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Jelena Đorđević, Goran T. Vladisavljević & Tatjana Trtić-Petrović

Liquid phase membrane extraction of targeted pesticides from manufacturing wastewaters in a hollow fiber contactor with feed-stream recycles

[a]Jelena Đorđević, [b]Goran T. Vladisavljević, [a]Tatjana Trtić-Petrović*

[a]Laboratory of Physics, Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia
[b]Chemical Engineering Department, Loughborough University, Loughborough, Leicestershire, UK

*Corresponding author:
Tatjana Trtić-Petrović
Laboratory of Physics
Vinča Institute of Nuclear Sciences
University of Belgrade
P.O. Box 522, 11001 Belgrade, Serbia
Fax: +381 11 644 7963
Telephone: +381 11 644 7700
E-mail address: ttrtic@vinca.rs

Abstract

A two-phase membrane extraction in a hollow fibre contactor with feed-stream recycle was applied to remove selected pesticides (tebufenozide, linuron, imidacloprid, acetamiprid and dimethoate) from their mixed aqueous solutions. The contactor consisted of 50 polypropylene hollow fibers impregnated with 5% tri-*n*-octylphosphine oxide in di-*n*-hexyl ether. For low polar pesticides with log $P > 2$ (tebufenozide and linuron), the maximum removal efficiency increased linearly from 85 to 96% with increasing the feed flow rate. The maximum removal efficiencies of more polar pesticides were significantly higher under feed recirculation (86%)

1

than in a continuous single pass operation (30%). It was found from the Wilson's plot that the mass transfer resistance of the liquid membrane can be neglected for low polar pesticides. The pesticide removals from commercial formulations were similar to those from pure pesticide solutions, indicating that built-in adjuvants did not affect the extraction process.

1. Introduction

Toxic chemicals originated from manufacturing wastewaters are considered as a threat to human health and ecological systems [1]. Wastewaters from pesticide formulating and manufacturing plants are one of the main sources of pollution [2]. Depending on the technology implemented in a wastewater treatment plant (WWTP), the pesticide concentration in final effluents can reach 500 mg dm^{-3} [3]. The European Union adopted the Water Framework Directive (WFD) to secure water resources [4]. The maximum allowable discharge concentration of a single pesticide in wastewater is typically 0.05 mg dm^{-1}, but may vary depending on the region and country [5].

Pesticide manufactures use different wastewater treatments to remove or destroy pesticide active ingredients in the wastewater. The treatment of these wastewaters includes a pre-treatment step (emulsion breaking, membrane filtration, and settling) to remove carriers and additives such as petroleum hydrocarbons, surfactants, antifoams and wetting agents, and the main treatment (activated carbon adsorption, chemical oxidation, chemical precipitation, and hydrolysis) to remove active pesticide ingredients [6]. Many of these methods pose clear disadvantages, such as low removal efficiency of pollutants, high energy consumption, high cost, disposal issues due to large amount of sludge, etc. The studies conducted on full-scale plants [7-9] confirmed that the removal efficiencies of pesticides in WWTPs are insufficient. Hence, there is an urgent need to develop more efficient technologies to reduce the current emissions of pesticides into aquatic environments.

Liquid membrane processes such as two-phase partitioning bioreactors, emulsion liquid membranes and supported liquid membranes can be a viable cost-effective alternative to biological treatment and solvent extraction for the removal and pre-concentration of

2

micropollutants from wastewater [10]. The application of hollow-fibre membrane contactors (HFMC) for liquid phase membrane extraction (LPME) has been studied extensively. The main advantages of HF-LPME are high surface area per unit module volume (up to 500 m^{-1}), large and stable interface under variable feed phase compositions and flow rates, no need for density differences leading to a greater choice of extraction solvents and a good opportunity for process automation [11].

HFMCs have been widely used for the removal of metals [10] and hydrocarbons [12-15] from wastewater. HF-LPME can be operated in a continuous flow mode or batchwise. If the specified degree of solute extraction cannot be achieved in a continuous flow HF-LPME process with a single pass of the feed stream through the contactor, the feed stream is recycled between the module and a mixed tank [16-18].

In our previous study, a continuous flow HF-LPME was used to remove pesticides of different chemical classes (acetamiprid, dimethoate, imidacloprid, linuron, and tebufenozide) from aqueous solutions [19]. The pesticides polarity expressed in terms of the n-octanol-water partition coefficient (log P) was in the range of 0.46-4.38. The pesticide removal efficiency, E_R, widely ranged from 6 to 95%, depending on the feed flow rate and the polarity of each pesticide. The mass transfer of low polar pesticides (log P > 3) in HF-LPME system was controlled by their rate of diffusion in the aqueous feed stream [19]. The mass transfer of these pesticides strongly depended on the feed stream flow rate and consequently, the applied system delivered better performances when operated under higher feed flow rate. The mass transfer of more polar pesticides (log P < 1.5) was mainly affected by their low log P values and the impact of the feed flow rate on the mass transfer rate was limited. For low polar pesticides, high E_R values were obtained in a continuous HF-LPME process, but for more polar pesticides, a continuous flow HF-LPME system was inefficient. The aim of this study is to investigate the removal of pesticides from pure aqueous solutions and synthetic wastewater samples consisting of a mixture of pesticides of different polarities using HF-LPME with recycling feed stream.

2. Experimental

2.1. *Materials*

The pesticides investigated in this work were acetamiprid (ACE, *N*-[(6-chloro-3-pyridyl)methyl]-*N'*-cyano-*N*-methyl-acetamidine), dimethoate (DIM, *O,O*-dimethyl *S*-[2-

3

(methylamino)-2-oxoethyl]dithiophosphate), imidacloprid (IMI, *N*-[1-[(6-chloro-3-pyridyl)methyl]-4,5-dihydroimidazol-2-yl]nitramide), linuron (LIN, 3-(3,4-dichlorophenyl)-1-methoxy-1-methylureum), and tebufenozide (TEB, *N*-tert-butyl-*N*′-(4-ethylbenzoyl)-3,5 dimethylbenzohydrazide). A commercial formulation of these pesticides with a purity of 95% was obtained from Galenika-Fitofarmacija (Serbia). Stock standard solutions of individual pesticides (200 mg dm^{-3}) were prepared in methanol and stored at -20°C. Aqueous working solutions (feed phases) containing 20 mg dm^{-3} of each pesticide were prepared daily by diluting the stock solutions with either Milli-Q water or tap water. Tri-*n*-octylphosphine oxide (TOPO), di-*n*-hexyl ether (DHE), methanol and HCl were of analytical grade, purchased from Sigma-Aldrich (USA). The Celgrad$^{®}$ X-20 polypropylene hollow fibres (HFs) with an inner and outer diameter of 280 and 660 µm, respectively, and porosity of 28% were obtained from Hoechst Celanese Co. (USA).

2.2. *Experimental setup and procedure*

A HFMC consisted of a cylindrical glass tube packed with 50 parallel HFs, glued together with epoxy resin at both ends. The effective length of each HF was 12.5 cm, the total effective inner surface area of the membrane was 15.4 cm^2 and the volume of the organic phase entrapped in the membrane pores, V_0 was 0.52 cm^3 [20].

The experimental setup shown in Figure 1 consists of a HFMC (C), two peristaltic pumps (P1 and P2) (Cole-Parmer, Masterflex), a feed reservoir (F) with magnetic stirrer (M), an acceptor phase reservoir (A), and Masterflex Norprene tubing (Cole-Parmer, PharMed). The membrane pores were impregnated with the organic phase (5% TOPO in DHE) by pumping the organic solution through the lumens of the HFs, after which both sides of the membrane were rinsed with water. The extra-capillary space of the module was loaded with the acceptor phase (2 mol dm^{-3} HCl), which was stagnant during extraction. The feed solution (20 cm^3) was pumped at 0.5-1.8 cm^3 min^{-1} from the feed reservoir through the lumens of the HFs and then back to the feed reservoir. During extraction, 0.05 cm^3 aliquots of the feed solution were taken every 5 or 10 min for analysis. All experiments were carried out at constant temperature of 22°C. After each experiment, the liquid phases were removed from the contactor by rinsing the lumens of the HFs with 5 cm^3 of methanol, followed by washing the lumens of the HFs and the membrane pores with water.

4

Figure 1. Schematic of the experimental set-up for HF-LPME under recirculation mode of operation: C – contactor, P1-P2 – peristaltic pumps, F – feed solution, A – acceptor solution, M – magnetic stirrer.

The HPLC analysis of the samples was performed using Agilent 1100 liquid chromatograph (USA) with Zorbax XDB-C18 column (4.6 mm × 250 mm, 3.5 μm particle size) and DAD detector at 254 nm. The flow rate was 0.7 cm^3 min^{-1} and an aliquot of 20 μl of the sample was injected into HPLC system. The mobile phase was a mixture of methanol (A) and deionized water (B) and the following gradient profile was run: 0.0 min 43% A and 57% B, then 7 min 70% A and 30% B, and 20 min the initial composition. The system was controlled by the Chemstation software.

3. Results and discussion

Five pesticides (ACE, DIM, IMI, LIN and TEB) were selected based on their significantly different chemical structure and physicochemical properties: ACE and IMI are neonicotinoids, DIM is an organophoshate, LIN is a substituted phenylurea, and TEB is a diacylhydrazine derivative. They are all insecticides, except LIN which is a herbicide. The selected pesticides can be divided into three groups based on their polarity: low polar pesticides, log P > 2 (LIN and TEB with log P of 3.12 and 4.38), moderately polar, 2 > log P > 1 (DIM with log P of 1.37) and polar pesticides, log P < 1 (IMI and ACE with log P of 0.56 and 0.8). They all exist in uncharged form over a wide pH range (2-9), since they are either very week acids or very week bases [21]. The composition of organic phase was found to significantly affect the removal efficiency of pesticides from the aqueous phase [21]. TOPO agent is able to form hydrogen-bound complexes with various solutes due to a lone pair of electrons on the oxygen atom, which can enhance the extraction of polar pesticides. The liquid membrane used in this work was 5% TOPO in DHE, selected for its ability to simultaneously extract various pesticides from the feed stream [19, 21].

3.1. *The influence of feed flow rate on the process performances*

In Figure 2, the pesticide concentrations in the feed reservoir at any time t (C_F^t) are plotted relative to their initial values (C_F^0) for the feed flow rate ranging from 0.5 to 1.8 cm^3 min^{-1}. The feed stream was recycled back to the feed reservoir after passing through the module to

5

improve the removal efficiency of the pesticides. The pesticide concentration decreased significantly with time indicating that the extraction step was efficient. Due to a steady decrease in the driving force for mass transfer, the pesticide concentration decreased exponentially and gradually reached a minimum limiting value. A decline in the pesticide concentration was the most rapid in the first 20 min and more pronounced at higher flow rates and for less polar compounds. The final pesticide concentration depended on the feed flow rate and the investigated pesticide. After 40 min of operation at the highest feed flow rate applied, the concentration of low polar pesticide TEB (Figure 2a) was just 4 % of its initial content. The pesticide concentration in the feed reservoir decreased more rapidly at the higher feed flow rates, due to more efficient mass transfer. The same trend was observed for medium polar compound DMT (Figure 2b) and polar compound ACE (Figure 2c), but the limiting pesticide concentrations and the time needed to reach them were higher. Less polar pesticides are more soluble in the liquid membrane and can be more efficiently removed from the feed stream. The minimum pesticide concentration in the feed phase ranged between 4 and 15% of C_F^0 and was established after 40 and 80 min of operation for low polar and polar compounds, respectively. The quantity of pesticides, which were back-extracted into the acceptor phase at the end of extraction, was less than 0.1%. Thus, almost all pesticide extracted from the feed stream was accumulated in the organic phase. However, a three-phase extraction system was selected because of the low holdup volume of the organic phase in the pores compared to the volume of the extra-capillary space and a high capacity of the organic phase [19].

Figure 2. The relative concentration of pesticide in the feed stream as a function of time at different feed flow rates for: (a) TEB, (b) DIM, and (c) ACE. The feed flow rate (cm³ ml⁻¹): ◊ – 0.5, ▽ – 0.8, △ – 1.1, ○ – 1.5, and □ – 1.8.

Figure 3 shows the effect of feed flow rate, Q_F on the maximum percentage of pesticide removal, $E_{R,max}$ calculated based on the pesticide concentration at quasi-steady state. $E_{R,max}$ depends on the polarity of the pesticide and Q_F. For low polar pesticides, $E_{R,max}$ was 90-96% for TEB and 85-95% for LIN, and increased linearly with increasing Q_F. At higher Q_F values, concentration polarisation was more supressed, leading to the lower pesticide concentrations in the aqueous phase near the interface and more efficient partitioning of the

6

pesticide from the aqueous phase into the organic phase. The highest $E_{R,max}$ was achieved for the most polar pesticide TEB, due to its highest solubility in the organic phase. The impact of Q_F on $E_{R,max}$ was more pronounced for polar pesticides (IMI and ACE). Low polar pesticides were efficiently removed even at the lowest Q_F due to their high partition coefficients. The polar pesticides required higher flow rates to counterbalance low partition coefficients. $E_{R,max}$ of ACE and IMI increased from 63 to 86% as Q_F increased from 0.5 to 1.8 cm^3 min^{-1}. In a single-pass HF-LPME system, $E_{R,max}$ for ACE and IMI was less than 20% at $Q_F = 1.8$ cm^3 min^{-1} [19]. On the other hand, the maximum removal efficiency of TEB in feed recycling and single-pass mode was nearly the same (95 and 96%), indicating that the extraction of TEB was dominated by partitioning and the effect of hydrodynamic conditions was limited.

Figure 3. The maximum removal efficiency of the pesticides as a function of feed flow rate: □ – TEB, ○ – LIN, △ – DIM, ▽ – ACE, ◊ – IMI.

3.2. *Overall mass transfer coefficient*

The mass transfer of a pesticide through liquid membrane consists of diffusion from a bulk of the aqueous feed phase to the membrane interface, partitioning between the organic and aqueous phase, diffusion through the organic phase entrapped within the membrane pores, and diffusion into the acceptor phase. In our previous work [19], the stripping of the pesticides in the acceptor phase was found to be less than 3%. The accumulation of low polar compounds such as LIN and TEB in the organic phase derives from their high partition coefficients, resulting in a high loading capacity of the organic phase for low polar pesticides. Therefore, diffusion in the acceptor phase can be neglected and the overall mass-transfer resistance, R_F is a sum of the resistances of the feed phase and the organic phase:

$$R_F = \frac{1}{K_F} = \frac{1}{k_F} + \frac{d_i}{k_M d_{LM} m_F} \tag{1}$$

where K_F is the overall mass transfer coefficient based on the feed phase driving force, k_F and k_M are the mass transfer coefficients in the feed and organic phase, d_{LM} is the log mean diameter of a hollow fibre, and m_F is the partition coefficient.

7

The estimation of K_F in recirculation mode is more challenging than in a single pass operation, because the concentrations of the solutes in the feed reservoir continuously vary with time until a quasi-state state is established when the net mass transfer rate is zero. The rate of decline of the pesticide concentration in the unsteady-state part of the process can be used to estimate K_F:

$$K_F = -\frac{Q_F}{A_i} ln\left[1 - \frac{V_F}{Q_F} \frac{d\,ln(C_F^0 / C_F^t)}{dt} \right] \quad (2)$$

where V_F is the total volume of the feed and A_i is the effective inner surface area of the membrane. Eq. (2) is a simplified form of the general solution [20], which is valid for high partition coefficients of the solutes.

The typical $ln(C_F^0 / C_F^t)$ vs. t plots used to determine K_F are shown in Figure S1 in the Electronic supplementary material. A linear relationship between $ln(C_F^0 / C_F^t)$ and t was obtained in all cases with $R^2 > 0.95$. The slopes of these lines are listed in Table S1 in the Electronic supplementary material. The K_F values were calculated using Eq. (2) based on the line gradients in Table S1. K_F was a linear function of Q_F in all cases with $R^2 > 0.97$ (Figure 4), indicating that $K_F \approx Q_F^b$, i.e. $Sh \propto Re^b$. For low polar pesticides, K_F strongly depended on the feed flow rate, with more than three-fold increase in K_F as a result of an increase in Q_F from 0.8 to 1.8 cm^3 min^{-1}. This behaviour indicates that R_F is controlled by the feed phase resistance and K_F can be regarded as equal to the mass transfer coefficient in the feed phase, $K_F \approx k_F$. K_F was less dependent on Q_F for moderately polar and polar pesticides than for low polar ones, with K_F increasing only by 40% for DIM and 10% for ACE and IMI over the Q_F range of 0.5-1.8 cm^3 min^{-1}.

Figure 4. The effect of the feed flow rate on the overall mass transfer coefficient for the targeted pesticides: □ – TEB, ○ – LIN, △ – DIM, ▽ – ACE, ◊ – IMI.

Two different modes of operation (feed recirculation and continuous feed) were compared using the overall mass transfer coefficient calculated in the present study and our previous work [19]. A significant increase in K_F was obtained for polar pesticides at all Q_F values. In

the case of low polar pesticides (TEB and LIN), an increase in K_F for both pesticides was observed only at $Q_F = 1.8$ ml min^{-1} (Table 1).

Table 1. Comparison of the overall mass transfer coefficients for the extraction of targeted pesticides in a continuous flow [19] and feed recirculation mode of operation.

Figure 5 shows the Wilson plots of $/1/K_F$ vs. $1/Q_F^b$ for the investigated pesticides. The values of b were the gradients of the best fit lines of K_F vs. Q_F (Figure 4) determined by the least squares method. The intercepts on the $1/K_F$ axis for TEB and LIN are close to zero indicating that the main resistance to the mass transfer of low polar pesticides is the resistance in the feed phase. The intercepts on the $1/K_F$ axis of DIM, ACE and IMI are 13.9, 19.4 and 19.7, respectively, clearly indicating a mass transfer resistance in the organic phase. The similar trends were observed for the same pesticides in HF-LPME with a single pass of the feed through the module [19].

Figure 5. Wilson plot of $1/K_F$ vs $1/Q_F^b$. Legend: $\square$ – TEB, $\bigcirc$ – LIN, $\triangle$ – DIM, ∇ – ACE, $\lozenge$ – IMI.

3.3. *Removal of pesticides from manufacturing wastewater sample*

Wastewaters from the pesticide manufacturing processes usually arise from the cleaning of equipment and process areas and contain active ingredients and various adjuvants. Although the amount of wastewater streams arising from the cleaning of equipment is limited, the regulatory limits for pesticide residues in these waters are typically very low, which means that a LPME under recirculation mode offering high removal efficiencies of pesticides at low water throughputs may be worthwhile.

Figure 6 shows the removal efficiencies of the investigated pesticides from a simulated pesticide wastewater, which was prepared by diluting a mixture of commercial formulations with tap water. The removal efficiencies from the mixture of commercial formulations were similar to those from pure pesticide solutions (Figure 3). Since $E_{R,max}$ values for pure pesticide solutions were close to $E_{R,max}$ for commercial formulations at any Q_F value,

9

adjuvants (inert ingredients) in the commercial formulations had no appreciable effect on the extraction of pesticides.

Figure 6. The removal efficiency of pesticides from diluted commercial pesticide formulations (20 mg dm^{-3} of each pesticide, V_F=20 cm^3, Q_F=1.1 cm^3 min^{-1} as a function of recirculation time. Legend: □ – TEB, ○ – LIN, △ – DIM, ▽ – ACE, ◊ – IMI.

The removal efficiency should be at least 99.75% to reduce the level of each pesticide from 20 to 0.05 mg dm^{-3}, which is the maximum allowable concentration of a single pesticide in the wastewater before discharge [5]. At the maximum feed flow rate used in this study, $E_{R,max}$ ranged from 86% for polar pesticides to 96% for low polar pesticides, which was insufficient to reduce the pesticide concentrations to 0.05 mg dm^{-3}. The efficiency of extraction of solutes from aqueous solutions in a HFMC process can be improved using two contactors in series, operated in such a way that a depleted aqueous phase from the first contactor is sent to the second contactor for further extraction [22]. The same extraction efficiency can be achieved in each stage if the same contact area is used in each contactor. Therefore, using several contactors in series, it is possible to decrease the pesticide concentration in the effluent stream to any level that may be required. Although a poor back-extraction of the pesticides is the main deficiency of the proposed HF-LPME process, it can be used to highly concentrate pesticides into the organic phase. The pesticides can be then effectively (> 95%) removed from the organic phase with methanol.

4. Conclusions

We have developed a simple and efficient method for the removal of pesticides from wastewater streams based on liquid phase membrane extraction in a hollow fibre contactor with feed-stream recycle. The removal efficiency of the selected pesticides strongly depended on their polarity, feed flow rate and operation mode. The removal of polar and moderately polar pesticides was significantly improved by recycling the feed stream between the contactor and a mixed reservoir compared to single-pass operation. At the feed flow rate of 1.8 cm^3 min^{-1}, the concentration of low polar pesticide TEB was reduced to 4% of its initial value after 40 min. The polar pesticides (ACE and IMI) are less soluble in the organic phase resulting in the maximum removal efficiency of 86% at 1.8 cm^3 min^{-1}. It was confirmed on the

10

Wilson's plot that the mass transfer resistance of the liquid membrane can be neglected for low polar pesticides. The removal efficiencies of the same pesticides from commercial formulations were similar to those from pure pesticide solutions, indicating that built-in adjuvants added to the commercial preparations did not affect the pesticide extraction process.

The throughput and efficiency of the investigated liquid phase membrane extraction process can be improved by increasing of back-extraction of the targeted pesticides and using full-scale industrial contactors connected in series or parallel. The effect of addition of ionic liquids in acceptor phase on back-extraction will be investigated.

Symbols

A_i [cm^2] effective inner surface area of membrane

C [mg dm^{-3}] concentration

d_{LM} [cm] log mean diameter of a hollow fibre

E_R [%] removal efficiency of pesticide

$E_{R,max}$ [%] maximum removal efficiency of pesticide

k [cm min^{-1}] Mass transfer coefficient

K [cm min^{-1}] Overall mass transfer coefficients

m_F organic-feed phase partition coefficient

Q [cm^3 min^{-1}] flow rate,

R [min cm^{-1}] overall mass transfer resistance

P n-octanol-water partition coefficient

V [cm^3] volume

Superscripts

t time

F   feed phase

o   organic phase

0   initial value

∞   value at quasi-steady state

ABBREVIATIONS

11

ACE - acetamiprid

DIM - dimethoate

HFMC - hollow fiber membrane contactor

IMI - imidacloprid

LIN - linuron

TEB - tebufenozide

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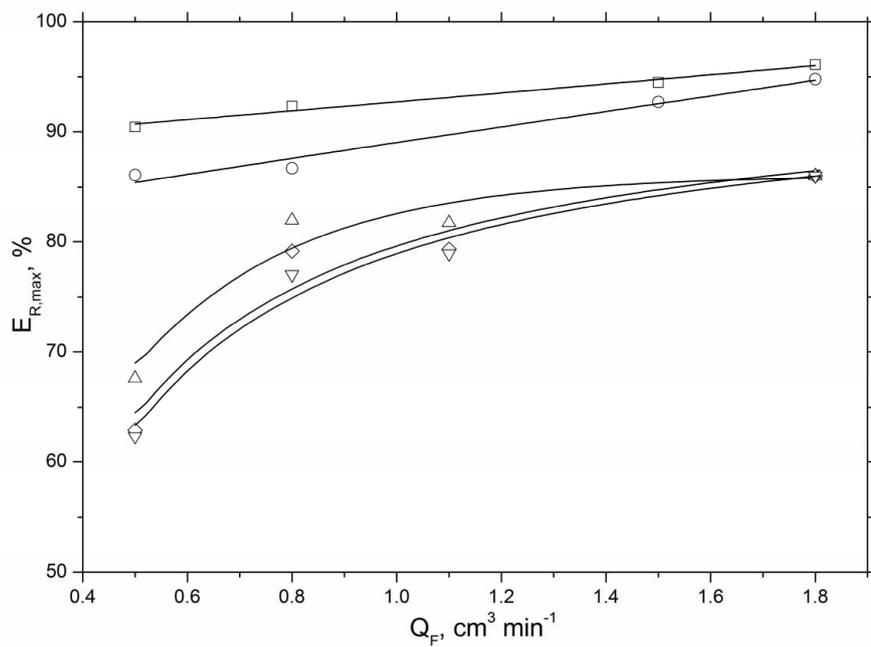
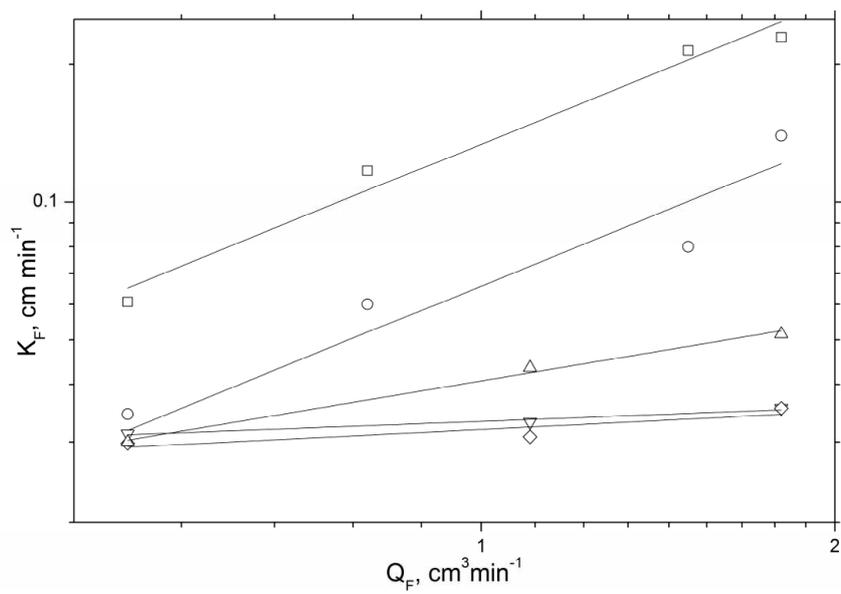The authors have declared no conflict of interest.

References

[1] Shannon MA, Bohn PW, Elimelech M, Georgiadis JG, Marinas BJ, Mayes AM. Science and technology for water purification in the coming decades. Nature 2008;452:301-310.

[2] Kasprzyk-Hordern B, Dinsdale RM, Guwy AJ. The removal of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters. Water Res. 2009;43:363-380.

[3] Chiron S, Fernandez-Alba A, Rodriguez A, Garcia-Calvo E. Pesticide chemical oxidation: state-of-the-art. Water Res. 2000;34:366-377.

[4] European Commission Council Directive on pollution caused by certain dangerous substances discharged into the aquatic environment. Offic. J Euro. Union: L64; 2006.

[5] Hamilton DJ, Ambrus Á, Dieterle RM, Felsot AS, Harris CA, Holland PT, Katayama A, Kurihara N, Linders J, Unsworth J, Wong S-S. Regulatory Limits for Pesticide Residues in Water. Pure Appl. Chem. 2003;75:1123-1155.

[6] Wang LK, Hung YT, Shammas NK. Physicochemical Treatment Processes, Humana Press Inc. New Jersey; 2005.

[7] Köck-Schulmeyer M, Villagrasa M, López de Alda M, Céspedes-Sánchez R, Ventura F, Barceló D. Occurrence and behavior of pesticides in wastewater treatment plants and their environmental impact. Sci. Total Environ. 2013;458-460:466-476.

[8] De Luca A, Dantas RF, Simões ASM, Toscano IAS, Lofrano G, Cruz A, Esplugas S. Atrazine Removal in Municipal Secondary Effluents by Fenton and Photo-Fenton Treatments. Chem. Eng. Technol. 2013;36:2155-2162.

[9] Ormad M, Miguel N, Mosteo R, Rodríguez J, Ovelleiro JL. Pesticides in the modern world - risks and benefits. In: Stoytcheva M (ed). InTech: Croatia; 2011; pp 453-470.

[10] Tandlich R. Liquid membranes, principles and applications in chemical separations and wastewater treatment. In: Kislik VS (ed). Elsevier: Amsterdam; 2010; Ch 8.

[11] Pabby AK, Sastre A M. State-of-the-art review on hollow fibre contactor technology and membrane-based extraction processes. J. Membr. Sci. 2013;430:263-303.

[12] Shen S, Kentish SE, Stevens GW. Effects of operational conditions on the removal of phenols from wastewater by a hollow-fiber membrane contactor. Sep. Purif. Technol. 2012;95:80-88.
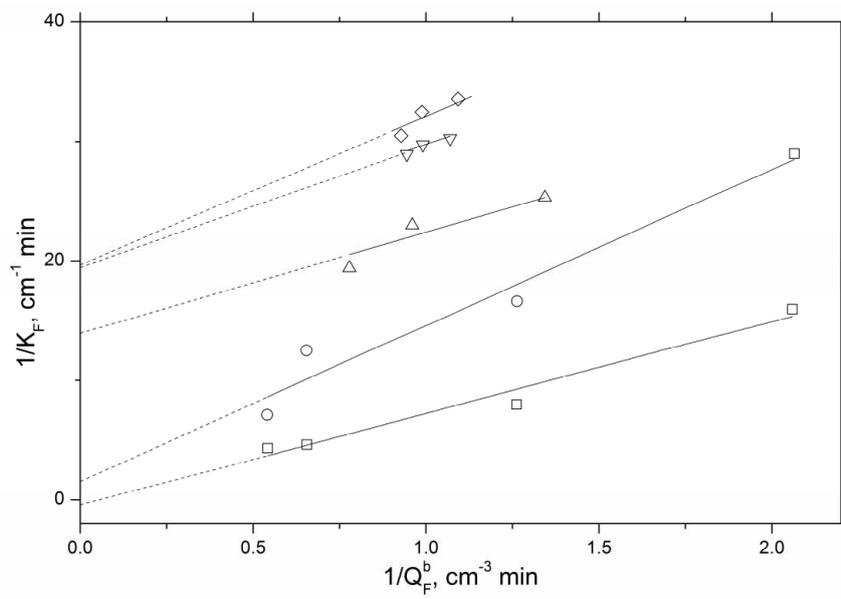
13

[13] Zidi C, Tayeb R, Dhahbi M. Extraction of phenol from aqueous solutions by means of supported liquid membrane (MLS) containing tri-n-octyl phosphine oxide (TOPO). J Hazard. Mater. 2011;194:62-68.

[14] Busca G, Berardinelli S, Resini C, Arrighi L. Technologies for the removal of phenol from fluid streams: A short review of recent developments. J. Hazard. Mater. 2008;160:265-288.

[15] Klaassen R, Jansen AE. The membrane contactor: environmental applications and possibilities. Environ. Progress. 2001;20:37-43.

[16] Qi Z, Cussler EL. Microporous hollow fibers for gas absorption : I. Mass transfer in the liquid. J. Membr. Sci. 1985;23:321-332.

[17] Trtić T M, Vladisavljević GT, Čomor J J. Single-stage and two-stage solvent extraction of Tl(III) in hollow-fiber contactors under recirculation mode of operation. Sep. Sci. Technol. 2001;36:295-312.

[18] Urtiaga A, Abellan MJ, Irabien JA, Ortiz I. Membrane contactors for the recovery of metallic compounds: modelling of copper recovery from WPO processes. J. Membr. Sci. 2005;257:161-170.

[19] Đorđević J, Vladisavljević GT, Trtić-Petrović T. Removal of the selected pesticides from a water solution applying hollow fiber liquid-liquid membrane extraction. Ind. Eng. Chem. Res. 2014;53:4861-4870.

[20] Prasad R, Sirkar KK. Membrane Handbook. In: Ho WSW, Sirkar KK (ed). Chapman & Hall, New York; 1992; pp 727-763.

[21] Trtić-Petrović T, Đorđević J, Dujaković N, Kumrić K, Vasiljević T, Laušević M. Determination of selected pesticides in environmental water by employing liquid-phase microextraction and liquid chromatography–tandem mass spectrometry. Anal. Bioanal. Chem. 2010;397:2233-2243.

[22] Trtić TM, Vladisavljević GT, Archimandritis SC, Varvarigou A, Čomor JJ. Influence of module arrangements on solvent extraction of thallium (III) in hollow fiber contactors. J. Sep. Sci. 2001;24:519-525.

14

Table 1. Comparison of the overall mass transfer coefficients for the extraction of targeted pesticides in a continuous flow [19] and feed recirculation mode of operation.

Q_F, cm^3 min^{-1}	Mode of operation	K_F, cm min^{-1}				
		TEB	LIN	DIM	ACE	IMI
0.5	Continuous	0.094	0.047	0.012	0.011	0.010
	Recirculation	0.041	0.030	0.037	0.032	0.029
0.8	Continuous	0.120	0.063	-	-	-
	Recirculation	0.168	0.060	-	-	-
1.1	Continuous	-	-	0.017	0.014	0.012
	Recirculation	-	-	0.043	0.033	0.031
1.8	Continuous	0.183	0.097	0.026	0.021	0.016
	Recirculation	0.229	0.140	0.051	0.035	0.035

15