Di-2-Ethylhexyl Phosphoric Acid Immobilization with Polysulfone Microcapsules for Cu(II) Extraction

M. Ciopec[*], C.M. Davidescu[*], A. Negrea[*], L. Lupa[*], P. Negrea[*], A. Popa[**]

[*] „POLITEHNICA" University of Timisoara, 2 Piata Victoriei, 300006 Timisoara, Romania,
e-mail: mihaela.ciopec@chim.upt.ro

[**] Romanian Academy, Institute of Chemistry, 24 Mihai Viteazul Blv., 300223 Timisoara, Romania

Abstract: This paper reports the results of the adsorption performance of Cu(II) removal from aqueous solutions by an impregnated resin, polysulfone microcapsules (PS) containing di-2-ethylhexyl phosphoric acid (D2EHPA). The adsorbent was obtained by solvent impregnated resin (SIR) method. The adsorption performance of the studied material was evaluated studying the effects of two physico-chemical parameters: contact time and Cu(II) initial concentration. The adsorption experiments were carried out following batch equilibrium techniques. The kinetic parameters of different models were calculated and discussed. The equilibrium adsorption data were modeled using Freundlich and Langmuir isotherm equations and the corresponding isotherm parameters were calculated and discussed in detail. The material showed good adsorption performance in the removal process of Cu(II) ions from aqueous solution.

Keywords: polysulfone microcapsules; removal; di-(2-ethylhexyl) phosphoric acid, copper

1. Introduction

Ion exchange now is a well-established technology, particularly in water purification and the concentration and removal of hazardous substances at very low concentrations in chemical process industries. For example, it has been applied for the recovery of copper from rayon spinning wastewater and the recovery of gold from cyanide solution in metallurgical industries [1].

Ion exchange resins have low selectivity in the extraction of metal ions and high saturation with ions different from those of interest, decreasing their yield. Highly selective chelating ion exchange resins have been developed, but these are only available for a limited number of metal ions and they are expensive in relation to the generation of polymers with selective ion groups. An interesting alternative to these processes is the use of solvent-impregnated resins (SIR) [2].

The concept of SIR is now well developed and has a strong place in extraction chromatography at analytical application scale and is of potential application at industrial scale [3, 4].

There are four methods available for the immobilization of the desired extractant into the polymeric supporting structure: the dry method, wet method, modified addition method and the dynamic column method [5-7].

The use of macro porous organic polymer supports, with a high surface area and good mechanical stability, is found more suitable for the removal of toxic elements from dilute solution, due to their faster kinetics, ease of regeneration and high adsorption capacity. The development and application of these systems in metal extraction processes has been intensively investigated for the purpose of applications on metal separation and recovery processes [8-17].

In this paper the adsorption performance of the D2EHPA impregnated polysulfone microcapsules (PS) has been investigated. In this purpose, the influence of two physicochemical parameters (contact time and initial concentration of Cu^{2+}) upon the Cu^{2+} adsorption onto PS was studied.

2. Experimental

The polysulfone microcapsules (PS) (Typical $M_n=26,000$, $T_g=190$ºC) by Sigma Aldrich was impregnated with di(2-ethylhexyl)phosphoric acid (D2EHPA) trough dry method. The DEHPA ~ 98.5% used as extractant, was supplied by BHD Chemicals Ltd Poole England and used as received. One gram of polysulfone microcapsules (PS) has been placed for 24 h in absolute ethanol (Chimopar Romania) containing 0.1 g/mL extractant (D2EHPA). The microcapsules have been separated through a porous filter using a vacuum pump, washed with water and dried at 50°C for 24 h [18].

In order to establish the adsorption performance of the D2EHPA impregnated polysulfone (PS), the influence of contact time and initial concentration of copper on the adsorption capacity was investigated.

The adsorption capacity q_t (mg/g) of the PS-D2EHPA towards Cu(II) ions was calculated with the following equation:

$$q = \frac{(C_0 - C_t)\,V}{m} \quad \text{[mg Cu(II)/g PS-D2EHPA]} \quad (1)$$

where C_0 and C_t are the concentrations of Cu(II) ions (mg/L) in the solution initially (t =0) and after a time t (min), respectively, V is the volume of the solution (L) and m is the mass of adsorbent employed (g).

The pH value for copper solutions was pH=5. The pH of the solutions was adjusted to the desired value using 0.05M/2 M NaOH solutions and was determined using a CRISON MultiMeter MM41.

The experiments were performed with samples of 0.1 g impregnated PS-D2EHPA in 25 mL 10 mg/L Cu^{2+} solutions, respectively. The samples have been shaken at different contact times (5, 15, 30, 45, 60, 90, 120, 240, 300 and 360 min).

The equilibrium studies were performed to study the influence of the initial Cu(II) ion concentrations (5, 10, 20, 30 and 40 mg Cu^{2+}/L) on the adsorption process, using the same adsorbent dosage and a 300 min contact time. For batch experiments a mechanical shaker bath MTA Kutesz Type 609/A, Hungary was used.

After contact time elapsed, the suspensions have been filtered and the residual concentration of Cu^{2+} ion in the filtrates has been determined through atomic absorption spectrometry using a Varian SpectrAA 280FS atomic absorption spectrometer.

Stock solution of Cu(II) was prepared using Merck Standard Solutions of Cu(NO3)2 , in HNO3 0.5 mol/L. All other chemicals used for experiments were of analytical reagent grade, and were used without further purification. Distilled water was used in all experiments.

3. Results and Discussion

3.1. Influence of contact time and kinetic studies

To attain the adsorption equilibrium time the results of the effect of stirring time on the adsorption capacity of PS-D2EHPA in the removal process of Cu(II) ions from aqueous solutions are presented in figure 1. It can be seen that the equilibrium is achieved after 300 minutes of shaking. For subsequent experiment, an equilibrium time of 300 minutes was chosen for the sake of convenience.
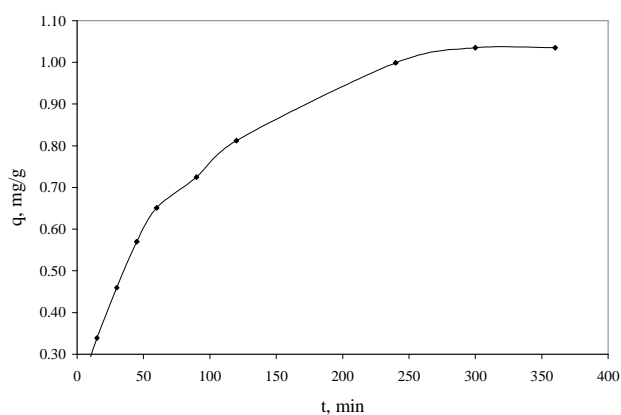

Figure 1. Effect of time on PS-D2EHPA adsorption capacity
m=0.1g, v=25mL, C_0=10mg/L Cu(II), pH=5

Kinetics of adsorption describing the solute uptake rate, which in turn governs the residence time of adsorption reaction, is one of the important characteristics defining the efficiency of adsorption.

In this study, Lagergren-first-order equation and pseudo-second-order equation were used to test the experimental data.

The pseudo-first-order kinetic model can be used to determine the rate constant for the adsorption process and the integrated form is expressed by the following equation [9-11, 18, 19]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

where: q_t and q_e represent the amounts of the Cu(II) adsorbed on the PS-D2EHPA at time t and at equilibrium time, respectively, mg/g; k_1 is the specific adsorption rate constant, min^{-1}.

The linear form of the pseudo-second-order rate expression, based on the solid phase sorption, is given by the following equation [9-11, 18, 19]:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \qquad (3)$$

where: $h = k_{s2} \cdot q_e^2$; k_2 is the pseudo-second-order constant, $min^{-1}(mg/g)^{-1}$. Other terms have their usual meanings.

Figure 2 displays the plot of $\ln(q_e-q_t)$ versus t for Cu(II) adsorption onto PS-D2EHPA. The slopes and intercept of the plot are used to estimate the pseudo-first-order rate constant (k_1) and the equilibrium adsorption capacity (q_e), respectively. A plot of t/q_t versus t should yield a straight line. From the intercept and slope (figure 3) are calculated the second-order rate constant (k_2) and the equilibrium adsorption capacity (q_e) for Cu(II) adsorption onto PS-D2EHPA.
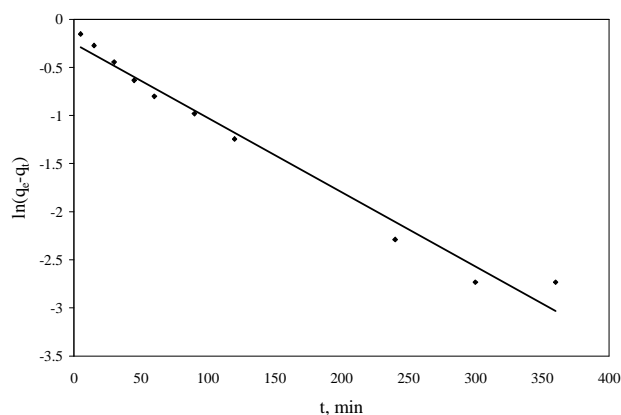

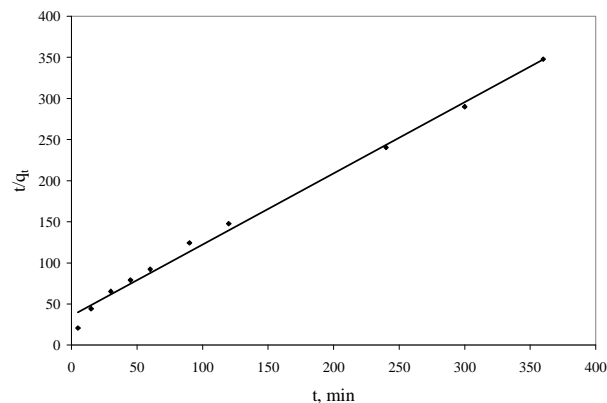
Figure 2. Pseudo-first-order kinetic plot

Figure 3. Pseudo-second-order kinetic plot

TABLE 1. Kinetic parameters for Cu(II) sorption onto PS-D2EHPA

q_e, exp, mg/g	Pseudo-first-order model			Pseudo-second-order model		
	q_e, calc, mg/g	k_1 min^{-1}	R^2	q_e, calc, mg/g	k_2 min^{-1}(mg/g)$^{-1}$	R^2
1.1	0.78	0.00077	0.9783	1.15	0.0213	0.994

The values of the constants, together with the regression coefficients (R^2) obtained in all cases are summarized in Table 1.

Data presented in Table 1 shows that the correlation coefficient for the pseudo-first-order kinetic model was lower than that obtained for the pseudo-second-order model, where the correlation coefficient is very close to 1. Furthermore, the value of the calculated equilibrium sorption capacity ($q_{e,calc}$) using the first-order model, is not close to the experimental value ($q_{e, exp}$). In the case of the pseudo-second-order model the theoretically predicted equilibrium sorption capacity is close to the value experimentally determined. This shows that the kinetics of Cu(II) removal by adsorption onto PS-D2EHPA resins is described by a pseudo-second-order expression. This suggests that the rate-determining step may be chemical adsorption or chemisorptions involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.

3.2. Influence of initial Cu(II) ion concentration and equilibrium studies

Adsorption isotherms are very powerful tools for the analysis of adsorption process.

Langmuir and Freundlich isotherm studies [7, 9-13, 17-19] were conducted in order to investigate the maximum adsorption capacity of the studied PS-D2EHPA resin towards Cu(II) ions.

The linear form of the Freundlich isotherm equation can be written as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (4)$$

and of the Langmuir isotherm as the following equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}, \qquad (5)$$

where: q_e is the amount of Cu(II) ions per gram of sorbent, mg/g; C_e is the the residual concentration of Cu(II) ions in the solution at equilibrium, mg/L; K_f and $1/n$ are characteristic constants that can be related to the relative adsorption capacity of the adsorbent and the intensity of adsorption, respectively; q_m is a measure of monolayer adsorption capacity [mg/g]; K_L is a constant related to the free energy of adsorption.

Adsorption isotherms establish the relationship between the equilibrium pressure or concentration and the amount of adsorbed by the unit mass of adsorbent at a constant temperature. The adsorption isotherm of Cu(II) is presented in figure 4.

The adsorption capacity increased with increasing equilibrium concentration of copper. Then, it approached a constant value at the high equilibrium concentration. The maximum adsorption capacity of copper determined experimental is 2.25 mg/g.
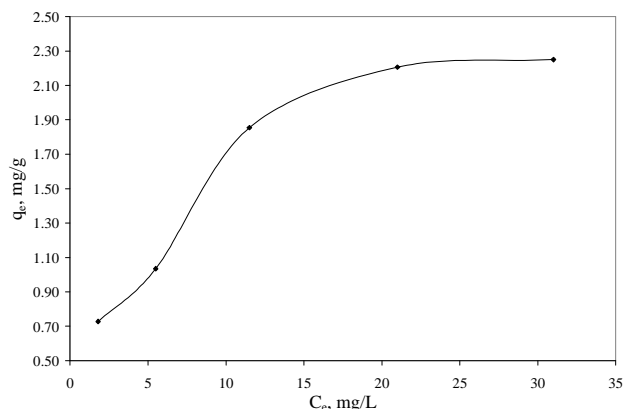

Figure 4. The adsorption isotherm of Cu(II)

The constants K_F and n of the Freundlich model, respectively, are obtained from the intercept and the slope of the linear plot of $\ln q_e$ versus $\ln C_e$ (figure 5). From the intercept and slope of the C_e/q_e versus C_e (figure 6) can be obtained the K_L and the maximum adsorption capacity of the PS-D2EHPA for Cu(II) adsorption. The Langmuir and Freundlich constants evaluated from the plots and their correlation coefficients are presented in Table 2.

The constant K_F can be defined as an adsorption coefficient, which represents the quantity of adsorbed metal ions for a unit equilibrium concentration. The slope $1/n$ is a measure of the adsorption intensity or surface heterogeneity. For $1/n = 1$, the partition between the two phases is independent on the concentration. The situation $1/n < 1$ is the most common and correspond to a normal L-type Langmuir isotherm, while $1/n > 1$ is indicative of a cooperative adsorption that involves strong interactions between the molecules of adsorbate. Values of $1/n < 1$ show favorable adsorption of Mu(II) ions onto PS-D2EHPA. The correlation coefficient is low suggesting a restriction on the use of Freundlich isotherm.

Correlation coefficient of the Langmuir plot is closer to 1. The essential feature of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L defined as:

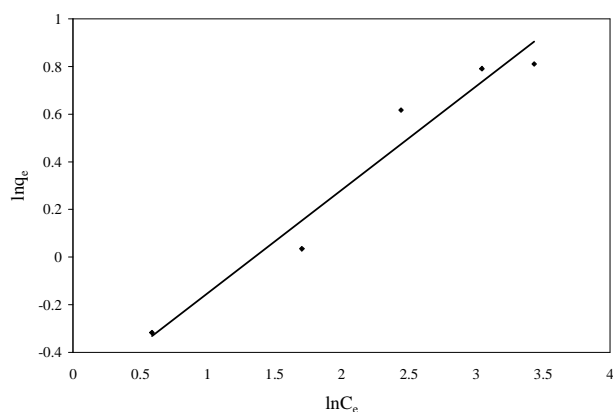$$R_L = \frac{1}{1 + K_L \cdot C_O} \qquad (6)$$

45

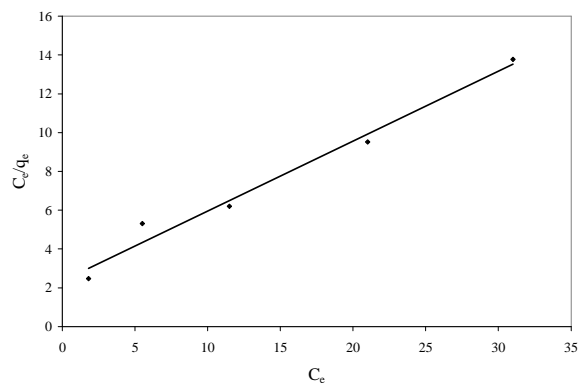Figure 5. Freundlich plot of Cu(II) adsorption onto PS-D2EHPA

Figure 6. Langmuir plot of Cu(II) adsorption onto PS-D2EHPA

TABLE 2. Parameters of different isotherm for the Cu(II) adsorption onto PS-D2EHPA

Freundlich isotherm			Langmuir isotherm		
K_F, mg/g	1/n	R^2	K_L, L/mg	q_m, mg/g	R^2
0.555	0.4348	0.9539	0.152	2.8	0.9794

The value of R_L indicates the shape of the isotherm: unfavorable, $R_L > 1$; linear, $R_L = 1$; favorable, $0 < R_L < 1$; and irreversible, $R_L = 0$. R_L values were found to be between 0 and 1 for all the concentration of Cu(II) ions, showing that the adsorption is favorable for the studied polymeric resins. One may also notice that the maximum adsorption capacity of the studied PS-D2EHPA resin calculated from the Langmuir plot ($q_{m, calc}$) for Cu(II) ions is close to the experimental values ($q_{m, exp}$). It is clear that the Langmuir isotherm model provide an excellent fit of the equilibrium adsorption data in the removal process of Cu(II) ions by adsorption onto PS-D2EHPA resin.

4. Conclusions

The present investigation shows that polysulfone microcapsules (PS) containing di-2-ethylhexyl phosphoric acid (D2EHPA) is an effective adsorbent for Cu(II) removal. The effects of process parameters such as contact time and initial concentration of Cu(II) on process equilibrium were studied. The equilibrium was obtained within 300 minutes.

By applying the kinetic model to the experimental data it was found that the adsorption of Cu(II) onto PS-D2EHPA follows the pseudo-second-order rate kinetics.

The linear Langmuir and Freundlich isotherm models were used to represent the experimental data and these could be relatively well interpreted by the Langmuir isotherm. R_L values between 0 and 1.0 further indicate a favourable adsorption of Cu(II) onto PS-D2EHPA. The monolayer adsorption capacity of Cu(II) calculated from Langmuir model was 2.8 mg/g.

ACKNOWLEDGEMENT

REFERENCES

1. Li-Chun L. and Ruey-Shin J., *Chemical Engineering Journal*, 112, **2005**, 211–218.
2. Ochoa N.A., Illanes C., Marchese J., Basualto C. and Valenzuela F., *Separation and Purification Technology*, 52, **2006**, 39–45.
3. Muscatello A.C. and Navratil J.D., *Journal of Radioanalytical and Nuclear Chemistry Letters*, 128, **1988**, 463-477.
4. Cortina J. L., Miralles N., Aguilar M. and Warshawsky A., *Reactive and Functional Polymers*, 27, **1995**, 61-73.
5. Rovira M., Hurtado L., Cortina J.L., Arnaldo J.S and Sastre A.M., *Reactive and Functional Polymers*, 38, **1998**, 279-287.
6. Muraviev D., Ghantous L. and Valiente M., *Reactive and Functional Polymers*, 38, **1998**, 259-268.
7. Mendoza R.N., Medina T.I.S., Vera A., Rodriguez M.A. and Guibal E., *Solvent Extraction and Ion Exchange*, 18, **2000**, 319-343.
8. Shafiqul A.M., Inoue K., Yoshizuka K., Dong Y. and Zhang P., *Hydrometallurgy*, 44, **1997**, 245-254.
9. Belkhouche N.E. and Didi M.A., *Hydrometallurgy*, 103, **2010**, 60-67.
10. Chabani M., Amrane A. and Bensmaili A., *Desalination*, 206, **2007**, 560-567.
11. Hosseini-Bandegharaei A., Hosseini M.S., Sarw-Ghadi M., Zowghi S., Hosseini E. and Hosseini-Bandegharaei H., *Chem. Eng. J.*, 160, **2010**, 190-198.
12. Mustafa S., Shah K.H., Naeem A., Waseem M.and Tahir M., *J. Hazard. Mater.*, 160, **2008**, 1-5.
13. Saha B., Gill R.J., Bailey D.G., Kabay N. and Arda M., *React. Funct. Polym.*, 60, **2004**, 223-244.
14. Shao W., Li X., Cao Q., Luo F., Li J.and Du Y., *Hydrometallurgy*, 91, **2008**, 138-143.
15. Zhu X. and Jyo A., *Sep. Sci. Technol.*, 36, **2001**, 3175-3189.
16 Chanda M., O`Driscoll K.F. and Rempel G.L., *React. Polym.*, 8, **1988**, 85-95.
17. An B., Steinwinder T.R. and Zhao D., *Water Research*, 39, **2005**, 4993-5004.
18. Benamor M., Bouariche Z., Belaid T., Draa M.T., *Sep. Purif. Technol.*, 59, **2008**, 74-84.
19. Yu Z., Qi T., Qu J., Wang L. and Chu, J., *J. Hazard. Mater.*, 167, **2009**, 406-412.