac{q_A}{C_0} \]  

(6.18)

where \( C_0 \) = influent solution concentration (meq/ml)  
\( q_A \) = uptake capacities of ions A (meq/g)

The distribution of multiple ions is not equal, and for a particular material one ion is preferred over the other, a process known as selectivity. Preference of one ion over another is governed by [21]:

- the ion with the greatest ionic charge;
- the ion with the smallest solvated equivalent volume;
- the ion that interacts most strongly with surface groups;
- the ion that forms the least complexes with co-ions present in solution.

6.1.4 Speciation

Constructing speciation diagrams for each pollutant studied is important in determining the nature of ions present in solution. Speciation is dependent on pH and solution concentration, hence the total concentration for each calculation and pH range of adsorption tests is given. The charge of a trace contaminant (anionic, cationic or neutral) affects the removal capacity of the
adsorbent. At low pH the iron oxide surface is positively charged, hence will attract anions and at high pH the surface is negatively charged and will attract cations.

Arsenate speciation

Arsenate can exist in four forms *i.e.* \( \text{H}_3\text{AsO}_4, \text{H}_2\text{AsO}_4^- \), \( \text{HAsO}_3^- \) and \( \text{AsO}_4^{3-} \). \( \text{H}_2\text{AsO}_4^- \) is the major species at \( \text{pH} < 7 \) (Equation 6.19) and \( \text{HAsO}_3^- \) dominates in the pH range 7–11 (Equation 6.20) and is usually found in aerobic surface water. The equations for pentavalent arsenic dissociation in water are given as [32]:

\[
\begin{align*}
\text{H}_3\text{AsO}_4 & \rightarrow \text{H}^+ + \text{H}_2\text{AsO}_4^- & \text{pKa} = 2.2 \\
\text{H}_2\text{AsO}_4^- & \rightarrow \text{H}^+ + \text{HAsO}_3^- & \text{pKa} = 7.08 \\
\text{HAsO}_3^- & \rightarrow \text{H}^+ + \text{AsO}_4^{3-} & \text{pKa} = 11.5
\end{align*}
\]

The pKa values given in Equations 6.19–6.21 are related to the dissociation constant \( (K) \), *i.e.* \( K = 10^{-pKa} \). The dissociation constant can then be expressed in terms of the ratio of the concentrations of the products divided by the reagents. The total concentration of arsenic in the solution, \( C_T \), was taken to be 2000 ppb (the maximum concentration of arsenic used in adsorption experiments) and is the sum of all the species.

The expressions for \( K \) and total arsenic concentration, \( C_T \), can be manipulated to determine the concentration of each species in terms of the dissociation constant, the total concentration and the concentration of the hydrogen ions (Equations 6.22–6.32, Figure 6.5). An example calculation for \( \text{H}_3\text{AsO}_4 \) is given below.
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\[ H_3AsO_4 \rightarrow H^+ + H_2AsO_4^- \]  \[ K_1 = \frac{[H_2AsO_4^-][H^+]}{[H_3AsO_4]} = 10^{-2.2} \quad (6.22) \]

\[ H_2AsO_4^- \rightarrow H^+ + HAsO_2^- \]  \[ K_2 = \frac{[HAsO_2^-][H^+]}{[H_2AsO_4^-]} = 10^{-7.08} \quad (6.24) \]

\[ HAsO_2^- \rightarrow H^+ + AsO_4^{3-} \]  \[ K_3 = \frac{[AsO_4^{3-}][H^+]}{[HAsO_2^-]} = 10^{-11.5} \quad (6.24) \]

\[ C_T = [H_3AsO_4] + [H_2AsO_4^-] + [HAsO_2^-] + [AsO_4^{3-}] \quad (6.25) \]

\[ [H_3AsO_4] = C_T - [H_2AsO_4^-] - [HAsO_2^-] - [AsO_4^{3-}] \quad (6.26) \]

\[ [H_3AsO_4] = \frac{C_T - K_1[H_3AsO_4]}{[H^+]^2} - \frac{K_1K_2[H_3AsO_4]}{[H^+]^4} \quad (6.27) \]

\[ [H_3AsO_4] = C_T/\left[1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2} + \frac{K_1K_2K_3}{[H^+]^3}\right] \quad (6.28) \]

Similarly, the remaining species are expressed as:

\[ [H_2AsO_4^-] = C_T/\left[1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]} + \frac{K_2K_3}{[H^+]^2}\right] \quad (6.29) \]

\[ [HAsO_2^-] = C_T/\left[1 + \frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + \frac{K_3}{[H^+]^2}\right] \quad (6.30) \]

\[ [AsO_4^{3-}] = C_T/\left[1 + \frac{[H^+]^3}{K_1K_2K_3} + \frac{[H^+]^2}{K_2K_3} + \frac{[H^+]}{K_3}\right] \quad (6.31) \]

\[ = C_T - [H_3AsO_4] - [H_2AsO_4^-] - [HAsO_2^-] \quad (6.32) \]

The pH of potable water is in the range 6.5–8.5, hence both HAsO_2^- and H_2AsO_4^- are present. The fraction of each species are approximately equal at pH 7 [33].

For each speciation diagram, (Figures 6.5–6.10) the pH range used for adsorption isotherms, 4–9, is marked with two vertical lines. In this range, pentavalent arsenic is present as H_2AsO_4^- and HAsO_2^-.
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Arсенитная спецификация

Арсенит считается более токсичным, чем As (V) [34] и более вероятен быть найден в анаэробной подземной воде. Он существует как H₃AsO₃, недиссоциированный слабый кислотный в pH диапазоне 2–9 (Уравнение 6.33), поэтому труднее удалять. Водопроводная вода часто пред-окисляется с помощью хлора или перманганата калия, чтобы convert As (III) to As (V) [35].

Как упоминалось в разделе 2.2.2, утилизация As (V) и окисление As (III) могут происходить в присутствии абиотических бактерий [36, 37]. Присутствие железа в осадочном камне также вызывает окисление As (III) [38].

\[
\begin{align*}
H_3\text{AsO}_3 & \rightarrow H^+ + H_2\text{AsO}_4^- & \text{pKa} = 9.22 \\
H_2\text{AsO}_4^- & \rightarrow H^+ + H\text{AsO}_2^- & \text{pKa} = 12.3
\end{align*}
\] (6.33) (6.34)
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A similar procedure was used to calculate the speciation diagram. (Figure 6.6. Equations 6.33–6.41) the expressions for each species are given:

\[
\begin{align*}
    H_3\text{AsO}_3 & \rightarrow H^+ + H_2\text{AsO}_3^- \\
    H_2\text{AsO}_3^- & \rightarrow H^+ + H\text{AsO}_2^- \\
\end{align*}
\]

\[
K_1 = \frac{[H_2\text{AsO}_3^-][H^+]}{[H_3\text{AsO}_3]} = 10^{-9.22} \quad (6.35)
\]

\[
K_2 = \frac{[H\text{AsO}_2^-][H^+]}{[H_2\text{AsO}_3^-]} = 10^{-12.3} \quad (6.36)
\]

\[
C_T = [H_3\text{AsO}_3] + [H_2\text{AsO}_3^-] + [H\text{AsO}_2^-] \quad (6.37)
\]

\[
[H_3\text{AsO}_3] = C_T \left[ 1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} \right] \quad (6.38)
\]

\[
[H_2\text{AsO}_3^-] = C_T \left[ 1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]} \right] \quad (6.39)
\]

\[
[H\text{AsO}_2^-] = C_T \left[ 1 + \frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} \right] \quad (6.40)
\]

\[
= C_T - [H_3\text{AsO}_3] - [H_2\text{AsO}_3^-] \quad (6.41)
\]

Figure 6.6: As (III) speciation diagram, total concentration 26.7 μmol/L
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Phosphate speciation

The dissociation of phosphate and phosphite in water are similar to arseniate and arsenite, the equations for pentavalent phosphorus are given as [39]:

\[
\begin{align*}
    \text{H}_3\text{PO}_4 & \rightarrow \text{H}^+ + \text{H}_2\text{PO}_4^- & \text{pKa} = 2.03 \\
    \text{H}_2\text{PO}_4^- & \rightarrow \text{H}^+ + \text{HPO}_2^{2-} & \text{pKa} = 7.19 \\
    \text{HPO}_2^{2-} & \rightarrow \text{H}^+ + \text{PO}_3^{-} & \text{pKa} = 12.03
\end{align*}
\]  

(6.42)  

(6.43)  

(6.44)

Using a similar method as for arsenic, a speciation diagram can be constructed (Figure 6.7). The total phosphorus concentration was 750 ppb (the maximum value used in adsorption experiments). The total molar concentration in the speciation calculations are approximately equal, 24-32 μmol/L. Full calculations for all subsequent speciation diagrams are given in Appendix A.

![Figure 6.7: P (V) speciation diagram, total concentration 24.2 μmol/L](image)

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The primary species in the pH range studied for the adsorption isotherms are \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \). At pH 7, the quantity of these two species are approximately equal, also found for arsenate (Section 6.1.4).

**Phosphite speciation**

The equations for phosphite are similar to arsenite, (Equations 6.33, 6.34) [39] and the speciation diagram is found in Figure 6.8.

\[
\begin{align*}
\text{H}_3\text{PO}_3 & \rightarrow \text{H}^+ + \text{H}_2\text{PO}_3^- & \text{pKa} = 1.8 & (6.45) \\
\text{H}_2\text{PO}_3^- & \rightarrow \text{H}^+ + \text{HPO}_3^{2-} & \text{pKa} = 6.13 & (6.46)
\end{align*}
\]

*Figure 6.8: P (III) speciation diagram, total concentration 24.2 \( \mu \text{mol/L} \)*
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Fluoride speciation

The equation for fluoride dissociation in water is as follows [39]:

\[ \text{HF} \rightarrow \text{H}^+ + \text{F}^- \quad \text{pKa} = 3.18 \]  \hspace{1cm} (6.47)

Hence a speciation diagram was constructed for a total fluorine concentration of 600 ppb (31.6 μmol/L), the maximum concentration used in adsorption experiments (Figure 6.9). In the pH range studied, F\(^-\) is the dominant species. Typical pH values of natural water are in the range 6.5 - 8.5, where the non-charged fluoride species is no longer present.

![Fluorine speciation diagram](image)

**Figure 6.9:** Fluorine speciation diagram, total concentration 31.6 μmol/L
Cadmium speciation

The equations for cadmium dissociation in water [40]:

\[ \text{Cd}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{Cd(OH)}^+ + \text{H}^+ \quad \text{pKa} = 10.1 \quad (6.48) \]
\[ \text{Cd}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Cd(OH)}_2(\text{aq}) + 2\text{H}^+ \quad \text{pKa} = 20.4 \quad (6.49) \]
\[ \text{Cd}^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{Cd(OH)}_3^- + 3\text{H}^+ \quad \text{pKa} = 33.3 \quad (6.50) \]
\[ \text{Cd}^{2+} + 4\text{H}_2\text{O} \leftrightarrow \text{Cd(OH)}_4^{2-} + 4\text{H}^+ \quad \text{pKa} = 47.4 \quad (6.51) \]

A speciation diagram was generated using Equations 6.48-6.51 for a total cadmium concentration of 3000 ppb, the maximum concentration used in adsorption experiments (Figure 6.10). Across the pH range studied, pH 4.9, cadmium is present as a divalent cation.

Figure 6.10: Cadmium speciation diagram, total concentration 26.7 \(\mu\text{mol/L}\)
6.2 Experimental procedure

The experimental procedures for both batch and column operations are given in the following section. The species studied in batch mode were arsenate, phosphate, fluoride and cadmium. All three iron oxide materials (NN, GEH and VL) were challenged with single species solutions up to a maximum concentration of approximately 25–30 μmol/L in the pH range 4-9. Analytical techniques used for each species in addition to an estimation of the error in determining the concentration are given.

Equilibrium concentrations of the anionic species studied were determined experimentally, at pH 4, 7 and 9. This would enable a comparison to be made of the experimental and theoretical maximum capacity computed using the Langmuir model.

Column runs were initially completed at pH 4 with an inlet concentration of 6.67 μmol/L arsenic. Subsequent column runs to observe the effect of anionic uptake capacity were operated at an elevated concentration of 133 μmol/L at neutral pH. All experimental parameters were maintained, e.g. flowrate and amount of adsorbent used. Binary and ternary mixtures were used to observe the competitive effect of other anions on the uptake capacity of arsenic. The experimental procedure for column regeneration by sodium hydroxide is also given.

6.2.1 Chemicals used

Arsenate and fluoride solutions were prepared using Na2AsO4 · 7H2O and KF respectively and were supplied by Fisons. Phosphate solutions were prepared using Na2HPO4 (Sigma). Aldrich supplied the cadmium (Cd(NO3)2 · 4H2O) and the standard solutions of sodium hydroxide, hydrochloric acid and palladium modifier (palladium nitrate, 10wt % solution in 10wt % nitric acid). The NN and VL samples were prepared from FeCl3·6H2O and FeCl3 anhydrous respectively, in addition to NaOH pellets, all purchased from Fisher, UK. The analytical reagents used for the colorimetric method for phosphate determination were ammonium molybdate and L-ascorbic acid (Fisons) and antimony potassium tartrate and concentrated sulphuric acid (Fisher).
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6.2.2 Analytical methods

Arsenic

Arsenic concentrations were determined by Varian GTA-100 graphite furnace atomic adsorption spectroscopy using a co-injected palladium modifier (0.1 % Pd + 0.25 % citric acid). The lamp current was set at 10 mA, slit width 0.5 nm and a wavelength of 193.7 nm was used. A deuterium lamp was used as background correction and argon (flowrate 3 L/min) as the carrier gas. For each run, a four point calibration curve was constructed automatically using 75 ppb As (V) bulk standard. The total volume of the sample was set at 30 µL, comprising 12 µL sample, 11 µL palladium modifier and 7 µL deionised water.

Samples were injected twice and the average of the two absorbance values taken. Two samples, one at a low concentration, 100 ppb, and another at a higher concentration of 2 ppm were injected ten times to determine the experimental error. The standard deviation of the two sets of ten samples were taken thus:

$$\text{error value} = \sqrt{\frac{\sum (\bar{x} - x_i)^2}{N}}$$  \hspace{1cm} (6.52)

where $\bar{x}$ = average value

$x_i$ = individual concentration value

$N$ = total number of values

The error value as determined by Equation 6.52 was 2 % for 100 ppb and 4 % for 2 ppm. Both the initial and equilibrium concentrations were measured using the same calibration curve. The steps for the ashing procedure are given in Appendix B.

Phosphate

Analysis was carried out using a colorimetric method (Murphy and Riley [41]). 125 ml 5 N sulphuric acid and 37.5 ml ammonium molybdate (20 g in 500 ml) were mixed in a 500 ml Duran glass flask. 75 ml of 0.1 M ascorbic acid was then added and the solution mixed. Finally, 12.5 ml of potassium antimonyl...
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tartrate (1 mg Sb/ml) was added. This solution enabled phosphorus analysis to be carried out with a Perkin Elmer Lambda 12 dual beam UV/VIS spectrophotometer, at a wavelength of 882 nm.

A new reagent was prepared for each batch of samples, as degradation occurs after more than 24 hours. Therefore, a new calibration curve was required for each run and the R² value were always greater than 0.99. To determine whether there was a time effect on absorbance values, the samples were reanalysed after 20 minutes. The difference between the two reading for several samples across the concentration range used was less than 4 %.

A reagent blank was prepared using 20 ml deionised water and 4 ml of the reagent added to a 25 ml volumetric flask, and the solution volume made up to 25 ml. Calibration standards of 250, 500, 750 and 1000 ppb phosphorus were also prepared using this method. A known quantity of each phosphorus sample was decanted into a 25 ml volumetric flask and the solution volume made up to 20 ml. 4 ml of the mixed reagent was added, the contents diluted to 25 ml and the flask left for 10 minutes for the complexation reaction to occur [41].

A correction was made to the absorbance using a blank, then the calibration samples and phosphorus samples were measured. 1 ml of each solution was transferred into a cuvette and the absorbance at 882 nm noted. A plot of log absorbance vs. log concentration (log(A₈₈₂) vs. log(Cₚ)) was constructed and the equation of the line of best fit was determined (Equation 6.53).

\[
\log(A₈₈₂) = m \log(Cₚ) + c \tag{6.53}
\]

where
- \( \log(A₈₈₂) \) = log absorbance at 882 nm
- \( m \) = gradient of the line
- \( \log(Cₚ) \) = phosphorus concentration (\(\mu\)g/L)
- \( c \) = intercept

Unknown values of phosphorus concentration can therefore be found using the equation below:

\[
Cₚ = 10^{(\log(A₈₈₂)−c)/m} \tag{6.54}
\]

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Fluoride

Analysis was carried out using a Dionex 4500i ion chromatograph with gradient pump and conductivity detector. An IonPac AS11 column (4x250 mm) with an IonPac AG guard column (4x50 mm) was used for isocratic separation (constant eluent concentration) using 21 mM sodium hydroxide. The flowrate of the eluent was maintained at 2 ml/min. An anion trap column was fitted before the pump to remove trace anion contaminants in the eluent. After the separating column, the eluent passed through an anion micromembrane suppressor (regenerant 50 mM H₂SO₄), then to the conductivity detector. The total run time was five minutes and the output graph was analysed by AI-450 chromatography software.

A four point calibration curve was constructed, with a maximum concentration of 1 ppm and an R² value of 0.999. Each sample was manually injected twice and an average value for the output was taken. Two samples, one at a low concentration, 100 ppb, and another at a higher concentration of 500 ppb were injected ten times to determine the experimental error. Using Equation 6.52, the error was 2.5 % at lower concentration and 5 % at higher concentration values.

Cadmium

The solutions were analysed using Spectra AA-200 flame emission atomic adsorption spectroscopy under oxidising conditions. An air/acetylene mix with an air flow 13.5 L/min was used. The lamp was set to 4 mA current and a wavelength 228.8 nm, slit width 0.5 nm, using no background correction. For each run both the initial and equilibrium concentrations were measured using the same calibration curve. A five point calibration curve was constructed using a bulk standard of 1 ppm. An error value for cadmium was determined by injecting two samples, namely 500 ppb and 3 ppm, ten times. The standard deviation was taken (Equation 6.52), the values were determined to be 3 % and 5 % respectively.
6.2.3 Batch experimental procedure for arsenic

Adsorption experiments were carried out at each pH value in the range 4-9 and for each material, namely NN, GEH and VL. Two 5 litre volumetric flasks of 100 ppb As (V) were prepared by dissolving Na₂H₂AsO₄·7H₂O (sodium arsenate), in deionised distilled water. The first flask, C₀₁ was used to prepare all of the NN samples in the range pH 4-9, i.e. six samples in all and GEH in the range pH 4-7. The second flask, C₀₂ was used to prepare the remaining GEH samples, i.e. at pH 8 and 9 and VL across the pH range 4-9.

In each case, 490 ml of solution was decanted into 500 ml Nalgene bottles and adjusted to the desired pH value by the addition of a known volume of approximately 0.1 M HCl or NaOH (titrated values by the manufacturer of 0.1021 M and 0.1033 M respectively), prior to the addition of 5 mg of material. The sorbent was weighed on a Sartorius BP210D balance, accuracy ±0.0005 g. The particle size of the material used was 150-300 μm.

The sample bottles were agitated at 25 ± 1°C in an orbital shaker and the pH maintained at its initial value by addition of acid or alkali twice a day. Any addition to the solution volume was noted and was < 0.5 % of the total batch volume. It was assumed that the solutions had reached equilibrium when there was no change in the pH. The arsenic capacity of the material was calculated as shown below.

\[ q = \frac{(C_o V_o - C_{eq} V_{eq})}{m} \]  

(6.55)

where

- \( q \) = adsorption capacity (mmol/g)
- \( C_o \) = initial concentration (mmol/L)
- \( V_o \) = initial volume of solution (L)
- \( C_{eq} \) = equilibrium concentration (mmol/L)
- \( V_{eq} \) = equilibrium volume (L)
- \( m \) = mass of dry adsorbent (g)
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Isotherms for all three samples were carried out in the pH range 4–9. This method was repeated for As (V) concentrations 200, 400, 500, 750, 1000 and 2000 ppb. A summary of the conditions is given in Table 6.2.

Table 6.2: Summary of final experimental conditions

<table>
<thead>
<tr>
<th>Variable</th>
<th>Sample value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (µm)</td>
<td>150–300</td>
</tr>
<tr>
<td>pH range</td>
<td>4–9</td>
</tr>
<tr>
<td>Concentration range (µM)</td>
<td>0–30</td>
</tr>
<tr>
<td>Volume (ml)</td>
<td>490</td>
</tr>
<tr>
<td>Mass of adsorbent (mg)</td>
<td>5</td>
</tr>
<tr>
<td>Reagents used to control pH</td>
<td>0.1 M NaOH, HCl</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25 ± 1</td>
</tr>
</tbody>
</table>

6.2.4 Batch experiments for other species studied

A similar batch experimental method (molar concentration and pH range, and weight:volume ratio of adsorbent:adsorbate) was used for each of the remaining species to be studied, namely, phosphate, fluoride and cadmium.

6.2.5 Maximum equilibrium value concentration

The equilibrium concentration value at three pH values, namely 4.7 and 9 was determined. 10 ml 21.8 mmol arsenate solution (as prepared for zeta potential analysis, Section 5.2.3) was transferred into a 25 ml Erlenmeyer flask. Three such flasks were prepared and the pH of the solutions were adjusted to 4.7 and 9 respectively by the addition of a known quantity of 0.1 M NaOH and 0.1 M HCl.

5 mg of sample NN, GEH and VL was weighed on a Sartorius BP210D balance, accuracy ±0.0005 g and transferred to each of the pre-adjusted flasks. The CV/m ratio used to determine the maximum value was approximately 16 times greater than the maximum used for batch adsorption isotherms.
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This method was repeated for similar molar concentrations of fluoride and phosphate, i.e. 27 flasks in total. The flasks were sealed with Parafilm and placed in an orbital shaker for four weeks at 25 °C. After which, the samples were washed in 25 ml of deionised distilled water then 25 ml 0.1 M NaOH. The samples were resealed with Parafilm and left overnight for elution to take place. The supernatant was removed and analysed for the respective anion, described in Section 6.2.2.

6.2.6 Mini-column experiments

Initial mini-column experiments

Approximately 0.2 g NN sample (150–300 μm) was weighed on a Sartorius BP210D balance, accuracy ±0.0005 g and transferred into a 1 ml nominal capacity empty solid phase extraction (SPE) column containing 20 μm polyethylene frit (Thames Restek, Windsor). A PTFE valve was attached to the bottom of the column and deionised water added. A vacuum was applied to remove any air trapped in the sorbent pores and any air bubbles in the bed were also removed. Another frit was added to the column after pre-treatment to promote an even flow distribution. The diameter of the column was 5.6 mm and the wetted bed height of adsorbent was 8 mm, hence the bed volume was 0.2 cm³ (calculated using Equation 6.14).

A column adapter was attached to the top of the column to allow PTFE tubing to be fitted into the column. The column was fed at room temperature with 500 ppb As (V) solution at pH 4 via a Watson-Marlow MHRE 22 multi-head peristaltic pump. This arsenic concentration value was chosen as arsenic levels of this order are found in aquatic environments.

Silicone rubber tubing, 1.5 mm bore was used for the pump head, 0.5 mm wall thickness, which resulted in a flowrate of 3.8 ml/hr. This was attached to Tygon PVC tubing and then PTFE tubing fed into the columns. An empty 6 ml SPE cartridge was used as an additional reservoir of feed.

Prior to the column being attached, the feed solution was fed through the tubing to remove any impurities from the rig. The effluent was fed to a sample collector, controlled by a Mitsubishi Fxo 14 PLC containing borosilicate glass
test tubes. The samples were collected every fifty minutes and the effluent was analysed for arsenate, using the SpectraAA 200 graphite furnace GTA 100. The pH of each sample was measured on a Mettler Toledo 340 pH probe calibrated at pH 4 and 10. A similar experimental method was used for a column containing GEH sample.

Single component

There was no evidence of any arsenic breakthrough after 35-40,000 bed volumes of 500 ppb As (V) solution had been passed through the two columns. Hence, a new set of experiments to test all three iron oxide samples were completed with a 0.133 mmol/L initial concentration at a neutral pH. Although such a high level of arsenic concentration is unlikely to be found in aquatic environments, it was necessary to increase the concentration to enable experiments to be carried out within a week. The flowrate was also increased slightly to 4.7 ml/hr for sufficient sample to be collected for multi component analysis.

For all subsequent column experiments, the same conditions were used (see Table 6.3). A photograph of the column set up is found in Figure 6.11.

**Table 6.3: Mini-column operating parameters**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (μm)</td>
<td>150-300</td>
</tr>
<tr>
<td>Mass of adsorbent (mg)</td>
<td>200</td>
</tr>
<tr>
<td>Column diameter (cm)</td>
<td>0.56</td>
</tr>
<tr>
<td>Bed height (cm)</td>
<td>0.8</td>
</tr>
<tr>
<td>Bed volume (cm³)</td>
<td>0.2</td>
</tr>
<tr>
<td>Flowrate (ml/hr)</td>
<td>4.7</td>
</tr>
<tr>
<td>Bed volume/hr</td>
<td>24</td>
</tr>
<tr>
<td>Superficial liquid velocity (m/s)</td>
<td>6.63x10⁻⁵</td>
</tr>
<tr>
<td>Empty bed contact time (mins)</td>
<td>2.52</td>
</tr>
<tr>
<td>Time per sample tube (mins)</td>
<td>50</td>
</tr>
<tr>
<td>pH range</td>
<td>7.6-7.8</td>
</tr>
<tr>
<td>Concentration (μmol/L)</td>
<td>133.5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>22 ±2</td>
</tr>
</tbody>
</table>
Chapter 6. Adsorption studies

Figure 6.11: Mini-column experimental set up
Multi component

Several mixtures of anions were prepared to observe the competitive effects of other anions on the arsenic uptake capacity. A similar experimental procedure was used for multi component column runs. Binary solutions of arsenate/phosphate, arsenate/fluoride and phosphate/fluoride were prepared. Equimolar solution concentrations of 0.133 mmol/L were used in each case, e.g. 0.133 mmol/L arsenate + 0.133 mmol/L phosphate at neutral pH, 7.6–7.8. In addition, 0.133 mmol/L ternary solution of arsenate/phosphate/fluoride was also used i.e. 0.133 mmol/L arsenate + 0.133 mmol/L phosphate + 0.133 mmol/L fluoride in column runs for all iron oxide samples.

Regeneration

An experimental procedure was developed to determine whether the loaded iron oxide samples could be regenerated. After the columns had been loaded with anions from the previous sets of experiments, 500 BV (100 ml) deionised distilled water was fed to the rig, to remove any remaining impurities. After which, 0.1 M NaOH was fed at 4.7 ml/hr for 8 hours, samples were collected every 30 minutes.

6.3 Results and Discussion

Three iron oxide materials were challenged with three anionic (arsenate, phosphate and fluoride) and one cationic (cadmium) species. One iron oxide was produced at Loughborough University, according to the experimental procedure outlined in Section 3.2.4, designated NN. Another material was also produced at Loughborough University, (see Section 3.2.5) although the finishing procedure was simpler, designated VL. The final iron oxide used was a commercially available sample supplied by GEH, Wasserchemie (GEH).

The uptake capacities for each species studied was determined in batch mode, up to a maximum concentration of approximately 28 ±4 μmol/L in the pH range 4–9. The data was fitted with both the Langmuir and Freundlich
isotherm models, each providing a reasonable fit. The monolayer values calculated from the Langmuir model were compared to those determined experimentally.

The effects of pH and type of material on the uptake capacity was studied and in conjunction with the physical and chemical characteristics found in chapters 4 and 5, possible mechanisms were postulated.

In column mode, the iron oxide samples were challenged with 0.133 µmol/L arsenic, to determine the arsenic capacity and breakthrough curve characteristics. Binary (arsenate/phosphate, arsenate/flouride and fluoride/phosphate) and ternary (arsenate/flouride/phosphate) mixtures were investigated to determine the effect of the presence of competing anions on the arsenic capacity and breakthrough curve characteristics. This enabled quantitative calculations of distribution coefficients of each species within multi component systems for each sample to be computed.

Elution of all column runs were completed within 60 bed volumes, under non-optimum conditions (a specified flowrate and concentration of NaOH). All iron oxide samples were able to be regenerated using 0.1 M NaOH, removing more than 85 % of all adsorbed species.

### 6.3.1 Arsenic isotherm data

For each iron oxide studied, the Langmuir and Freundlich parameters with their respective correlation coefficients are given in Tables 6.4 and 6.5 and isotherms in the pH range 4–9 in Figures 6.12–6.14. The theoretical values for monolayer coverage calculated by the Langmuir model (see Equation 6.1) can be compared to an equilibrium value, experimentally determined at three pH values, namely 4, 7 and 9 (see Table 6.6).

The Langmuir model under-predicts the monolayer coverage value (a) for all materials across the pH range. At low pH, the values in Tables 6.4 and 6.6 are comparable. The difference between the experimental value and predicted value increases with increasing pH and a values for sample NN being better predicted than the other two samples.
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The changes in the type of arsenic complex binding with the surface is dependent on surface loading (number of available sites) and pH. These changes are explained further in the following sections. This may be due to the limitations of the Langmuir model, which does not take into account the degree of crystallinity, the change in speciation or changes in the surface charge. Hence the Langmuir model does not provide a very close fit to the data, as changes in surface complexation are not taken into account.

Table 6.4: Parameters for the Langmuir model $a$ (mmol/g) and $b$ (L/mmol) and correlation coefficients ($R^2$) for all samples for arsenate adsorption

<table>
<thead>
<tr>
<th>pH</th>
<th>NN a</th>
<th>b</th>
<th>R²</th>
<th>GEH a</th>
<th>b</th>
<th>R²</th>
<th>VL a</th>
<th>b</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.210</td>
<td>180</td>
<td>0.986</td>
<td>1.180</td>
<td>158</td>
<td>0.982</td>
<td>0.955</td>
<td>113</td>
<td>0.984</td>
</tr>
<tr>
<td>5</td>
<td>0.908</td>
<td>174</td>
<td>0.987</td>
<td>0.981</td>
<td>148</td>
<td>0.981</td>
<td>0.855</td>
<td>69</td>
<td>0.988</td>
</tr>
<tr>
<td>6</td>
<td>0.641</td>
<td>223</td>
<td>0.975</td>
<td>0.646</td>
<td>201</td>
<td>0.976</td>
<td>0.815</td>
<td>42</td>
<td>0.993</td>
</tr>
<tr>
<td>7</td>
<td>0.626</td>
<td>138</td>
<td>0.992</td>
<td>0.512</td>
<td>176</td>
<td>0.994</td>
<td>0.921</td>
<td>17</td>
<td>0.980</td>
</tr>
<tr>
<td>8</td>
<td>0.584</td>
<td>102</td>
<td>0.997</td>
<td>0.482</td>
<td>150</td>
<td>0.982</td>
<td>0.897</td>
<td>52</td>
<td>0.985</td>
</tr>
<tr>
<td>9</td>
<td>0.578</td>
<td>81</td>
<td>0.987</td>
<td>0.378</td>
<td>142</td>
<td>0.977</td>
<td>0.711</td>
<td>18</td>
<td>0.979</td>
</tr>
</tbody>
</table>

Table 6.5: Parameters for the Freundlich model, $k$ ((mmol/g)(L/mmol)$^{1/n}$) and $n$, and correlation coefficients ($R^2$) for all samples, for arsenate adsorption

<table>
<thead>
<tr>
<th>pH</th>
<th>NN k</th>
<th>n</th>
<th>R²</th>
<th>GEH k</th>
<th>n</th>
<th>R²</th>
<th>VL k</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>10.71</td>
<td>1.74</td>
<td>0.964</td>
<td>11.02</td>
<td>1.66</td>
<td>0.960</td>
<td>8.72</td>
<td>1.74</td>
<td>0.988</td>
</tr>
<tr>
<td>5</td>
<td>8.63</td>
<td>1.69</td>
<td>0.959</td>
<td>9.72</td>
<td>1.62</td>
<td>0.946</td>
<td>10.30</td>
<td>1.54</td>
<td>0.956</td>
</tr>
<tr>
<td>6</td>
<td>5.08</td>
<td>1.88</td>
<td>0.972</td>
<td>5.25</td>
<td>1.82</td>
<td>0.953</td>
<td>7.41</td>
<td>1.58</td>
<td>0.956</td>
</tr>
<tr>
<td>7</td>
<td>5.69</td>
<td>1.65</td>
<td>0.974</td>
<td>4.31</td>
<td>1.76</td>
<td>0.960</td>
<td>6.99</td>
<td>1.53</td>
<td>0.967</td>
</tr>
<tr>
<td>8</td>
<td>4.90</td>
<td>1.60</td>
<td>0.979</td>
<td>3.39</td>
<td>1.82</td>
<td>0.950</td>
<td>8.82</td>
<td>1.31</td>
<td>0.971</td>
</tr>
<tr>
<td>9</td>
<td>4.56</td>
<td>1.56</td>
<td>0.956</td>
<td>5.36</td>
<td>1.43</td>
<td>0.899</td>
<td>6.57</td>
<td>1.32</td>
<td>0.950</td>
</tr>
</tbody>
</table>
The correlation coefficients were higher for the Langmuir model; hence, in Figures 6.12–6.14, the points are the experimental data and the lines describe the Langmuir fit of the data. As was demonstrated in Section 5.3.2, the surface of iron oxide can be positively or negatively charged, depending on the pH of the system, i.e. that the surface is amphoteric. For activated alumina, which is similar to iron in that it is amphoteric, Lin and Wu [42] found that both the Freundlich and Langmuir models fitted, although the latter gave a more suitable fit.

<table>
<thead>
<tr>
<th>pH</th>
<th>q (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NN</td>
</tr>
<tr>
<td>4</td>
<td>1.30</td>
</tr>
<tr>
<td>7</td>
<td>0.89</td>
</tr>
<tr>
<td>9</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Figure 6.12: Sample NN arsenic uptake capacity, pH range 4–9
Chapter 6. Adsorption studies

Figure 6.13: Sample GEH arsenic uptake capacity, pH range 4–9

Figure 6.14: Sample VL arsenic uptake capacity, pH range 4–9
Effect of pH

The arsenic isotherms for each material were examined in the pH range 4 - 10. From Figures 6.12-6.14, the uptake decreases as the pH increases, as would be expected for anion exchange. Driehaus et al. [43] also found for a granular ferric hydroxide that arsenate adsorption decreased with increasing pH. Similar results were also found for two-line ferrihydrite [44] and goethite [45].

Arsenate under most pH conditions is present as a negative species (Figure 6.5). The isoelectric point IEP for the samples is approximately near neutral, pH 7-8 (see Section 5.3.2). Hence at pH 4, the surface is positively charged and will attract anions. For protonated anions such as arsenate and phosphate, ligand exchange may be accompanied by a deprotonation at the surface, resulting in a bidentate inner-sphere bonding (two bonds with the iron oxide surface, see Equations 6.56-6.57) [40]. Evidence from Section 5.2.3, i.e. the isoelectric point of all three samples was lower in the presence of arsenate and phosphate, also indicates the presence of inner-sphere complexes. Figure 6.15 illustrates both monodentate and bidentate bonding using arsenate complexes.

![Arsenate surface complexes](image)

Figure 6.15: Arsenate surface complexes [46]
As the pH increases, the degree of positive surface charge decreases, lowering the attractive forces towards anionic species. Neutral adsorption occurs through proton dissociation from the acid surface. Adsorbed species obtain a proton from solution to equilibrate with the solution [47]. At pH > IEP there is some arsenic adsorption despite there being mutual repulsion between the negative surface and anionic species. Hence, the energy gained by the surface in forming new bonds with the anion must be greater than the repulsive forces, for any adsorption to occur. In addition, the speciation of arsenate changes from $H_2AsO_4^{-}$ to $HAsO_4^{2-}$, increasing the negative charge of the species. Removal at higher pH by specific adsorption is possible, if the undissociated acid donates a proton to the surface hydroxyl group to form water that can be displaced by the anion [48]:

$$\equiv FeO\, +\, HAsO_4^{2-} \leftrightarrow \equiv FeHAsO_4^{2-} + OH^-$$  \hspace{1cm} (6.58)

$$\equiv FeHAsO_4^{2-} \leftrightarrow \equiv FeAsO_4^{2-} + H^+$$  \hspace{1cm} (6.59)

Any cationic counter-ions ($Na^+$) would be attracted to the surface at pH > IEP, would balance the negative charge due to $\equiv FeHAsO_4^{2-}$. Lower capacity compared to site availability is due to the bidentate surface formation and electrostatic repulsion [49].

**Effect of material**

All iron oxide samples tested exhibited a similar arsenic capacity, the highest at pH 4. NN had the highest removal capacity ($\sim 1$ mmol/g) followed by GEH and VL, both approximately 0.9 mmol/g. This is in agreement with the ions released chart (Figure 5.7, Section 5.3.1), which indicated that the NN surface possessed a higher quantity of positive surface sites. Specific surface
area does not appear to affect the uptake capacity, as sample NN possessed a specific surface area greater than VL, but smaller than GEH. The degree of crystallinity however, appears to have some bearing on the isotherm results, from a reduction in the availability of surface sites or bonding energy [50].

Waychunas et al. [51] determined that bidentate ligands were the primary species on akaganeite with very little monodentate bonding. Higher quantities of monodentate coverage were evident on amorphous material, such as ferrihydrite, but less common in more crystalline polymorphs, *i.e.* goethite and akaganeite [52]. Hence a higher capacity would be expected in materials that are more amorphous. This concurs with the trend in capacity (NN>GEH~VL) and results from XRD analysis from Section 4.4.6 indicating crystallinity (VL~GEH>NN). Some maintain, however, that crystal structure has no effect on adsorption capacity [53, 54].

**Effect of speciation**

As seen from Figures 6.5-6.8, the speciation of arsenate and phosphate are very similar across the entire pH range. Hiemstra and Van Riemsdijk [55] calculated the relative surface speciation of phosphate on goethite at equilibrium levels of $10^{-7}$ M and $10^{-4}$ M phosphorus, see Figure 6.16.

From FT-IR spectroscopy there is evidence of three adsorbed species, dependent on anion loading and pH. Protonated bidentate species at low pH predominate, in the mid pH range bidentate species and monodentate species at high pH. Bidentate bonding is preferred over monodentate (single bond with the surface) at low pH as two bonds form with the surface, which contributes the highest to balancing the charges and releases the most electrostatic energy. At high pH, the species with the mean centre of change furthest away from the surface is preferred, *i.e.* monodentate [55].

Similarly with increasing surface loading, the electrostatic charge increases in the diffuse layer, increasing the negative repulsion. Hence, the species that contributes the least negative charge to the outer plane is preferred, *i.e.* bidentate. Waychunas et al. [52] have found Fe$_2$O$_2$AsO$_2$ bidentate species dominant at low concentration $< 200$ mmol/g [46], with monodentate species also evident.
Figure 6.16: Relative surface speciation of phosphate at (a) $10^{-7}$ and (b) $10^{-4}$ M phosphorus [55]

This may explain the existence of two parts of the arsenic isotherms (Figures 6.12-6.14). At low surface loading, the dominant species is monodentate. As the amount of arsenate on the surface increases, bidentate species dominate, hence lowering the overall capacity as two active surface sites are required.
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Possible uptake mechanism

It is generally agreed that for both aluminium and iron oxides, anion uptake occurs via ligand exchange with surface hydroxyls and/or surface aquo groups. Direct evidence for ligand exchange is given by infra red spectroscopy [56, 57], X-ray adsorption near edge spectroscopy (XANES) [58] and extended X-ray adsorption fine structure (EXAFS) analysis [46, 51, 52, 59].

It is assumed that ligand exchange occurs where the anion forms an inner-sphere complex with the metal cation on the oxide surface, which was bound to the hydroxyl group. To maintain the overall electroneutrality of the surface, cations and anions from the background electrolyte form outer-sphere complexes on the boundary with the diffuse swarm [6] (Figure 6.17).

Figure 6.17: Possible complexes at the iron oxide surface [60]
A possible mechanism, analogous to phosphate adsorption described by Goldberg and Sposito is given below [6]:

\[
\equiv \text{FeOH} + \text{H}_3\text{AsO}_4 \leftrightarrow \equiv \text{FeH}_2\text{AsO}_4 + \text{H}_2\text{O} \quad (6.60)
\]

\[
\equiv \text{FeOH} + \text{H}_3\text{AsO}_4 \leftrightarrow \equiv \text{FeHAsO}_4^- + \text{H}_2\text{O} + \text{H}^+ \quad (6.61)
\]

\[
\equiv \text{FeOH} + \text{H}_3\text{AsO}_4 \leftrightarrow \equiv \text{FeAsO}_4^- + \text{H}_2\text{O} + 2\text{H}^+ \quad (6.62)
\]

Allowing for bidentate bonding [61]:

\[
2(\equiv \text{FeOH}) + \text{H}_3\text{AsO}_4 \leftrightarrow \equiv \text{Fe}_2\text{HAsO}_4 + 2\text{H}_2\text{O} \quad (6.63)
\]

\[
2(\equiv \text{FeOH}) + \text{H}_3\text{AsO}_4 \leftrightarrow \equiv \text{Fe}_2\text{AsO}_4^- + 2\text{H}_2\text{O} + \text{H}^+ \quad (6.64)
\]

### 6.3.2 Phosphate isotherm data

For each material studied, the Langmuir and Freundlich parameters in addition to their correlation coefficients are given in Tables 6.8 and 6.9 and isotherms for the pH range 4–9 in Figures 6.18–6.20. Both the Freundlich and the Langmuir model gave a suitable description of the data. The theoretical values calculated by the Langmuir model can be compared to an equilibrium value experimentally determined at three pH values, namely 4, 7 and 9 (Table 6.7).

The trend seen for arsenate is reversed for phosphate adsorption, i.e. the Langmuir model over-estimates the uptake capacity for all materials across the pH range. Similar molar concentration values were used to enable a comparison of uptake capacity between all species studied. Comparing Figures 6.12–6.14 and 6.18–6.20 it can be seen that the isotherms for phosphate adsorption are more linear than for arsenate. Hence, some \( a \) values may be unrealistically high, as capacities were not determined at higher concentrations, indicating a limitation of the Langmuir model.

Other parameters which might affect the goodness of fit of the Langmuir model, such as changes in the surface complexes, dependent on pH and surface loading, would be expected to be similar to arsenate.
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However, as found previously (Section 6.3.1), the Langmuir model gave a better fit of the experimental data. Hence, in Figures 6.18–6.20, the points represent experimental data and lines the Langmuir approximation of the data.

Table 6.7: Maximum values for phosphate

<table>
<thead>
<tr>
<th>pH</th>
<th>q (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NN</td>
</tr>
<tr>
<td>4</td>
<td>1.09</td>
</tr>
<tr>
<td>7</td>
<td>0.74</td>
</tr>
<tr>
<td>9</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Table 6.8: Parameters for the Langmuir model $a$ (mmol/g) and $b$ (L/mmol) and correlation coefficients ($R^2$) for all samples, for phosphate adsorption

<table>
<thead>
<tr>
<th>pH</th>
<th>a</th>
<th>b</th>
<th>$R^2$</th>
<th>a</th>
<th>b</th>
<th>$R^2$</th>
<th>a</th>
<th>b</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.136</td>
<td>69</td>
<td>0.990</td>
<td>1.16</td>
<td>56</td>
<td>0.991</td>
<td>1.070</td>
<td>82</td>
<td>0.998</td>
</tr>
<tr>
<td>5</td>
<td>1.316</td>
<td>37</td>
<td>0.994</td>
<td>1.896</td>
<td>22</td>
<td>0.997</td>
<td>1.542</td>
<td>33</td>
<td>0.998</td>
</tr>
<tr>
<td>6</td>
<td>1.877</td>
<td>17</td>
<td>0.996</td>
<td>2.685</td>
<td>12</td>
<td>0.981</td>
<td>1.563</td>
<td>25</td>
<td>0.997</td>
</tr>
<tr>
<td>7</td>
<td>4.143</td>
<td>5</td>
<td>0.999</td>
<td>3.058</td>
<td>8</td>
<td>0.998</td>
<td>3.271</td>
<td>8</td>
<td>0.995</td>
</tr>
<tr>
<td>8</td>
<td>0.620</td>
<td>39</td>
<td>0.987</td>
<td>1.380</td>
<td>13</td>
<td>0.998</td>
<td>9.728</td>
<td>2</td>
<td>0.999</td>
</tr>
<tr>
<td>9</td>
<td>0.676</td>
<td>26</td>
<td>0.996</td>
<td>0.607</td>
<td>28</td>
<td>0.992</td>
<td>3.308</td>
<td>5</td>
<td>0.998</td>
</tr>
</tbody>
</table>

Table 6.9: Parameters for the Freundlich model, $k$ ((mmol/g)(L/mmol)$^{1/n}$) and $n$, and correlation coefficients ($R^2$) for all samples, for phosphate adsorption

<table>
<thead>
<tr>
<th>pH</th>
<th>k</th>
<th>n</th>
<th>$R^2$</th>
<th>k</th>
<th>n</th>
<th>$R^2$</th>
<th>k</th>
<th>n</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>14.09</td>
<td>1.33</td>
<td>0.995</td>
<td>13.20</td>
<td>1.31</td>
<td>0.996</td>
<td>8.73</td>
<td>1.57</td>
<td>0.996</td>
</tr>
<tr>
<td>5</td>
<td>14.39</td>
<td>1.23</td>
<td>0.992</td>
<td>20.49</td>
<td>1.12</td>
<td>0.997</td>
<td>12.79</td>
<td>1.30</td>
<td>0.996</td>
</tr>
<tr>
<td>6</td>
<td>14.37</td>
<td>1.16</td>
<td>0.997</td>
<td>23.39</td>
<td>1.04</td>
<td>0.997</td>
<td>12.31</td>
<td>1.21</td>
<td>0.996</td>
</tr>
<tr>
<td>7</td>
<td>16.35</td>
<td>1.06</td>
<td>0.998</td>
<td>17.18</td>
<td>1.06</td>
<td>0.996</td>
<td>14.45</td>
<td>1.13</td>
<td>0.992</td>
</tr>
<tr>
<td>8</td>
<td>10.54</td>
<td>1.10</td>
<td>0.983</td>
<td>11.01</td>
<td>1.08</td>
<td>0.999</td>
<td>16.48</td>
<td>1.03</td>
<td>0.999</td>
</tr>
<tr>
<td>9</td>
<td>12.08</td>
<td>1.01</td>
<td>0.979</td>
<td>9.28</td>
<td>1.07</td>
<td>0.988</td>
<td>24.37</td>
<td>0.90</td>
<td>0.975</td>
</tr>
</tbody>
</table>
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Figure 6.18: Sample NN phosphorus uptake capacity, pH range 4–9

Figure 6.19: Sample GEH phosphorus uptake capacity, pH range 4–9
Figure 6.20: Sample VL phosphorus uptake capacity, pH range 4–9

Effect of pH

A similar trend was found for phosphate as for arsenate, *i.e.* the capacity decreases with increasing pH (Figures 6.18–6.20). Similar equations concluded for arsenate can be constructed for phosphate adsorption at low pH with a positively charged iron surface (see Equations 6.56–6.59) [40]:

\[
\begin{align*}
\text{FeOH} + \text{H}_2\text{PO}_4^- & \leftrightarrow \text{FeH}_2\text{PO}_4^- + \text{OH}^- \\
\text{FeH}_2\text{PO}_4^- & \leftrightarrow \text{FeHPO}_4^{2-} + \text{H}^+ 
\end{align*}
\]  

(6.65)  

(6.66)

As the pH increases, the degree of positive surface charge decreases, lowering the attractive forces towards anionic species. At pH > IEP, both the surface and the ions (primarily HPO$_4^{2-}$ rather than H$_2$PO$_4^-$) in solution are negatively charged, hence there is no coulombic attraction.
Adsorption occurs if the undissociated acid donates a proton to the surface hydroxyl group to form water that can be displaced by the anion [48]:

\[
\equiv \text{FeOH} + \text{HPO}_4^{2-} \leftrightarrow \equiv \text{FeHPO}_4^{2-} + \text{OH}^- \quad (6.67)
\]

\[
\leftrightarrow \equiv \text{FePO}_4^{2-} + \text{H}_2\text{O} \quad (6.68)
\]

The overall phosphate adsorption capacity was approximately 25% lower than arsenate. The chemistry of arsenate and phosphate are similar (Figures 6.5 and 6.7) and it would be expected that a similar process would describe the adsorption mechanism (Equations 6.60-6.62). The effective ionic radii at 25 °C for both arsenic and phosphorus are both approximately 4 Å [62]. However, Lumsdon et al. [57] determined that the arsenate was a larger ligand than phosphate (As—O bond 8-14% longer than P—O determined by FT-IR analysis), hence arsenate interacts more strongly with OH⁻ at the surface and is preferred.

Jain and Loeppart [63] discovered that phosphate adsorption was slightly lower on ferrihydrite, indicating that arsenate is preferred over phosphate. If As (V) is desorbed by P (V), only a proportion is removed which indicates that there are different sites available for arsenate and phosphate [64]. Hingston et al. [45] also concluded that for goethite, there were surface sites common to both anions, and others that one or other preferentially adsorbs onto.

Manning and Goldberg [65] found that the uptake of both phosphate and arsenate are similar for goethite at near neutral pH. This is in agreement with the results from this study found that uptake capacities were ~ 0.48 mmol/g and ~ 0.45 mmol/g for arsenic and phosphorus respectively. The similarity in uptake may be due to the change in bonding type, as the pH increases monodentate bonding increases at the surface. Hence, the iron oxide surface appears to have a similar affinity for both arsenate and phosphate monodentate complexes.
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Effect of material

The trend for phosphate uptake and sample type was similar to that of arsenate i.e. NN gave the highest uptake, 0.75 mmol/g, followed by ~ 0.65 mmol/g for both GEH and VL. As for arsenate, this trend follows the degree of crystallinity of the iron oxide materials studied, the most amorphous (NN) with the highest capacity, decreasing with increasing crystallinity.

FT-IR evidence indicates that on more crystalline material, such as goethite and akaganeite, bidentate bonding is the sole type of phosphate species adsorbed [66]. However, Figure 6.16 illustrates that some monodentate species can exist at higher pH and lower anion loading. Hence a similar trend is expected for phosphate, that monodentate species are less likely to form on more crystalline material, due to the different surface sites available [51].

Effect of speciation

Bidentate species are preferred at low pH as more electrostatic energy is released by two bonds formed with the iron oxide surface, and hence is more stable than monodentate bonding [67]. Similarly at high pH, a larger species is preferred as repulsion forces are lower. Monodentate species are more evident at lower surface loading, with bidentate species preferred at higher loading as they contribute least negative charge to the diffuse layer by having the mean centre of charge nearer the surface [68]. Hence this provides an explanation to the over-prediction of the Langmuir model, due to dependence of surface coverage on bonding mechanism and the observation of two sections in the phosphate isotherms (Figures 6.18-6.20).

Possible uptake mechanism

As mentioned previously, the chemistry of phosphate is very similar to arsenate. Goldberg and Sposito suggest the uptake mechanism is as follows [69].
Chapter 6. Adsorption studies

\[
\begin{align*}
\equiv \text{FeOH} + \text{H}_3\text{PO}_4 & \leftrightarrow \equiv \text{FePO}_4\text{H}_2 + \text{H}_2\text{O} \\
\equiv \text{FePO}_4\text{H}_2 & \leftrightarrow \equiv \text{FePO}_4\text{H}^- + \text{H}^+ \\
\equiv \text{FePO}_4\text{H}^- & \leftrightarrow \equiv \text{FePO}_4^{2-} + \text{H}^+
\end{align*}
\]

(6.70)  

(6.71)

Allowing for bidentate species [70]:

\[
\begin{align*}
2(\equiv \text{FeOH}) + \text{H}_3\text{PO}_4 & \leftrightarrow \equiv \text{Fe}_2\text{PO}_4\text{H} + 2\text{H}_2\text{O} \\
\equiv \text{Fe}_2\text{PO}_4\text{H} & \leftrightarrow \equiv \text{Fe}_2\text{PO}_4^- + \text{H}^+
\end{align*}
\]

(6.72)  

(6.73)

6.3.3 Fluoride isotherms

For each material studied, the Langmuir and Freundlich parameters and respective correlation coefficients are given in Tables 6.10 and 6.11 and isotherms for the pH range 4–9 in Figures 6.21–6.23. The theoretical values calculated by the Langmuir model can be compared to an equilibrium value, experimentally determined at three pH values, namely 4, 7 and 9, see Table 6.12.

Similar to the trend noted for phosphate adsorption, the Langmuir model generally over-estimates the uptake capacity for all materials across the pH range. Similar molar concentrations were used to enable a comparison of the respective uptake capacities of arsenate and fluoride. However, problems were encountered implementing the Langmuir equation at low fluoride concentrations (600 ppb), resulting in almost linear isotherms (Figures 6.21–6.23). Hence, some \(a\) values may be unrealistically high, as capacities were not determined at higher concentrations, indicating a limitation of the Langmuir model.

Both the Langmuir and the Freundlich isotherm models gave a suitable fit of the data, however, the \(R^2\) coefficients were higher for the Langmuir fit. Hence, in Figures 6.21–6.23, the points represent experimental data and the solid lines the Langmuir model.
Table 6.10: Parameters for the Langmuir model \( a \) (mmol/g) and \( b \) (L/mmol) and correlation coefficients \( R^2 \) for all samples, for fluoride adsorption

<table>
<thead>
<tr>
<th>pH</th>
<th>NN</th>
<th>a</th>
<th>b</th>
<th>R²</th>
<th>GEH</th>
<th>a</th>
<th>b</th>
<th>R²</th>
<th>VL</th>
<th>a</th>
<th>b</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td></td>
<td>2.508</td>
<td>118</td>
<td>0.997</td>
<td></td>
<td>3.191</td>
<td>73</td>
<td>0.998</td>
<td></td>
<td>2.255</td>
<td>164</td>
<td>0.994</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>2.581</td>
<td>69</td>
<td>0.998</td>
<td></td>
<td>2.644</td>
<td>73</td>
<td>0.998</td>
<td></td>
<td>2.151</td>
<td>93</td>
<td>1.000</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>2.653</td>
<td>42</td>
<td>0.999</td>
<td></td>
<td>2.606</td>
<td>43</td>
<td>1.000</td>
<td></td>
<td>3.568</td>
<td>31</td>
<td>0.988</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>4.355</td>
<td>17</td>
<td>0.991</td>
<td></td>
<td>2.865</td>
<td>26</td>
<td>1.000</td>
<td></td>
<td>2.970</td>
<td>29</td>
<td>0.996</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>10.628</td>
<td>4.8</td>
<td>0.993</td>
<td></td>
<td>5.938</td>
<td>9</td>
<td>0.998</td>
<td></td>
<td>16.673</td>
<td>3</td>
<td>0.999</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>1.936</td>
<td>18</td>
<td>0.979</td>
<td></td>
<td>3.630</td>
<td>9</td>
<td>0.995</td>
<td></td>
<td>6.725</td>
<td>6</td>
<td>0.992</td>
</tr>
</tbody>
</table>

Table 6.11: Parameters for the Freundlich model \( k \) ((mmol/g)(L/mmol)\(^{1/n}\)) and \( n \), and correlation coefficients \( R^2 \) for all samples, for fluoride adsorption

<table>
<thead>
<tr>
<th>pH</th>
<th>NN</th>
<th>k</th>
<th>n</th>
<th>R²</th>
<th>GEH</th>
<th>k</th>
<th>n</th>
<th>R²</th>
<th>VL</th>
<th>k</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td></td>
<td>15.17</td>
<td>1.85</td>
<td>0.994</td>
<td></td>
<td>15.96</td>
<td>1.83</td>
<td>0.994</td>
<td></td>
<td>14.06</td>
<td>1.93</td>
<td>0.982</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>16.22</td>
<td>1.66</td>
<td>0.998</td>
<td></td>
<td>17.63</td>
<td>1.64</td>
<td>0.994</td>
<td></td>
<td>12.81</td>
<td>1.80</td>
<td>0.998</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>15.24</td>
<td>1.43</td>
<td>0.999</td>
<td></td>
<td>15.09</td>
<td>1.56</td>
<td>0.999</td>
<td></td>
<td>18.36</td>
<td>1.47</td>
<td>0.991</td>
</tr>
<tr>
<td>7</td>
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<td>1.16</td>
<td>0.986</td>
<td></td>
<td>15.02</td>
<td>1.43</td>
<td>0.999</td>
<td></td>
<td>19.50</td>
<td>1.35</td>
<td>0.999</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>52.97</td>
<td>0.96</td>
<td>0.975</td>
<td></td>
<td>8.65</td>
<td>0.66</td>
<td>0.989</td>
<td></td>
<td>25.79</td>
<td>1.19</td>
<td>0.995</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>35.05</td>
<td>0.93</td>
<td>0.987</td>
<td></td>
<td>21.42</td>
<td>1.08</td>
<td>0.995</td>
<td></td>
<td>76.51</td>
<td>0.85</td>
<td>0.975</td>
</tr>
</tbody>
</table>

Table 6.12: Maximum values for fluoride

<table>
<thead>
<tr>
<th>pH</th>
<th>NN</th>
<th>GEH</th>
<th>VL</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2.64</td>
<td>2.88</td>
<td>2.35</td>
</tr>
<tr>
<td>7</td>
<td>1.67</td>
<td>1.73</td>
<td>1.62</td>
</tr>
<tr>
<td>9</td>
<td>1.58</td>
<td>1.62</td>
<td>1.50</td>
</tr>
</tbody>
</table>
Effect of pH

Adsorption of fluoride onto iron oxide samples is strongly pH dependent. As the pH increases, the fluoride capacity decreases. At pH > 6, fluoride removal decreases further as a result of stronger competition from hydroxide ions on the adsorbent surface. The decrease is particularly sharp above pH ≈ 6 as the surface charge becomes more negative. Hence, to adsorb onto the surface, the fluoride ions would have to overcome electrostatic forces as there would be a higher density of negative charge very near the surface, hence greater electrostatic repulsion [68]. A similar result for the effect of pH was noted by Meeussen et al. [71] for fluoride uptake by goethite.

For small ions like F\(^-\) that are similar to OH\(^-\) ions, there is a greater tendency to displace hydroxyls in solution, i.e. the charge is primarily balanced in solution. Fluoride is also a fully dissociated acid, therefore cannot contribute a proton to the surface to enable ligand exchange with surface water. [72].

![Figure 6.21: Sample NN fluoride uptake capacity, pH range 4 - 9](image-url)
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Figure 6.22: Sample GEH fluoride uptake capacity, pH range 4–9

Figure 6.23: Sample VL fluoride uptake capacity. pH range 4–9
Effect of material

The fluoride uptake capacity for each material is almost identical, approximately 1.8 mmol/g. Across the pH range studied fluoride is present as a monovalent species, $F^-$ (Figure 6.9), hence an exchange with a surface hydroxyl is likely.

The fluoride capacity is almost double that for arsenic and three times that for phosphate. The effective ionic radius of fluoride at 25 °C is smaller than that of arsenate and phosphate, namely 3.5 Å. Hence the fluoride ion would be able to penetrate smaller pores that would not be accessible to the larger species. This gives further indication that the arsenate and phosphate species adsorb primarily as bidentate species at pH $< \text{IEP}$.

The calculated $a$ values (Table 6.10) and experimental uptake capacities (Table 6.12) indicate a change in the trend in uptake capacities, i.e. sample GEH has the largest capacity followed by NN and VL. At low to intermediate concentrations, fluoride reacts with singly co-ordinated hydroxyl groups [71]. With increasing concentration, doubly co-ordinated $\text{OH}^-$ groups are also exchanged [73]. Hence, GEH may have a higher quantity of singly co-ordinated sites, and have a greater affinity for fluoride over the other two samples.

Possible uptake mechanism

The fluoride ion is much smaller than the equivalent species for either arsenate or phosphate, and a mechanism of simple exchange with a hydroxide ion can be postulated. A two step ligand exchange reaction [74]:

\[
\equiv \text{FeOH} + H^+ \leftrightarrow \equiv \text{FeOH}_2^+ \tag{6.74}
\]

\[
\equiv \text{FeOH}_2^+ + F^- \leftrightarrow \equiv \text{FeF} + \text{H}_2\text{O} \tag{6.75}
\]

Combined gives:

\[
\equiv \text{FeOH} + H^+ + F^- \leftrightarrow \equiv \text{FeF} + \text{H}_2\text{O} \tag{6.76}
\]
Chapter 6. Adsorption studies

6.3.4 Cadmium isotherm data

For each material studied, the Langmuir and Freundlich parameters and respective correlation coefficients are given in Tables 6.13 and 6.14 and isotherms for the pH range 4–9 (Figures 6.24–6.26). Both models gave a reasonable fit, although generally the Freundlich model described the isotherm data better.

Dzombak and Morel [75] determined that for low cadmium concentrations (< 10^{-6} M), the Langmuir model was followed and at medium concentrations (10^{-6}-10^{-3} M), the data was better described by the Freundlich model. This could explain why, to some degree, both models provided a suitable fit. Hence, in Figures 6.24–6.26, the points represent experimental data and the solid lines the Freundlich model.

Table 6.13: Parameters for the Langmuir model \( a \) (mmol/g) and \( b \) (L/mmol) and correlation coefficients (R^2) for all samples, for cadmium adsorption

<table>
<thead>
<tr>
<th>pH</th>
<th>a</th>
<th>b</th>
<th>R^2</th>
<th>a</th>
<th>b</th>
<th>R^2</th>
<th>a</th>
<th>b</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>-2.63</td>
<td>-8.23</td>
<td>0.988</td>
<td>0.67</td>
<td>26.16</td>
<td>0.981</td>
<td>-0.63</td>
<td>-21.15</td>
<td>0.992</td>
</tr>
<tr>
<td>5</td>
<td>0.65</td>
<td>113.0</td>
<td>0.925</td>
<td>3.82</td>
<td>11.78</td>
<td>0.984</td>
<td>3.40</td>
<td>15.18</td>
<td>0.999</td>
</tr>
<tr>
<td>6</td>
<td>1.26</td>
<td>97.07</td>
<td>0.971</td>
<td>2.68</td>
<td>27.44</td>
<td>0.989</td>
<td>3.95</td>
<td>23.66</td>
<td>0.979</td>
</tr>
<tr>
<td>7</td>
<td>58.48</td>
<td>3.35</td>
<td>0.988</td>
<td>1.66</td>
<td>78.08</td>
<td>0.985</td>
<td>2.13</td>
<td>80.2</td>
<td>0.993</td>
</tr>
<tr>
<td>8</td>
<td>1.19</td>
<td>441.8</td>
<td>0.980</td>
<td>1.13</td>
<td>227.5</td>
<td>0.948</td>
<td>1.76</td>
<td>135.6</td>
<td>0.997</td>
</tr>
<tr>
<td>9</td>
<td>1.18</td>
<td>849.4</td>
<td>0.966</td>
<td>0.95</td>
<td>658.7</td>
<td>0.907</td>
<td>1.47</td>
<td>323.0</td>
<td>0.997</td>
</tr>
</tbody>
</table>

Table 6.14: Parameters for the Freundlich model, \( k \) ((mmol/g)(L/mmol)^{1/n}) and \( n \), and correlation coefficients (R^2) for all samples, for cadmium adsorption

<table>
<thead>
<tr>
<th>pH</th>
<th>k</th>
<th>n</th>
<th>R^2</th>
<th>k</th>
<th>n</th>
<th>R^2</th>
<th>k</th>
<th>n</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>15.5</td>
<td>0.92</td>
<td>0.981</td>
<td>9.8</td>
<td>1.09</td>
<td>0.994</td>
<td>40.1</td>
<td>0.85</td>
<td>0.995</td>
</tr>
<tr>
<td>5</td>
<td>12.9</td>
<td>0.78</td>
<td>0.989</td>
<td>17.9</td>
<td>1.20</td>
<td>0.989</td>
<td>30.2</td>
<td>1.09</td>
<td>0.983</td>
</tr>
<tr>
<td>6</td>
<td>17.9</td>
<td>0.72</td>
<td>0.984</td>
<td>27.0</td>
<td>1.19</td>
<td>0.979</td>
<td>28.8</td>
<td>1.25</td>
<td>0.987</td>
</tr>
<tr>
<td>7</td>
<td>14.46</td>
<td>0.61</td>
<td>0.978</td>
<td>25.1</td>
<td>1.32</td>
<td>0.980</td>
<td>15.6</td>
<td>1.58</td>
<td>0.992</td>
</tr>
<tr>
<td>8</td>
<td>8.156</td>
<td>0.44</td>
<td>0.991</td>
<td>19.6</td>
<td>1.52</td>
<td>0.994</td>
<td>11.53</td>
<td>1.85</td>
<td>0.981</td>
</tr>
<tr>
<td>9</td>
<td>7.180</td>
<td>0.38</td>
<td>0.990</td>
<td>11.94</td>
<td>1.92</td>
<td>0.989</td>
<td>9.25</td>
<td>2.21</td>
<td>0.989</td>
</tr>
</tbody>
</table>
Chapter 6. Adsorption studies

Figure 6.24: Sample NN cadmium uptake capacity, pH range 4–9

Figure 6.25: Sample GEH cadmium uptake capacity, pH range 4–9
Figure 6.26: Sample VL cadmium uptake capacity, pH range 4–9

Effect of pH

Thus far only anion adsorption has been studied. However, the point of zero charge occurs at a near neutral pH (see Section 5.3.2), it would be expected that at high pH, the negatively charge oxide surface would attract cations. Cadmium was chosen to determine the degree of uptake, and the effect of the type of material in the pH range 4–9.

The uptake capacity for cadmium increases with increasing pH. Cadmium is predominantly Cd$^{2+}$ across the pH range studied (Figure 6.10), hence it would be attracted to a negative surface, i.e. pH $> \text{IEP}$. There is a sharp decrease in adsorption below pH 6, as the surface becomes positively charged. A similar drop in the cadmium uptake was noted by Benjamin and Leckie [76].

This phenomenon is more marked in this case than for the anions studied, hence could be an indication that the energy associated with new bonds formed at the oxide surface is lower and is therefore less likely that electrostatic energy will be overcome. In addition, the cadmium species is fully dissociated and cannot contribute a hydroxyl group to balance the surface charge.
Chapter 6. Adsorption studies

Effect of material

The material possessing the highest cadmium uptake capacity was NN (~1.4 mmol/g) and both GEH and VL samples were ~1.3 mmol/g. Therefore the uptake capacity is greater than arsenate and phosphate but less than fluoride. The iron oxide surface appears to possess an almost equal amount of positive and negative surface sites, depending on the pH.

Both Spadini et al. [77] and Venema et al. [78] indicate that cadmium uptake is a combination of monodentate and bidentate species from FT-IR and spectroscopic data. Cowan et al. also suggested a combination of inner- and outer-sphere complexes, although this conclusion was based solely on model fitting, rather than experimental evidence [79]. This concurs with the cadmium uptake capacity compared to the anionic species studied. It is lower than fluoride which is bound by monodentate species and higher than the bidentate dominated surface species of arsenate and phosphate.

There is also evidence that the type of cadmium species that complexes with the iron oxide surface changes with surface loading. At low surface coverage, the monodentate species is more evident. With increasing concentration, bidentate species are preferred [80].

Possible uptake mechanism

Dzombak and Morel developed a model that included surface precipitation, to allow for non-Langmuirian behaviour. This model would be more suited to higher concentrations, i.e. greater than $10^{-6}$ M, where precipitation is more likely as surface sites become saturated [75]. However, the maximum concentration used in this study is < $10^{-6}$ M, a more likely uptake mechanism is a combination of bidentate bonding and adsorption, followed by hydrolysis as suggested by Benjamin and Leckie [76]:

$$2(\equiv FeOH) + Cd^{2+} \leftrightarrow \equiv Fe_2O_2Cd + 2H^+ \quad (6.77)$$

$$\equiv FeOH + Cd^{2+} + H_2O \leftrightarrow \equiv FeOCdOH + H_2O \quad (6.78)$$
6.4 Mini-column results

6.4.1 Initial mini-column experiments

In the first set of experiments samples NN and GEH were used in column mode. the operating parameters are given in Table 6.15. After at least 35,000 bed volumes of 500 ppb arsenic-bearing solution (\( \text{Na}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O} \)) was passed through, there was still no sign of any breakthrough, i.e. the ratio of effluent concentration to initial concentration was less than 5%. Hence, the initial solution concentration was increased twentyfold to reduce the amount of time required for each run. The flowrate was also slightly increased from 3.8 ml/hr to 4.7 ml/hr allowing sufficient sample to be collected for multi component analysis. All other experimental conditions were maintained.

Table 6.15: Initial mini-column operating parameters

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (( \mu \text{m} ))</td>
<td>150–300</td>
</tr>
<tr>
<td>Mass of adsorbent (mg)</td>
<td>200</td>
</tr>
<tr>
<td>Column diameter (cm)</td>
<td>0.56</td>
</tr>
<tr>
<td>Bed height (cm)</td>
<td>0.8</td>
</tr>
<tr>
<td>Bed volume (cm(^3))</td>
<td>0.2</td>
</tr>
<tr>
<td>Flowrate (ml/hr)</td>
<td>3.8</td>
</tr>
<tr>
<td>Bed volume/hr</td>
<td>19</td>
</tr>
<tr>
<td>Empty bed contact time (mins)</td>
<td>3.11</td>
</tr>
<tr>
<td>Time per sample tube (mins)</td>
<td>50</td>
</tr>
<tr>
<td>pH range</td>
<td>7.6–7.8</td>
</tr>
<tr>
<td>Concentration (( \mu \text{mol/L} ))</td>
<td>6.6.7</td>
</tr>
<tr>
<td>Temperature ((^\circ\text{C}))</td>
<td>22 ±2</td>
</tr>
</tbody>
</table>

6.4.2 Subsequent mini-column experiments

There were a number of factors of the column experiments which decreased the performance. The first aspect was the size of column. It was necessary to use the smallest column available, as the uptake capacity for arsenic was so large, the mass of adsorbent required for each run was minimised.
Another option if the mass of sorbent increases is to increase the feed concentration. However, this was already increased twentyfold to 10 ppm, a value possibly found in aquatic environments. If the feed concentration was further increased to compensate for the larger mass, it would become unrealistic.

The ratio of column diameter:particle diameter was also a compromise between avoiding very small (100 μm) particles which would induce packing problems and lead to channelling [28] and maximising the \( d_{col}:d_p \) ratio to minimise the wall effects (\( d_{col}:d_p > 10 \)) [22]. As a consequence of the previous two parameters, namely the mass of adsorbent and column diameter, the aspect ratio \( L_{col}:d_{col} \) is perhaps lower than ideal. The value used in column experiments was 1.4:1, which would decrease the column performance.

A balance must be made between maximising the contact time between the feed solution and adsorbent, hence increasing the column utilisation, and flow resistance and high flowrate if the aspect ratio is too high. A maximum value to avoid flowrate perturbations is 3:1 [22].

The relatively high flowrate of 24 BV/hr was necessary to enable sufficient sample to be collected. The efficiency of the column is reduced with a reduced contact time and is characterised by a flatter breakthrough curve.

Nevertheless, all operating parameters were held constant throughout the column experiments, both single and multi component runs. Hence breakthrough values determined for each experiment should be comparable. Several experiments were repeated and difference in breakthrough values was less than 8%.

**Breakthrough values**

The breakthrough values (calculated as 5% of the inlet concentration) for each anion used in each column run are given in Table 6.16. Subsequently, the adsorbent is considered to be exhausted and would be replaced or regenerated.

Distribution coefficients \( (K_d) \) for each column run were determined. A higher value indicates a stronger affinity towards the adsorbent. These values are given in Table 6.17, where \( X^- \) is the amount in milliequivalents of the anion on the solid and in solution. From Equation 6.18 the distribution coefficient for arsenic for As/F system is found by:
K_d = \frac{q_A}{C_0} = \frac{0.126}{9.38 \times 10^{-5}}
= 1345

Table 6.16: Breakthrough capacities for mini-column experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Column run</th>
<th>Breakthrough capacity (BV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As</td>
<td>F</td>
</tr>
<tr>
<td>NN</td>
<td>As</td>
<td>850</td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td>450</td>
</tr>
<tr>
<td>GEH</td>
<td>As</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td>500</td>
</tr>
<tr>
<td>VL</td>
<td>As</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td></td>
</tr>
</tbody>
</table>

Single component

From Tables 6.16 and 6.17 and Figures 6.27–6.29, it is evident that all three iron oxide samples have a high affinity for arsenate with similar breakthrough values. One noticeable difference in Figures 6.27–6.29 is the pH profiles. Sample NN remains at near neutral conditions, the pH lower during adsorption as H^+ ions are released (Equations 6.60–6.62). As breakthrough commences, the pH approaches the initial value as the surface becomes saturated with arsenic.

The pH profile of sample NN drops at 500 bed volumes, which could indicate a change in the type of bonding mechanism. The speciation diagram (Figure 6.5 reveals that at near neutral conditions, there is an equal amount of H_\text{As-O}_\text{4}^- and H_\text{2AsO}_\text{4}^- . For samples GEH and VL, which produce a much lower pH profile, the dominant species is H_\text{2AsO}_\text{4}^- . The higher proportion of H_\text{As(O}_\text{4})^- .
Table 6.17: Distribution coefficients for mini-column experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Column run</th>
<th>As</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>NN</td>
<td>As</td>
<td>1574</td>
<td>235</td>
<td>728</td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td>1345</td>
<td>286</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td>1016</td>
<td></td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td>1003</td>
<td>351</td>
<td>1011</td>
</tr>
<tr>
<td>GEH</td>
<td>As/P/F</td>
<td>1360</td>
<td>607</td>
<td>969</td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td>1232</td>
<td></td>
<td>1542</td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td>1007</td>
<td>425</td>
<td>1063</td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td>1183</td>
<td>758</td>
<td>988</td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td>1272</td>
<td></td>
<td>1132</td>
</tr>
<tr>
<td>VL</td>
<td>As</td>
<td>1576</td>
<td></td>
<td>1099</td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td>1183</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td>1272</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td>1078</td>
<td>582</td>
<td></td>
</tr>
</tbody>
</table>

would increase the likelihood of bidentate bonding with the iron oxide surface. The proportion of bidentate bonding increases with increasing surface loading, releasing water rather than H\(^+\) ions (Equations 6.63–6.64).

Samples GEH and VL however, produce a pH profile dropping to approximately pH 4. One possible difference between the samples is the equilibrium pH of each material in water and its chloride capacity (Table 5.2, see Section 5.2.4 for experimental procedure for determination of the chloride capacity).

With increasing chloride content the equilibrium pH drops. Rahman and Patterson [81] also found the pH of the wash water for akaganeite was acidic, approximately pH 3. The chloride present in the pores and on the surface slowly leaches into the solution as hydrochloric acid. The difference in pH could also account for the slightly higher breakthrough values of both samples GEH and VL over NN, as a lower pH would increase the positive charge on the iron oxide surface and the attractive forces would increase. The effect would not be so pronounced in batch mode, as the pH was adjusted regularly to compensate for any HCl released for the surface.
Figure 6.27: Sample NN breakthrough curve. concentration 0.133 mmol/L As and pH profile, initial pH = 7.7
Figure 6.28: Sample GEH breakthrough curve, concentration 0.133 mmol/L As and pH profile, initial pH = 7.7
Figure 6.29: Sample VL breakthrough curve, concentration 0.133 mmol/L As and pH profile, initial pH = 7.7
6.4.3 Multi component

Binary and ternary column runs were completed to determine the effect of competitive ions on the breakthrough capacity of arsenic. The operating conditions used for single component runs were maintained for multi component experiments are outlined in Table 6.3.

Arsenate-phosphate

The presence of equimolar phosphate markedly decreased the arsenate breakthrough values of all three materials, compared to single component values (Table 6.16 and Figures 6.30–6.32). As phosphate and arsenate are chemically similar, it would be expected that phosphate would compete for similar sites, reducing arsenic uptake [82]. Distribution coefficients of each material indicate selectivity towards arsenate, as values for arsenate are higher than phosphate (Table 6.17). This concurs with the isotherm data, in that arsenate capacity is greater than phosphate capacity by around 25 % (Section 6.3.2). The reason being that arsenate is a larger ion and therefore interacts more strongly with hydroxide groups on the iron oxide surface and hence is preferred [57].

The difference in the pH profile between sample NN and GEH and VL is again observed. This could account for the greater decrease in arsenate breakthrough, as at higher pH, the presence of both arsenate and phosphate increases the negative charge and hence depresses the arsenate uptake [63]. Manning and Goldberg [65] also found that arsenate and phosphate uptake to be equal at near neutral conditions. The distribution coefficients increase with decreasing pH (Table 6.17), where the surface is more positive, hence more arsenate and phosphate are adsorbed onto the iron oxide surface. Both samples GEH and VL have similar breakthrough values and distribution coefficients.

The mechanism for phosphate uptake is given in Equations 6.69–6.71, showing that pH is lower as phosphate and arsenate are removed. As breakthrough commences, the pH approaches the initial value as the surface becomes saturated with arsenate and phosphate. Also, with increasing surface loading, bidentate bonding becomes increasingly important which releases water (Equations 6.72–6.73).
Figure 6.30: Sample NN breakthrough curve, concentration 0.133 mmol/L As, 0.133 mmol/L P and pH profile, initial pH = 7.7
Figure 6.31: Sample GEH breakthrough curve, concentration 0.133 mmol/L As, 0.133 mmol/L P and pH profile. initial pH = 7.7
Figure 6.32: Sample VL breakthrough curve, concentration 0.133 mmol/L As, 0.133 mmol/L P and pH profile. initial pH = 7.7
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Arsenate-fluoride

The arsenate breakthrough values are not so greatly affected by the presence of fluoride as compared to phosphate. From the isotherm data, fluoride capacity is approximately twice that of arsenate (Section 6.3.3), hence there must be a strong preference for arsenate. Fluoride is not a triprotic acid and therefore does not compete for similar sites as arsenate. Arsenate is able to form bidentate bonds with the iron oxide surface which is the preferred mechanism at pH < IEP, releasing the most electrostatic energy and is more stable than a monodentate bond [67].

There is a marked difference between the breakthrough values of sample NN and the other two samples in an equimolar binary arsenate/fluoride system. There is a much greater separation between arsenate and fluoride on sample NN (Table 6.17). This could be due to the difference in pH profiles (Figures 6.33–6.35). At near neutral pH values, fluoride ions compete strongly with hydroxide ions, hence fluoride uptake is drastically reduced. In addition, fluoride is a fully dissociated acid and cannot contribute a proton to the surface to enable ligand exchange with the surface water to occur.

Fluoride uptake occurs by Equation 6.76, hence as water is released on fluoride adsorption, this minimises the reduction in pH seen compared to arsenate/phosphate system. There is some chromatographic elution, which is another indication that arsenate is preferred over fluoride, as previously adsorbed fluoride is replaced by arsenate. There is therefore a rapid increase in fluoride concentration, exceeding the influent value. This is particularly evident for sample GEH, which has the highest distribution coefficient for arsenate, indicating that arsenate replaces previously adsorbed fluoride on the iron oxide surface.

The column pH drops during the chromatographic peaking, as more arsenate is able to react with the surface and release a proton. With increasing surface loading, bidentate bonding increases, hence water is released and the pH approaches the influent value. The effect is not seen for the other two samples GEH and VL, as the column pH is much lower and would mask any slight drop in pH.
Figure 6.33: Sample NN breakthrough curve, concentration 0.133 mmol/L As, 0.133 mmol/L F and pH profile, initial pH = 7.7
Figure 6.34: Sample GEH breakthrough curve, concentration 0.133 mmol/L As, 0.133 mmol/L F and pH profile, initial pH = 7.7
Figure 6.35: Sample VL breakthrough curve. concentration 0.133 mmol/L As, 0.133 mmol/L F and pH profile, initial pH = 7.7
Fluoride-phosphate

The separation between fluoride and phosphate is higher than for arsenate and fluoride. For each column run, fluoride breaks through more quickly (Figures 6.36-6.38) and hence the difference in distribution coefficients are greater (Table 6.17). Sample VL is triple that of arsenate/fluoride and both samples NN and GEH, $K_d$ is higher for phosphate than arsenate. There is also a greater degree of chromatographic elution compared to the As/F system.

All these factors are evidence that phosphate has a greater affinity for iron oxide in a binary system containing fluoride compared to arsenate. One possible explanation is that surface heterogeneity (surface sites with preference towards anion over another) is more pronounced in a multi component adsorption system, particularly when competing ions are dissimilar, and kinetics play an increasingly important role [83]. Hence the kinetics of phosphate adsorption may be faster than arsenate, and a greater amount adsorbs onto the iron oxide at the same flowrate.

Sample NN has the lowest breakthrough value, due to the near neutral pH which reduces the fluoride uptake compared to GEH and VL. A characteristic drop in the pH profile is again observed on chromatographic elution. This enables more phosphate to be adsorbed onto the surface, causing a drop in pH as $H^+$ is released.
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Figure 6.36: Sample NN breakthrough curve, concentration 0.133 mmol/L F, 0.133 mmol/L P and pH profile, initial pH = 7.7
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Figure 6.37: Sample GEH breakthrough curve. concentration 0.133 mmol/L F, 0.133 mmol/L P and pH profile. initial pH = 7.7
Figure 6.38: Sample VL breakthrough curve, concentration 0.133 mmol/L F, 0.133 mmol/L P and pH profile, initial pH = 7.7
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Arsenate-fluoride-phosphate

A similar effect seen in the previous section is observed in the ternary system, i.e. the affinity sequence is phosphate > arsenate > fluoride (Figures 6.39–6.41). The breakthrough capacities of both arsenate and phosphate are unaffected by the presence of fluoride, (i.e. the capacities for both the binary As/P and ternary systems are equal, see Table 6.16).

The distribution coefficients indicate that phosphate is slightly preferred over arsenate, and has a marginally higher separation from fluoride than As (V) (Table 6.17). Sample NN has the greatest difference in $K_d$ values followed by GEH and VL. Hence, all three species compete on NN for similar sites, with arsenate and phosphate being preferred as they are able to form stronger bidentate bonds.

Another parameter affecting the distribution coefficients is the difference in pH profiles for the three materials, as previously indicated. A neutral system pH favours arsenate and phosphate adsorption, whereas at lower pH, exhibited in GEH and VL column runs, all three species are able to adsorb onto a positive iron oxide surface.

Chromatographic elution of fluoride is further evidence that it is the least preferred ion. The drop in pH that accompanies chromatographic elution for sample NN is due to more arsenate and phosphate replacing the adsorbed fluoride and protonating the surface. At higher surface loading, bidentate species tend to be adsorbed and exchanged with surface water (formed by a proton donated by arsenate or phosphate combining with a surface hydroxyl).

From Figures 6.39–6.41 it is evident that both arsenate and phosphate are competing for similar sites and are able to partially desorb each other, hence the fluctuations in the effluent concentration of each ion. The distribution coefficients are approximately equal, hence have a similar affinity for the iron oxide surface. Barrow [64] observed a similar phenomena, as phosphate added to an iron oxide system pre-loaded with arsenate only desorbed a proportion of the arsenate adsorbed. Hence the selectivity sequence for the iron oxide materials studied appear to be As $\sim$ P $\gg$ F.
Figure 6.39: Sample NN breakthrough curve, concentration 0.133 mmol/L As, 0.133 mmol/L F, 0.133 mmol/L P and pH profile. Initial pH = 7.7
Figure 6.40: Sample GEH breakthrough curve, concentration 0.133 mmol/L As, 0.133 mmol/L F, 0.133 mmol/L P and pH profile. initial pH = 7.7
Figure 6.41: Sample VL breakthrough curve, concentration 0.133 mmol/L As, 0.133 mmol/L F, 0.133 mmol/L P and pH profile. initial pH = 7.7
Other potential competing ions

The values for some trace anionic species in two types of post-treated tap water are given in Table 6.18. This gives an indication of the magnitude and variability of competitive ions in natural waters.

Table 6.18: Typical concentrations of various anionic species in two types of tap water

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (ppm)</th>
<th>Derbyshire</th>
<th>Leicestershire</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenate</td>
<td>0.022</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td>94</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>17</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Fluoride</td>
<td>0.01</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>Nitrate</td>
<td>4</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Sulphate</td>
<td>187</td>
<td>110</td>
<td></td>
</tr>
</tbody>
</table>

Sulphate does not greatly affect As (V) [43] or P (V) uptake, due to the difference in the surface bonding mechanism, the former two ions are able to form strong inner-sphere bonds, whereas sulphate only binds at the surface via outer-sphere complexes, hence it cannot compete for surface sites [63].

Manning and Goldberg [65] found that molybdate (a diprotic acid) affected As (V) in the pH range 4-6, however at pH > 7, adsorption of arsenate increased. An increase in the solution ionic strength causes a reduction in the thickness of the electric double layer, lowering the repulsive forces, enabling a greater amount of arsenate to be adsorbed. This phenomenon was also seen for arsenate adsorption on ferrihydrite in the presence of sulphate [63].

Silicate affected arsenate adsorption at pH > IEP as adsorption increases with increasing pH, hence becoming increasingly competitive [49, 82]. Selenite also forms inner-sphere complexes, hence reduces both arsenate and phosphate adsorption, although both the latter ions has a higher affinity [84]. Specifically adsorbed ions are preferred over those that form outer-sphere complexes e.g. nitrate and chloride [72], hence arsenate and phosphate adsorption are not particularly affected by the presence of these type of ions.
6.4.4 Regeneration

The regeneration efficiency of the column runs was determined using 0.1 M NaOH. Prior to elution, the columns were washed with 500 BV (100 ml) of deionised distilled water. The experimental set up was similar to that for the anion loading experiments (see Section 6.2.6). The regenerant was fed to the columns via a Watson-Marlow pump and the same flowrate was used as in the previous column runs, i.e. 4.7 ml/hr. The time for each test tube was set to 30 minutes to enable sufficient sample to be analysed. The analysis method for arsenate, phosphate and fluoride has previously been outlined (Section 6.2.2) and elution profiles can be found in Figures 6.42-6.46.

The elution efficiencies for each column experiment is given in Table 6.19. These efficiencies were calculated by determining the quantity from elution divided by the amount of each anion adsorbed on the column using mass balance equations. For 0.1 M NaOH, these values were in the range 85–107 %. Arsenate and phosphate had similar average efficiencies, 95 % and 94 % respectively, and fluoride a slightly higher value, 96 %.

Table 6.19: Elution efficiencies for mini-column experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Column run</th>
<th>As</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>NN</td>
<td>As</td>
<td>97</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td>95</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td>97</td>
<td></td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td></td>
<td>100</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td>95</td>
<td>98</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td></td>
<td></td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td>95</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td>95</td>
<td></td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td></td>
<td>107</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td>92</td>
<td>96</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td></td>
<td></td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td>95</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td></td>
<td>101</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td></td>
<td></td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td></td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>GEH</td>
<td>As</td>
<td>97</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td>95</td>
<td>97</td>
<td></td>
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<tr>
<td></td>
<td>As/P</td>
<td>95</td>
<td></td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td></td>
<td>100</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td>95</td>
<td>98</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td></td>
<td></td>
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<td>As/P</td>
<td>95</td>
<td></td>
<td>98</td>
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<tr>
<td></td>
<td>F/P</td>
<td></td>
<td>107</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td>92</td>
<td>96</td>
<td>95</td>
</tr>
<tr>
<td>VL</td>
<td>As</td>
<td></td>
<td></td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td>95</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td></td>
<td>101</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td></td>
<td></td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td></td>
<td>86</td>
<td></td>
</tr>
</tbody>
</table>

205
The enrichment ratio i.e. the amount adsorbed per bed volume:amount eluted per bed volume calculated at 60 bed volumes is given in Table 6.20. A higher $1/E$ reveals that less eluent is required to regenerate the material, reducing the total running costs. A lower flowrate would increase efficiency and $1/E$ values and give sharper, narrower peaks with greater separation between the species [85]. However, it was necessary to have such a high flowrate to enable sufficient sample to be collected.

Table 6.20: Enrichment values for mini-column experiments, after 60 bed volumes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Column run</th>
<th>$1/E$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>As</td>
</tr>
<tr>
<td>NN</td>
<td>As</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td>14</td>
</tr>
<tr>
<td>GEH</td>
<td>As</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>As/F</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td>14</td>
</tr>
<tr>
<td>VL</td>
<td>As</td>
<td>26</td>
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<tr>
<td></td>
<td>As/F</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>As/P</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>F/P</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>As/P/F</td>
<td>16</td>
</tr>
</tbody>
</table>

Fluoride is adsorbed as a monodentate species whereas both As and P both form bidentate bonds with the iron oxide surface, the latter is a stronger bond, therefore more difficult to elute [67]. Fluoride does not appear to effect the elution profile of the As/F or P/F binary systems (Figures 6.44–6.45), although the enrichment ratio for fluoride is very low.

Arsenate elution is affected by the presence of other ions, particularly phosphate as the enrichment ratio decreases by at least 50% in both binary and ternary mixtures. This evidence suggests that there is an increase in the number of bidentate bonds with the iron oxide surface (two bonds which are more strongly held) for both arsenate and phosphate. Equimolar arsenate and phos-
Chapter 6. Adsorption studies

Phosphate would compete for similar sites, decreasing the available active surface, increasing the ratio of bidentate bonds.

It is evident from Figure 6.43 and Table 6.20 that phosphate is more strongly held than arsenate as it takes a longer time to elute from the column and gives lower 1/E values. This is a surprising result as arsenate has a greater selectivity than phosphate towards the iron oxide surface as determined from the column experiments. A higher quantity of bidentate bonds formed by phosphate would increase the elution time.

This trend is reversed in the ternary system (Figure 6.46), as arsenate is more strongly held, with increased elution time. The presence of fluoride reduces the available sites for arsenate and phosphate adsorption, hence increasing the surface loading, therefore the number of bidentate bonds particularly for arsenate. Bidentate bonds are stronger than monodentate bonds, which are more prominent at lower surface loading, hence the elution time increases.

Joshi and Chaudhuri [86] used 0.2 M NaOH to elute 94–99 % arsenate from iron-coated sand. In addition Ghosh and Yuan [87] used 0.5 % NaOH to successfully remove arsenate from activated alumina (AA). Elution efficiencies were lower than for iron oxide material in this study, as AA has such a high affinity for arsenate, with approximately 3 % AA was lost during the regeneration cycle. Jackson and Miller [88] found that hydroxide ions were the most effective extractant (>80%) for As (V) from both ferrihydrite and goethite. It was found that elution efficiency was lower for more crystalline material.

These results indicate that the material could be regenerated and reused if desired. Only one cycle of anion loading was implemented for each sample, hence the effect of a recycled adsorbent on the uptake capacity has not been quantified. One possibility is to use a once-through cycle, after which the adsorbent is sent to landfill, the method currently used after activated alumina regeneration [20]. The brine used to elute As (V) is precipitated with iron (III) salts, the resulting sludge dried to reduce the volume. The standard EP test revealed an As (V) leachate of 1.5 mg/L, which is acceptable (limit is < 5 mg/L).

All iron oxide samples were tested across a pH range 4–9 to determine whether Fe³⁺ ions were liberated. 50 ml of deionised distilled water was transferred
using a 50ml pipette into three 100 ml Erlenmeyer flasks and the pH adjusted to 4, 7 and 9 respectively by the addition of 0.1 M NaOH or HNO₃. The pH was measured on a Mettler Toledo 340 pH probe, calibrated at pH 4 and 10. 50 mg sample NN was weighed on a Sartorius BP210D balance, accuracy ±0.0005 g and transferred to each flask. The particle size of the material used was 150–300 μm. The flasks were sealed with Parafilm and left in an orbital shaker at room temperature (22 ± 2° C) for two weeks.

This procedure was repeated for samples GEH and VL, i.e. 9 samples in total. After which the supernatant material from each flask was tested for the presence of Fe (III) ions using a Dionex 4500i Ion Chromatograph with gradient pump and conductivity detector.

Neither sample NN nor GEH released any Fe (III) and sample VL only slightly dissolved (0.04 mg/L Fe (III)). The threshold limit value of Fe (III) in drinking water is 0.2 mg/L [89]. This presents a distinct advantage to using iron oxide rather than activated alumina (AA), which on regeneration, redissolves and approximately 3% AA is lost [87]. Recently there have been concerns over the quantity of Al (III) released; a high quantity of Al (III) has been linked to elevated risk of Alzheimer’s disease [90]. AA has been shown previously to be an effective adsorbent for arsenic removal [91,92], although Pierce and Moore found that amorphous ferric hydroxide possesses 5–10 times greater capacity for arsenic than AA [54].

![Arsenate elution curve for all samples](image_url)
Figure 6.43: Arsenate-phosphate elution curve for all samples
Figure 6.44: Arsenate-fluoride elution curve for all samples
Figure 6.45: Fluoride-phosphate elution curve for all samples
Figure 6.46: Arsenate-fluoride-phosphate elution curve for all samples
6.5 Conclusions

Adsorption experiments have been carried out in both batch and column modes. Single ion uptake capacities have been determined for all three iron oxide materials studied. For the anionic species studied (arsenate, phosphate and fluoride), adsorption increased with decreasing pH, in the range 4–9. The highest uptake capacity for all anionic species occurred at pH 4, due to the iron oxide surface possessing the highest positive charge, hence strongly attracting the negative species.

Conversely for the cationic species studied (cadmium), the uptake capacity increased with increasing pH, in the range 4–9. The highest uptake was at pH 9, where the iron oxide surface is most negative, hence the attractive forces towards a positive species is the strongest.

Both the Langmuir and Freundlich isotherm models fitted the data reasonably well, although for the anionic species the Langmuir model gave a better fit of the data. The limitations of this model in describing the isotherm data became evident on comparison of theoretical and experimentally determined maximum adsorption capacities.

Potential problems were highlighted for both phosphate and fluoride adsorption, as the isotherms were almost linear, resulting in unrealistically high maximum adsorption capacities. This was due to the restriction in the range of concentration used to enable a comparison to be made of the anionic uptake capacities over an equimolar concentration range.

Empirical models, such as the Langmuir and Freundlich, do not take into account the nature of the complexation at the iron oxide surface nor provide a description of the electric double layer. It was postulated that from the speciation diagrams for phosphate and arsenate, in addition to spectroscopic information provided in the literature, that there were different binding mechanisms that were affected by surface loading and pH.

At low loading the percentage of monodentate bonds increase as there is less competition for surface sites. As the concentration increases, bidentate bonds are preferred as they are more stable and release the most electrostatic energy. Hence, as seen for the arsenate and phosphate, there are two sections of the
Chapter 6. Adsorption studies

isotherm, depending on concentration, marking the transition between monodentate and bidentate bonding. This is a further indication of the limitation of the Langmuir model.

Also at low pH, bidentate (two bonds with the iron oxide surface) was preferred, as the pH increased, monodentate complexes become more evident, as the repulsive forces are lower towards a negative surface. The formation of bidentate complexes at the surface would reduce the number of available sites, hence the capacity for arsenate and phosphate would be lower, compared to fluoride which is bound solely by monodentate complexes.

This is evident from the capacities found for the anionic species, fluoride possessed the highest capacity (1.8 mmol/g), followed by arsenate (0.9–1 mmol/g) and phosphate (0.65–0.75 mmol/g). Arsenate is a larger ligand interacting more strongly with the iron oxide surface and therefore is preferred over phosphate.

Cadmium uptake capacity was less than fluoride but greater than arsenate and phosphate, indicating that both negative and positive surface sites are present on the iron oxide materials studied, depending on the system pH. This concurs with zeta potential measurements, with an isoelectric point of 7–8. It was suggested that there was a combination of bidentate and monodentate species, dependent on pH and surface loading. It is probable that there is a higher quantity of monodentate complexes, hence increasing the available surface sites for adsorption compared to both arsenate and phosphate.

Cadmium adsorption was best described by the Freundlich isotherm. The effect of surface loading on the nature of the surface complex would also contribute to the heterogeneity of the isotherm data. The isotherm model fit is dependent on the concentration of solution, and could also be fitted reasonably well by the Langmuir model.

The degree of crystallinity appeared to have an effect on the uptake capacities, particularly of arsenate and phosphate. Sample NN had a higher uptake capacity for both arsenate and phosphate, with both samples GEH and VL having similar capacities. This is due to the type of sites available on more crystalline material which favours bidentate bonding, hence reducing further the available adsorption sites.
Competitive effects of other anions on the arsenic uptake capacity were also determined in column experiments. The same experimental conditions were maintained to enable a comparison of breakthrough capacities of a single ion system (arsenate) to binary and ternary systems with phosphate and fluoride to be made.

Limitations of the experimental set up on column utilisation was noted. Restrictions were made on the influent concentration and mass of sorbent that resulted in non-optimum conditions. The flowrate was necessarily high to enable sufficient sample to be collected. A compromise was made on the column diameter:particle diameter ratio to minimise wall effects and reducing any potential channelling problems.

Distribution coefficients were calculated from each column run to observe effects of the relative uptake of each anion in binary and ternary mixtures. As might be expected, arsenate removal was most strongly affected by phosphate by almost halving the breakthrough capacity. In both As/F and As/P binary systems, arsenate had a greater affinity towards the iron oxide surface.

The pH profile of sample NN was quite different to the other two samples, consistently throughout the column experiments. This effect was attributed to the amount of chloride present in each sample. Both samples GEH and VL possessed a much higher quantity of chloride, which reduced the solution pH, by slow release of HCl.

This disparity in column pH is particularly evident in both the As/F and P/F column runs for sample NN, as fluoride breaks through almost immediately. At near neutral pH, the fluoride uptake rapidly decreases, as it is a fully dissociated acid and cannot contribute a proton necessary to enable ligand exchange to occur. At lower column pH values, as in samples GEH and VL, fluoride is able to compete more readily for surface sites.

As arsenate is chemically similar to phosphate, there was a similar trend for the P/F binary system, with phosphate preferred over fluoride, with a greater difference in distribution coefficients than arsenate in the As/F column run. Sample NN gave the greatest separation, with similar trends in pH profiles for all samples studied. The higher affinity for phosphate over arsenate in a binary system with fluoride could be due to the faster kinetics of phosphate.
adsorption over arsenate, as kinetics play a greater role in a multi component system when the species are dissimilar.

The ternary system (arsenate-phosphate-fluoride) produced a surprising result, since the presence of both phosphate and fluoride caused the affinity of arsenate and phosphate to be almost equal, with phosphate slightly preferred over arsenate. This could be evidence of the faster kinetics of phosphate adsorption over arsenate. It is also observed that some partial desorption of phosphate and arsenate occurs, as the effect of competition for surface sites is accentuated by the presence of fluoride.

Elution of each column experiment was carried out by the addition of 0.1 M sodium hydroxide. All three anions were successfully desorbed from iron oxide, with measured efficiencies in the range 85–107 %. Fluoride was the most easily desorbed as only monodentate, rather than bidentate bonds are formed, which are more easily overcome.

The elution process was not optimised and the adsorbent was not further challenged with anions to determine uptake capacity after regeneration. There was no evidence that iron was redissolved in the pH range 4–9, with only sample VL at pH 9 releasing 0.04 mg/L, well below standards for drinking water. This presents a distinct advantage of iron oxide as a potential adsorbent over activated alumina (AA), as concerns have been raised over the dissolution of Al (III) in water and links to Alzheimers disease. In addition, the strong affinity for AA towards arsenate reduces uptake capacity after regeneration.
References


REFERENCES


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REFERENCES


Chapter 7

Overall conclusions and further work

7.1 Overall conclusions

An iron oxide material was developed at Loughborough University to be used within both batch and column operations (sample NN). The experimental method was optimised to increase the particle size and robustness of the precipitate produced by reacting hydrous ferric chloride and sodium hydroxide. A freeze-thaw rig was used to control the rate of freezing to −1 °C hour and the material thawed in a fridge to maximise the size of granules produced.

This material was compared with another sample, also produced at Loughborough University via a larger-scale process, with a simpler post-treatment process; the iron oxide produced was left to air dry rather than undergo any freeze-thaw process (sample VL). This resulted in large, solid chunks of material which were crushed to size, rather than discrete granular material. A further iron oxide was selected for comparison, a commercially available product, supplied by GEH, Wasserchemie (sample GEH).

All three iron oxides were characterised physically and chemically, and appeared to be robust, unaggregated material, although were more powdery on the surface compared to a synthetic akaganeite. The difference in production method became evident when the specific surface area and pore size distri-
Chapter 7. Overall conclusions and further work

butions were determined by nitrogen porosimetry. BET specific surface area analysis showed that all samples fell in the range 250–300 m²/g. Both sample NN and VL possessed a high degree of macroporosity, as determined by the DFT method due to the methods used for production. Poor pH control and degree of crystallinity affects the pore size distribution.

X-ray diffraction (XRD) revealed that the amount of chloride in the samples affected the XRD output. VL contained the most chloride and was more crystalline, followed closely by GEH. Sample NN contained very little chloride and was the most amorphous material. pH also affected the crystallinity, and samples GEH and VL appeared to consist of more than one iron oxide phase, due to the production pH > 5.

pH titrations and zeta potential measurements of each sample were carried out. the latter repeated with anionic species present, namely arsenate, phosphate and fluoride. Hence, the point of zero net proton charge (PZNPC) and the isoelectric point (IEP) for each material was calculated. The former parameter varied in the range 4.2–6.5 with sample NN possessing the highest PZNPC, followed by GEH and VL. These values were not greatly affected by altering the background electrolyte concentration (0.1, 0.01 and 0.001 M NaNO₃).

A trend was noted in the drift of PZNPC and chloride content of each material. On adding samples GEH and VL to water, the equilibrium pH values were 4 and 3.5 respectively. Both materials contained a reasonable amount of chloride (0.61 and 1.15 mmol/g) which releases slowly on contact with water.

The IEP however was not significantly affected by the presence of chloride, all samples were approximately equal, in the range 7–8. This is possibly due to the internal surface being more negatively charged due to the adsorbed chloride. This would not be observed by zeta potential analysis, since this method measures the surface potential at the slipping plane, some distance from the surface.

The zeta potential was also determined in the presence of the anionic species used in adsorption experiments, namely arsenate, phosphate and fluoride. Both arsenate and phosphate reduced the IEP by forming inner-sphere complexes at the surface. The greater negative charge is balanced by a greater uptake of H⁺.
Chapter 7. Overall conclusions and further work

It was less clear with fluoride whether inner-sphere complexes were formed as measurements were not taken around the pK\text{a} value of fluoride, where most uptake occurs. Also fluoride is chemically different from arsenate and phosphate because it cannot contribute a proton to the negative surface at pH > IEP, hence it is not so easily adsorbed onto the iron oxide surface.

Adsorption experiments with the anionic species mentioned increased the uptake capacity with decreasing pH, as expected for anion adsorption. Negative species (as determined by speciation diagrams constructed for each moiety studied) are more strongly attracted to the surface at low pH. Both arsenate and phosphate are able to adsorb at pH > IEP as they are able to contribute a proton to the surface to enable ligand exchange with water to occur. Fluoride adsorption decreases sharply below the IEP.

The nature of the material affects arsenate and phosphate uptake. More crystalline materials are more likely to form bidentate (two bonds) complexes at the surface that suppress uptake capacity. Hence, for both arsenate and phosphate, sample NN has a higher capacity (1 mmol/g and 0.75 mmol/g) than both samples GEH and VL (approximately 0.9 mmol/g and 0.65 mmol/g) respectively. Arsenate capacity is higher for all samples than phosphate since it is a larger ligand and can interact more strongly with the iron oxide surface and therefore arsenate is preferred.

Fluoride uptake, however, was not affected by the material type, as all samples had an uptake capacity of 1.8 mmol/g as fluoride forms monodentate bonds with the surface. Hence, the uptake is much greater than for arsenate and phosphate, as both form bidentate bonds with decreasing pH and increasing surface loading.

The two types of bonding could explain the difficulties in fitting the Langmuir or Freundlich equations to the sample data. These empirical models do not take into account surface complexation or any electric double layer considerations. However, the Langmuir model fitted the anion isotherm data best and Freundlich the cationic (cadmium) data.

Cadmium uptake increased with increasing pH, as the surface becomes more negative attracting positive ions. The iron oxide surface appears to have an almost equal number of positive and negative surface sites, depending on pH
as cadmium uptake was 1.3–1.4 mmol/g. Cadmium is attached by both monodontate and bidentate species, with monodontate complexes having a greater role as the pH increases. Hence, cadmium capacity is greater than arsenate and phosphate, but less than fluoride. Limitations of the Freundlich model are noted as bidentate bonding increases with increasing surface loading.

The effect of other anions on the arsenate uptake capacity was determined in column mode. The same experimental conditions were used as for arsenate, and no attempt was made to optimise the operating parameters. The experimental shortfalls were also discussed. Distribution coefficients were determined for each experiment.

Arsenate uptake was more strongly affected by the presence of phosphate than fluoride, as the former is chemically similar to arsenate and is able to compete for similar sites. Arsenate has a greater affinity in both As/F and As/P column runs. The pH profile of samples GEH and VL runs were very different to sample NN, as the raised chloride content caused the pH to drop as HCl was slowly leached. Hence both phosphate and fluoride were able to compete more strongly for surface sites, hence the relative affinity for arsenate was much lower.

The pH effect was most strongly observed in both As/F and P/F runs as fluoride broke through very quickly. Fluoride exhibited chromatographic elution, both arsenate and phosphate displaced previously adsorbed fluoride. At near neutral conditions, fluoride is fully dissociated hence cannot donate a proton to the surface for ligand exchange.

Phosphate appeared to have a stronger affinity than arsenate in a binary P/F and As/F system. This could be due to the faster kinetics of phosphate adsorption, enhancing the uptake capacity. In the ternary system (As/P/F), the distribution coefficients for As and P were almost equal. The reduced availability of surface sites for adsorption could increase the amount of bidentate bonding, further suppressing uptake capacity. There appeared to be some mutual desorption of both phosphate and arsenate, indicating the similarity in affinities.

The evidence of the presence of bidentate bonding in both the As/P and As/P/F column experiments is in the delayed elution of arsenate in As/P and
phosphate in As/P/F. A stronger bond is formed with bidentate complexes, hence is more difficult to elute. The regeneration process with 0.1 M NaOH was successful with > 85 % being eluted. Fluoride was more easily eluted. Further evidence of the selectivity and type of surface complexes formed. The solution process was not optimised and the adsorbents only went through a single cycle of adsorption-regeneration.

All the experiments have indicated that the iron oxide samples tested are suitable adsorbents for both anionic and cationic species, depending on the solution pH. The materials are stable in water, iron was not detected in solution at pH 4, 7 and 9. Sample VL redissolved very slightly, 0.04 mg/L. well within the 0.2 mg/L limit for drinking water.

This presents a distinct advantage over activated alumina, an adsorbent often used for water treatment. Concerns have been raised over the amount of soluble Al (III) in water that have been linked to Alzheimer's disease and the high affinity for arsenate limits the regeneration efficiency to approximately 90 %. In addition, ferric salts have a higher removal capacity for arsenate and amorphous ferric hydroxide possesses 5-10 times greater capacity for arsenic than activated alumina.

### 7.2 Further work

This study has shown that an iron oxide material can be used to successfully remove both anionic and cationic pollutants. Due to ease of use, low cost of production and disposal method, iron oxide could be an industrially viable adsorption media. However, there are several areas which could be investigated further to optimise the adsorption process and understand further the uptake mechanisms and effect of competing ions on uptake capacity.

Column experiments should be carried out to optimise the process by decreasing the flowrate and particle size and increasing the aspect ratio and inlet concentration. Equimolar binary and ternary systems with 0.133 mmol/L total concentration should be completed to enable mass transfer coefficients to be calculated.
Further anionic species should be studied for the competitive effects on arsenate uptake in column operation. For example, both molybdate and silicate are expected to affect arsenate removal. The pH effects on arsenate, phosphate and fluoride systems should be studied by reducing the influent pH to 4, to enable a more accurate comparison of samples NN, GEH and VL to be made.

The elution process should be investigated, by reducing the flowrate to enhance the separation of species to determine relative affinity for each species to the iron oxide surface. The concentration and type of eluent should also be examined. The ability of other anionic species to desorb pre-loaded iron oxide material with arsenate should be investigated as an alternative means of determining the preference of one species over another.

Leach tests should be developed for pre-loaded iron oxide material with the anionic species studied. This would confirm the suitability of the spent adsorbent to be sent to landfill, rather than a regeneration process.

The kinetics of arsenate, phosphate and fluoride uptake should be determined, both as single ion solutions and as binary and ternary solutions. Hence, the competitive effects exhibited from column experiments may be further explained and the rate of uptake modelled.

The effect of mixed solutions of anionic and cationic species should also be studied. It would be expected that the presence of both positive and negative species would enhance the anionic uptake, depending on solution pH.
Appendix A

Speciation calculation

A.1 Phosphate calculations

\[ \text{H}_3\text{PO}_4 \rightarrow \text{H}^+ + \text{H}_2\text{PO}_4^- \quad K_1 = \frac{[\text{H}_2\text{PO}_4^-][\text{H}^+]}{[\text{H}_3\text{PO}_4]} = 10^{-2.03} \quad (A.1) \]

\[ \text{H}_2\text{PO}_4^- \rightarrow \text{H}^+ + \text{HPO}_4^{2-} \quad K_2 = \frac{[\text{HPO}_4^{2-}][\text{H}^+]}{[\text{H}_2\text{PO}_4^-]} = 10^{-7.19} \quad (A.2) \]

\[ \text{HPO}_4^{2-} \rightarrow \text{H}^+ + \text{PO}_4^{3-} \quad K_3 = \frac{[\text{PO}_4^{3-}][\text{H}^+]}{[\text{HPO}_4^{2-}]} = 10^{-12.03} \quad (A.3) \]

\[ C_T = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] \quad (A.4) \]

\[ [\text{H}_3\text{PO}_4] = C_T \left[ 1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1K_2}{[\text{H}^+]^2} + \frac{K_1K_2K_3}{[\text{H}^+]^3} \right] \quad (A.5) \]

\[ [\text{H}_2\text{PO}_4^-] = C_T \left[ 1 + \frac{[\text{H}^+]}{K_1} + \frac{K_2}{[\text{H}^+]} + \frac{K_2K_3}{[\text{H}^+]^2} \right] \quad (A.6) \]

\[ [\text{HPO}_4^{2-}] = C_T \left[ 1 + \frac{[\text{H}^+]^2}{K_1K_2} + \frac{[\text{H}^+]}{K_2} + \frac{K_3}{[\text{H}^+]^3} \right] \quad (A.7) \]

\[ [\text{PO}_4^{3-}] = C_T \left[ 1 + \frac{[\text{H}^+]^3}{K_1K_2K_3} + \frac{[\text{H}^+]^2}{K_2K_3} + \frac{[\text{H}^+]}{K_3} \right] \quad (A.8) \]

\[ = C_T - [\text{H}_3\text{PO}_4] - [\text{H}_2\text{PO}_4^-] - [\text{HPO}_4^{2-}] \quad (A.9) \]
A.2 Phosphite calculations

\[ \begin{align*}
\text{H}_3\text{PO}_3 & \rightarrow \text{H}^+ + \text{H}_2\text{PO}_3^- \\
\text{K}_1 &= \frac{[\text{H}_2\text{PO}_3^-][\text{H}^+]}{[\text{H}_3\text{PO}_3]} = 10^{-1.8} \quad (A.10) \\
\text{H}_2\text{PO}_3^- & \rightarrow \text{H}^+ + \text{HPO}_3^{2-} \\
\text{K}_2 &= \frac{[\text{HPO}_3^{2-}][\text{H}^+]}{[\text{H}_2\text{PO}_3^-]} = 10^{-6.13} \quad (A.11)
\end{align*} \]

\[ \begin{align*}
\text{C}_T &= [\text{H}_3\text{PO}_3] + [\text{H}_2\text{PO}_3^-] + [\text{HPO}_3^{2-}] \\
[\text{H}_3\text{PO}_3] &= \frac{\text{C}_T}{1 + \frac{\text{K}_1}{[\text{H}^+]} + \frac{\text{K}_1\text{K}_2}{[\text{H}^+]^2}} \quad (A.13) \\
[\text{H}_2\text{PO}_3^-] &= \frac{\text{C}_T}{1 + \frac{[\text{H}^+]}{[\text{K}_1]}} \quad (A.14) \\
[\text{HPO}_3^{2-}] &= \frac{\text{C}_T}{1 + \frac{[\text{H}^+]^2}{\text{K}_1\text{K}_2} + \frac{[\text{H}^+]}{\text{K}_2}} \quad (A.15) \\
&= \text{C}_T - [\text{H}_3\text{PO}_3] - [\text{H}_2\text{PO}_3^-]
\end{align*} \]

A.3 Fluoride calculations

\[ \begin{align*}
\text{HF} & \rightarrow \text{H}^+ + \text{F}^- \\
\text{K}_1 &= \frac{[\text{F}^-][\text{H}^+]}{[\text{HF}]} = 10^{-3.18} \quad (A.17)
\end{align*} \]

\[ \begin{align*}
\text{C}_T &= [\text{HF}] + [\text{F}^-] \quad (A.18) \\
[\text{HF}] &= \frac{\text{C}_T}{1 + \frac{\text{K}_1}{[\text{H}^+]}} \quad (A.19) \\
[\text{F}^-] &= \frac{\text{C}_T}{1 + \frac{[\text{H}^+]}{[\text{K}_1]}} \quad (A.20) \\
&= \text{C}_T - [\text{HF}] \quad (A.21)
\end{align*} \]
A.4 Cadmium calculations

\[
\text{Cd}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{Cd(OH)}^+ + \text{H}^+ \quad \text{(A.22)}
\]

\[
K_1 = \frac{[\text{Cd(OH)}^+][\text{H}^+]}{[\text{Cd}^{2+}]} = 10^{-10.1}
\]

\[
\text{Cd}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Cd(OH)}_2(\text{aq}) + 2\text{H}^+ \quad \text{(A.23)}
\]

\[
K_2 = \frac{[\text{Cd(OH)}_2(\text{aq})][\text{H}^+]^2}{[\text{Cd}^{2+}]} = 10^{-20.4}
\]

\[
\text{Cd}^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{Cd(OH)}_3^- + 3\text{H}^+ \quad \text{(A.24)}
\]

\[
K_3 = \frac{[\text{Cd(OH)}_3^-][\text{H}^+]^3}{[\text{Cd}^{2+}]} = 10^{-33.3}
\]

\[
\text{Cd}^{2+} + 4\text{H}_2\text{O} \leftrightarrow \text{Cd(OH)}_4^{2-} + 4\text{H}^+ \quad \text{(A.25)}
\]

\[
K_4 = \frac{[\text{Cd(OH)}_4^{2-}][\text{H}^+]^4}{[\text{Cd}^{2+}]} = 10^{-47.4}
\]

\[
C_T = [\text{Cd}^{2+}] + [\text{Cd(OH)}^+] + [\text{Cd(OH)}_2(\text{aq})] + [\text{Cd(OH)}_3^-] + [\text{Cd(OH)}_4^{2-}] \quad \text{(A.26)}
\]

\[
[Cd^{2+}] = \frac{C_T}{1 + \frac{K_1}{[\text{H}^+]}} \quad \text{(A.27)}
\]

\[
[Cd(OH)^+] = \frac{C_T}{1 + \frac{[\text{H}^+] + K_2}{K_1[H^+]} + \frac{K_3}{K_1[H^+]^2} + \frac{K_4}{K_1[H^+]^3}} \quad \text{(A.28)}
\]

\[
[Cd(OH)_2(\text{aq})] = \frac{C_T}{1 + \frac{[\text{H}^+]^2}{K_2} + \frac{K_1[H^+]}{K_2[H^+]^2} + \frac{K_3}{K_2[H^+]^3} + \frac{K_4}{K_2[H^+]^4}} \quad \text{(A.29)}
\]

\[
[Cd(OH)_3^-] = \frac{C_T}{1 + \frac{[\text{H}^+]^3}{K_3} + \frac{K_1[H^+]}{K_3[H^+]^2} + \frac{K_3}{K_3[H^+]^3} + \frac{K_4}{K_3[H^+]^4}} \quad \text{(A.30)}
\]

\[
[Cd(OH)_4^{2-}] = \frac{C_T}{1 + \frac{[\text{H}^+]^4}{K_4} + \frac{K_1[H^+]}{K_4[H^+]^2} + \frac{K_3[H^+]}{K_4[H^+]^3} + \frac{K_4}{K_4[H^+]^4}} \quad \text{(A.31)}
\]
Appendix B

Ashing steps for Varian GTA-100 graphite furnace

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<th>Step</th>
<th>Temperature (°C)</th>
<th>Time (s)</th>
<th>Flow (L/min)</th>
<th>Store signal (S), read steps (R)</th>
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