Removal of metal ions from aqueous solutions by sorption onto microcapsules prepared by copolymerization of ethylene glycol dimethacrylate with styrene

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A B S T R A C T

The removal of Cd(II) and Cu(II) ions from aqueous solutions was studied by sorption onto microcapsules prepared by copolymerizing ethylene glycol dimethacrylate (EGDMA) and styrene (ST). The microcapsules were prepared by an *in situ* radical polymerization method by adding the extractant compound, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester, and the monomers to the continuous aqueous phase.

The extractant was immobilized within the microcapsules (MCs) which presented a spherical shape with rough surface. High productions of MCs with an important retention of extractant were achieved. Microcapsules constituted by a copolymer of 65% EGDMA and 35% ST presented best capacity of sorption of both metals. These MCs presented sufficient degree of cross-linking and a suitable balance of hydrophilic–hydrophobic character.

The experimental data from chemisorption of metals onto the microcapsules fitted well the applied pseudo-second-order kinetics model. The alkylphosphonic extractant presented a higher rate constant and a higher equilibrium sorption capacity for Cd(II) than for Cu(II) at the pH used in this study.

1. Introduction

It is well known that the development of industrial activities in most countries generates huge quantities of a variety of wastes, including effluents of mining and chemical industries. Most of these residuals are acidic waste waters containing in many cases variable amounts of dissolved metals which must be removed owing to their toxic characteristics or recovered due to their intrinsic value, especially if they constitute useful and scarce metals. The challenge is how to extract them from this kind of aqueous solutions by using simple and economical methods. The current available extraction technologies for metallic ions are the use of chemical precipitants, the employment of ionic exchange solid resins (IX) [1], solvent extraction with liquid extractants (SX) [2], membrane-based technologies as solid supported liquid membranes [3], emulsion liquid membranes [4], and the utilization of natural and synthetic adsorbents [5,6]. All of them present advantages and limitations which oblige to pursue looking for newer and more efficient and technically feasible alternatives.

For example, there is no doubt that SX processing is in these days by far the most important industrial method to separate and recover metallic ions from aqueous solutions being easily applied in large-scale continuous steps. However, many difficulties appear in its practical operation, for example the loss of extractant due to reasons such as entrainment and crud formation, solubility of organic solvent into the metal-containing aqueous feed phase and volatilization of the diluents employed to dissolve the extractant and the phase modifier [7].

The immobilization of the extractant in a solid polymeric matrix would constitute a practical manner to overcome these disadvantages. There are two known methods to retain the extractant in a solid phase: the use of solvent impregnated resins (SIRs) [8] and the employ of polymeric microcapsules (MCs) [9–12]. In recent years both methods have attracted the attention of several researchers with the purpose of applying them in the separation and recovery of metals from aqueous solutions. SIRs contain an extractant in a macroporous polymeric resin, and microcapsules are synthesized by an *in situ* radical polymerization of an organic monomer and an extractant. SIRs and MCs behave as granular adsorbents hav-

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ing the properties of both IX solid resins (suitable to treat dilute solutions) and liquid extractants used in SX processing (high extraction capability), becoming highly selective if an appropriate liquid extractant is selected to be immobilized in them to uptake the desired metal.

Up to date, in hydrometallurgy it has had major advances in the use of SIRs than microcapsules as much in their preparation as in their application in specific areas [13,14]. In general, SIRs are simpler to produce than microcapsules; however the polymerization of these solid matrices allows a better control of the size of the microcapsules and their porous structure. Furthermore, the stability of the extractants in the porous structure of microcapsules is much better than that observed in SIRs.

Particularly, MCs and their applications have been investigated in many fields like agricultural [15], pharmaceutical [16] and chemical industries [17], however is in hydrometallurgy where they would present an attractive potential of use, basically in the separation, removal and recovery of metals from aqueous solutions. In this field, the interesting point is that the extractants encapsulated in the microspheres are the same commercial compounds used for industrial SX plants, but in this case retained inside the pores and on the surface of the microcapsules. In this way, a very stable solid–liquid interface is achieved and a minimal inventory of organic solvent is required to achieve the extraction of the same amount of metal. Microcapsules present some advantages as solid supports for extractants, among them, the existence of a large interfacial area as compared to other separation systems and a very easy separation of metal-loaded MCs from the treated solution by conventional filtration or sedimentation.

Some researchers have focused their works with the goal to produce microcapsules using common monomers and polymerization initiators [18,19]. Meanwhile other investigators have been working in the study of the metal sorption rate behavior by using different kinetics models. Kamio et al. [20] investigated the extraction behavior of gallium and indium with microcapsules containing an organophosphorus extractant. The chemical reactions that govern the metal extraction equilibrium were proposed and their constants and separation factors were also determined. In other work, Kamio et al. [21] studied the initial sorption rates of the same system and measured the activation energy of sorption. It was concluded that both chemical reaction of metal with the extractant at the MCs surface and diffusion processes affect the rate-determining step. The metal sorption would proceed according the following sequential steps: diffusion of metallic ion in the liquid-film neighbor to the microsphere, the chemical reaction on the microcapsule surface and the intraparticle diffusion of the metal-complex inside the microcapsule.

In this work, the removal of Cd(II) and Cu(II) using microcapsules containing the compound, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, have been studied. The microcapsules were prepared by copolymerization of styrene (ST) with ethylene glycol dimethacrylate (EGDMA) by using the oil in water suspension method. In the literature it has not found information on the use of EGDMA to prepare this type of microcapsules, which would present several interesting characteristics.

The synthesis of MCs under different experimental conditions and the determination of microencapsulated extractant were studied first. Furthermore, the characterization of the yielded microspheres by means of scanning electron microscopy (SEM) and porosimetry was accomplished. Finally metallurgical sorption tests of both metals from single acid aqueous solutions were carried out in batchwise. Equilibrium and kinetics information derived from these experimental results are analyzed and discussed.

2. Materials and methods

2.1. Reagents and solutions

2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester, $C_{16}H_{35}O_3P$, (commercially known as PC-88A) supplied by Daihachi Chemical Industry Co. Japan, was used without further purification being indicated by the producer a purity that averages 95%. This compound is an acid extractant that acts by cation exchange which presents a specific gravity of 0.948 (20 °C) and whose structure has been shown previously [22]. Styrene (C_8H_8, molecular weight 104.15) and ethylene glycol dimethacrylate ($C_{10}H_{14}O_4$, molecular weight 198.2) supplied by Aldrich were used as monomers to prepare the microcapsules. Their purities were more than 98% and were used as received. The structures of these monomers are shown in Fig. 1. Reagent grade benzoyl peroxide was employed as polymerization initiator. All other chemicals, including toluene as solvent for the organic compounds and arabic gum were of reagent grade.

Stock solutions of Cd(II) and Cu(II) were prepared by dissolving $CdCl_2 \cdot 2.5H_2O$ and $CuSO_4 \cdot 5H_2O$ (Merck r.g.) in distilled water and whose initial pH were adjusted around a value of 4.0 and measured with a pH electrode.

2.2. Preparation of microcapsules

The syntheses of microcapsules were carried out in a batch-type reactor having a 1.0 L capacity. A mixture of distilled water and arabic gum was added as the continuous phase being stirred by a mechanical stirrer Ika-Werk RW 20 at 600 rpm, which has a two-blades propeller that assured a suitable dispersion of organic phase. The organic solution composed of the monomers; the polymerization initiator and the organophosphonic acid extractant were added when the temperature of this aqueous solution reached 70 °C. This mixture acts as the dispersed phase. Both phases (continuous and dispersed) were intensely agitated for 3 h in nitrogen atmosphere to reach a high conversion of monomers to polymer. The resulting microcapsules were filtered and repeatedly washed with distilled water and then dried at room temperature.

2.3. Characterization of microcapsules

The measurement of the content of the organophosphonic extractant retained within the microcapsules was carried out by the same potentiometric titration method reported in our previous works [23]. 1.0 g of microcapsules was mixed with 50 cm³ of methanol and was left for 1 week. Then the microcapsules were separated from the organic liquid by vacuum filtration. The alcoholic solution was divided into 10 cm³ portions and each portion was titrated with a 0.05 mol/L NaOH solution using an OAKTON 500 pH meter.

The microcapsules containing 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester were observed by scanning electron
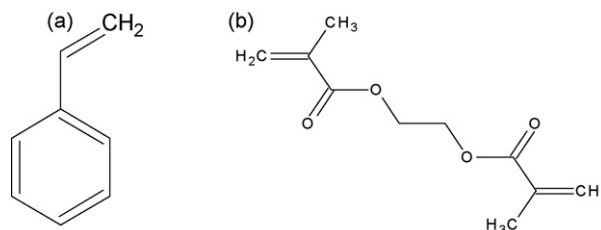

Fig. 1. Structure of the monomers (a) styrene and (b) ethylene glycol dimethacrylate.

Table 1
Synthesis of microcapsules as a function of solid matrix composition[*]

	MC-No. (%ST–%EGDMA)						
	MC-1 (100–0%)	MC-2 (86–14%)	MC-3 (70–30%)	MC-4 (50–50%)	MC-5 (35–65%)	MC-6 (20–80%)	MC-7 (0–100%)
Aqueous phase (g)							
Distilled water	220.57	220.39	220.62	220.61	220.59	220.50	220.50
Arabic Gum	4.52	4.50	4.50	4.50	4.54	4.51	4.50
Organic phase (g)							
Styrene	3.78	3.17	2.20	1.49	0.97	0.52	–
Ethylene glycol dimethacrylate	–	0.95	1.84	2.74	3.11	3.59	4.14
Benzoyl peroxide	0.9093	0.9015	0.9070	0.9041	0.9049	0.9066	0.9005
PC-88A	2.51	2.51	2.45	2.43	2.41	2.43	2.44
Theoretical weight	7.1993	7.5315	7.336	7.5641	7.3903	7.4466	7.4805
Toluene	7.12	7.30	7.40	7.41	7.26	7.20	7.20
Results							
MCs weight (g) (% yield)	1.13 (15.70)	5.402 (71.70)	6.196 (84.46)	6.740 (89.11)	6.303 (85.23)	6.740 (90.51)	6.58 (89.05)
Retained extractant (%)	–	–	92.65	95.03	84.11	89.15	87.15
(mmol PC-88A/g MC)			1.197	1.121	1.051	1.050	1.050

[*] Conditions used for the Synthesis of microcapsules: 70 °C; 600 rpm; 3 h.

microscopy (SEM) in an apparatus JEOL, JSM 6380LV following a normal procedure which includes a prior gold-coating of microcapsules before their analysis with the purpose of minimizing the eventual surface charging effect. The pore diameter, the void fraction and the surface area were determined by means of BET porosimetry with a Micromeritics ASAP 2010 porosimeter.

2.4. Extraction of metals from aqueous solutions

In order to test the feasibility to extract metallic ions from aqueous solutions with the microcapsules, the next step was to carry out some metal uptake equilibrium and kinetics experiments. The experiments were carried out in a batchwise by contacting 0.2 g of microcapsules containing the extractant and 25 cm³ of the aqueous solution containing either cadmium or copper ions in a Polyscience orbital-shaker apparatus. The equilibrium sorption runs were carried out during 24 h, which was considered as enough time to allow equilibrium to be reached. The kinetics experiments were done by measuring the variation of the metals concentration in the feed solution with time. In all experiments, once the microcapsules loaded with metals were filtrated from the raffinate, the metal concentration in this resulting aqueous solution was measured by atomic absorption spectrophotometry in a PerkinElmer 3110 apparatus. The amount of metal adsorbed onto the microspheres was calculated from the mass balance between initial and equilibrium metal concentrations in the aqueous solutions.

3. Results and discussion

3.1. Preparation of microcapsules

First the production of MCs was determined varying the proportion between the two monomers employed in this study, namely styrene and ethylene glycol dimethacrylate. It is clear by observing their chemical structures that styrene is more hydrophobic than EGDMA however this compound would present improved characteristics as an excellent cross-linker. Microcapsules were prepared by changing the monomer feed composition between 0 and 100% of each monomer. The copolymerization reaction was carried out at 70 °C in a reactor under nitrogen and by using mechanical stirring at a speed of 600 rpm during 3 h. In all cases, the aqueous phase consisting of a mixture of distilled water and arabic gum had the same composition. The same amounts of benzoyl peroxide as radical initiator and alkylphosphonic as extractant were used as organic

phase in all polymerization runs. The monomer feed composition, polymerization conditions as well as the yield of microcapsules obtained in each experiment are listed in Table 1. It was appreciated that the amount of MCs obtained was practically independent of the proportion of ethylene glycol dimethacrylate employed, where high production yield of microspheres was reached in all experiments. This result is different from that accomplished in a previous study, where we attempted to prepare microcapsules whose polymeric matrix was constituted by a styrene–divinylbenzene copolymer. This matrix is highly hydrophobic due to the presence of divinylbenzene. Moreover, it has a more compact structure due to the fact that divinylbenzene is a short molecule with a rigid structure. In that case, the production of MCs was enhanced as the proportion of divinylbenzene monomer was increased. These results are compared in Fig. 2 with those obtained in this work confirming that ethylene glycol dimethacrylate is a better cross-linker than divinylbenzene. Although divinylbenzene is more hydrophobic than dimethacrylate monomer, the results of retention tests of extractant inside the solid matrix indicated that the ethylene glycol dimethacrylate–styrene copolymer was sufficiently hydrophobic to retain in a stable form the alkylphosphonic extractant in its porous structure. Furthermore, EGDMA presents not only a higher cross-linking ability but also a higher reactivity with the other monomer
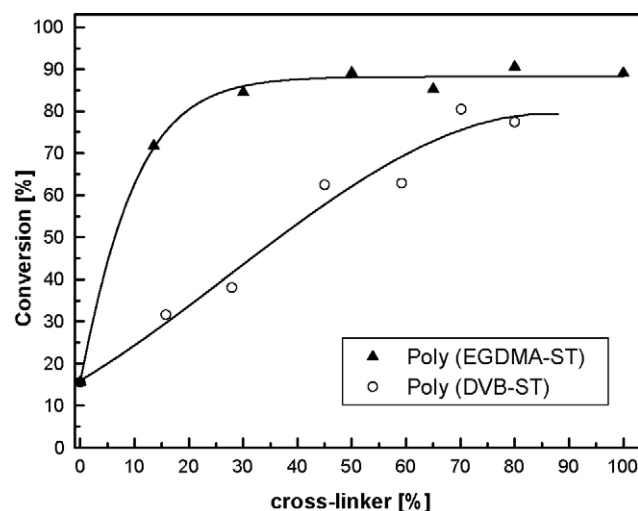

Fig. 2. Dependence of microcapsule production on the composition of polymer matrix.
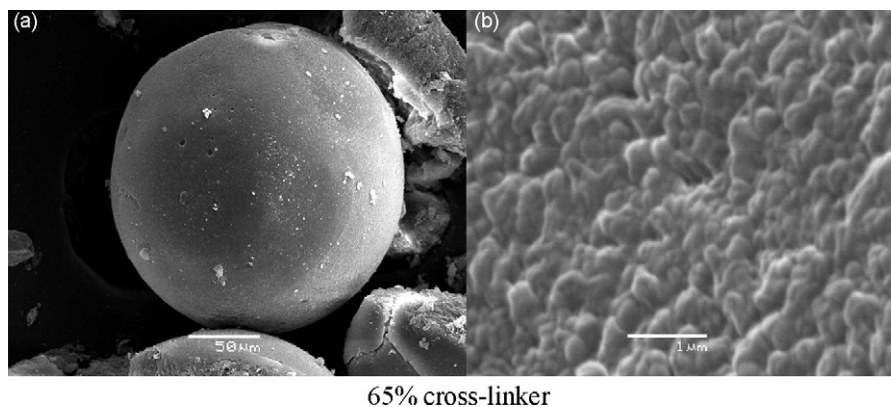
65% cross-linker

Fig. 3. SEM micrographs of microcapsules: (a) whole image of the microcapsule, (b) surface structure.

(styrene) than that of DVB, producing a very stable solid polymeric structure suitable to encapsulate the extractant.

3.2. Characterization of microcapsules

Typical SEM micrographs of the microcapsules obtained are shown in Fig. 3 (MC-5 in Table 1). Fig. 3(a) shows the whole image of the microcapsule and Fig. 3(b) the detail of its surface structure. They are almost spherical and their surface are quite rough. The physical properties of a synthesized microcapsule (MC-5) including its surface area, pore volume and pore size are shown in Table 2. Besides, the microcapsules presented a diameter of about 67 μm measured with a Mastersizer 2000, with a normal narrow size distribution and a rather good dispersity among them. It was also observed that in some cases the microcapsules tend to aggregate between them. This effect can be overcome using a higher stirring speed during the synthesis or by increasing the amount of dispersant used in their preparation.

The relation between the quantity of the alkylphosphonic extractant retained within the microcapsules and the mass fraction of ethylene glycol dimethacrylate employed in the synthesis are also shown in Table 1. As seen in this table, the extractant retained in the microspheres was high and practically constant being independent from the proportion of methacrylate monomer used to prepare the microcapsules averaging a value in the range of 1.05–1.20 mmol of extractant per gram of microcapsule. The results obtained from potentiometric titration confirms that most of the extractant used in the preparation of the microcapsules was immobilized within and on the surface of the microspheres. Any leakage of the extractant from the microcapsules was observed under the acidic conditions used for these experiments (around pH 4.0). This indicated that the hydrophobicity of microcapsules prepared with these monomers is suitable in order to retain the organic-soluble phosphonic extractant in this polymeric structure.

3.3. Removal of metals from aqueous solutions

When microcapsules are used for metal uptake from aqueous solutions, it is interesting to measure their metal loading ratio which becomes a value feasible to compare with the chemical sorption capacity of other adsorbents. We have defined the metal loading ratio as the weight of metal encapsulated to the molar mass of extractant held in the microcapsules, expressed as (mg metal/mol extractant). In order to explore the extraction ability of 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester for Cd(II) and Cu(II), many solid–liquid sorption experiments on each single metal solution were carried out, where the metal loading ratio was measured. The extraction of both metals as a function of time for different type of microcapsules are plotted in Fig. 4. These experiments were carried out using microspheres synthesized from a polymer matrix consisting of a minimum of 30% of EGDMA. Microcapsules containing less than that proportion of the cross-linker were not quite suitable, as can be seen in Table 1. This figure shows that a higher extraction of Cd(II) was achieved with respect to that of Cu(II) at pH 4.0, independent from the composition of the polymeric matrix that conforms the microcapsule. These results confirm that the extractant compounds preserve their capacity for metal extraction as function of the acidity of the treated

Table 2
Physical properties of synthesized microcapsules

|	
Surface area	
Single point surface area at P/P_o 0.20042717	12.0263 m²/g
BET surface area	14.5339 m²/g
BJH adsorption cumulative surface area of pores between 17.0000 and 3000.0000 Å diameter	15.2978 m²/g
BJH desorption cumulative surface area of pores between 17.0000 and 3000.0000 Å diameter	13.1090 m²/g
Pore volume	
Single point adsorption total pore volume of pores less than 751.8152 Å diameter at P/P_o 0.9974	0.02325 cm³/g
BJH adsorption cumulative volume of pores between 17.0000 and 3000.0000 Å	0.05056 cm³/g
BJH desorption cumulative volume of pores between 17.0000 and 3000.0000 Å	0.04885 cm³/g
Pore size	
Average pore diameter (4V/A by BET)	64.0082 Å
BJH adsorption average pore diameter (4V/A)	132.2022 Å
BJH desorption average pore diameter (4V/A)	149.0569 Å
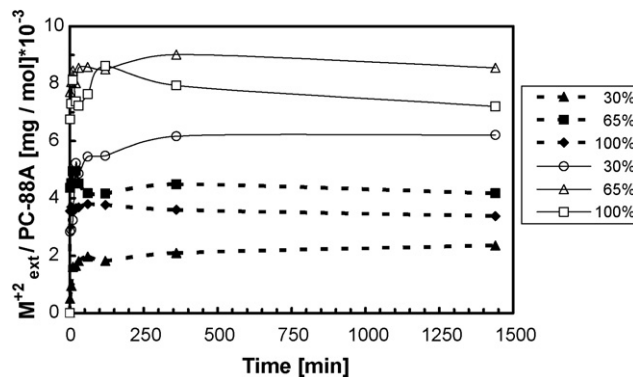
Fig. 4. Dependence of metal extraction with time as a function of EGDMA content in the polymer matrix, (—) Cd(II); (- - -) Cu(II).
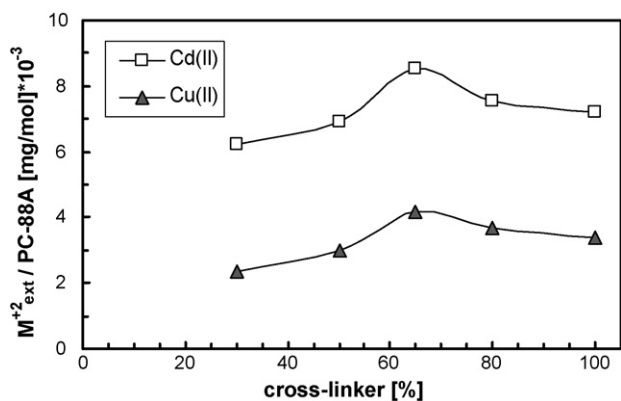
Fig. 5. Effect of the amount of cross-linker used in the synthesis of microcapsules on the metal loading ratio.

aqueous solution, regardless of the extraction system. PC-88A is an organophosphorus acid extractant. These kind of compounds are able to form stable complex with these metals, specially with cadmium in acid solutions, as it has been reported previously Basualto et al. [24] and Reddy et al. [25], although their copper loading capacity is lower. This has brought about the preference of the use of β-hydroxyoxime-type extractant for this metal uptake. This figure also shows that in general microcapsules with a minimum of 60% of ethylene glycol dimethacrylate in their structure present an enhanced metal extraction capacity confirming the existence of a good hydrophilic–hydrophobic balance and flexibility feature of this monomer. Fig. 5 shows the effect of the copolymer composition used as adsorbents on the metal loading ratio for both metals in batch extraction with the microcapsules. It is seen that the Cd(II) loading capacity was higher than that of Cu(II), where both curves show the same tendency reaching a maximum extraction of metals with MCs constituted by a minimum of 60% of EGDMA followed by a slight decrease for microspheres with a higher proportion of ethylene glycol dimethacrylate. This fact would indicate that in spite of good cross-linking property of EGDMA, an excess of this monomer in the solid structure of microcapsules would cause a decrement of their hydrophobicity affecting the retention of the extractant, coherently with the results shown in Table 3.

Many adsorption rate models have been studied trying to explain the experimental results obtained in a number of works whose aim has been focused on the sorption of existing metallic ion contaminants in aqueous solutions onto different natural or synthetic adsorbents. In most of these cases the sorption process includes a chemical reaction between the adsorbent and the metal to remove by a mechanism called chemisorption. The extractants bond to the metal through the formation of coordination compounds, salt formation, or ion-pair formation, thereby extracting them from their dilute solutions. The global mechanism also includes the diffusion of metal ions through aqueous film and diffusion of metal complexes through the pores of microcapsules, becoming any of them the rate-determining step of the overall pro-

cess. Then, the extraction of metal ions by microcapsules would be ruled by a mass transfer process accompanied by chemical reaction that allows the metal ions to be separated and concentrated from the aqueous feed solution toward the acceptor aqueous.

In a previous work concerned with the sorption behavior of Ga(III) and In(III) and lanthanides into a microcapsule loaded with the alkylphosphonic extractant used herein, our results indicated that both chemical reaction and diffusion processes would affect the rate-determining step [21,26]. Zhang et al. [27] studied the equilibrium and kinetics of adsorption of copper ions from aqueous solutions onto a starch/acrylonitrile copolymer-type adsorbent. They found that the adsorption process obey a first-order reversible kinetics. On other hand, Sari et al. [28] have studied the equilibrium, kinetics and thermodynamics of adsorption of Pb(II) from aqueous solution onto a kaolinite clay. They showed that the kinetics obey a pseudo-second-order expression based on the intraparticle diffusion step as the controlling factor. Of special interest are the studies of Ho [29], in which the author makes a complete review of second-order models for adsorption system based on the solid adsorption capacity of adsorbents more than on the concentration of the sorbate in the aqueous solution. The model has been applied as much to the adsorption of gases onto a solid as to describe ion exchange reactions of dissolved pollutants in aqueous solutions. Other authors have described chemisorption process based on solution concentration under reversible or irreversibles chemical reaction of first-order or second-order. However, Sobkowsk and Czerwinski [30] have concluded that the first-order rate equation only could be applied for low surface concentration of species adsorbed onto a solid surface, meanwhile second-order rate expression could also be applied to higher concentrations of adsorbate on the surface. It is important to predict the kinetics at which pollutants species are uptaken from their solutions since the rate of sorption process would allow to design a practical system to remove undesired species from actual polluted waters.

It would be reasonable to think that when the microcapsules are prepared by the chemical method employed in this study which is based on the copolymerization of the monomers in the presence of the extractant in an organic diluent at 70 °C, the solvent is finally evaporated allowing the extractant to remain in the microcapsules, practically at a pure state and by the way that presenting a high concentration on the surface and inside the pores of the microspheres. Under these conditions and according to Ho and Sobkowsk, we assume that a pseudo-second-order kinetics could be applied to our experimental data. The metallic ion, M^{2+}, would react on the surface of the microcapsule loaded with the acid extractant, HX, which exists in its dimerized form [23,31,32] and according to the following cation-exchange reaction shown in Eq. (1).

$$M^{2+}_{(aq)} + 2(HX)_{2(sol)} = MX_2 \cdot 2(HX)_{(sol)} + 2H^+_{(aq)} \tag{1}$$
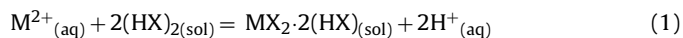
$(HX)_2$ and $MX_2 \cdot 2(HX)$ indicate the dimerized extractant and the metal-extractant complex. Besides, (sol) and (aq) denote the solid surface of microcapsules and aqueous solution, respectively.

Table 3
Parameters of kinetics model applied to Cu(II) and Cd(II) adsorption onto microcapsules loaded with the alkylphosphonic extractant

ST/EGDMA	Cu(II)			Cd(II)		
	q_e ($\times 10^4$ mol/g PC-88A)	k (mol Cu(II)/g PC-88A s)	R^2	q_e ($\times 10^4$ mol/g PC-88A)	k (mol Cd(II)/g PC-88A s)	R^2
70/30	12.17	9.11	0.9989	18.13	12.69	0.9999
50/50	15.40	27.68	0.9998	20.05	47.42	0.9999
35/65	21.48	22.76	0.9997	24.91	48.39	0.9998
20/80	18.73	15.54	0.9987	21.94	16.02	0.9995
0/100	17.37	18.58	0.9997	20.96	12.70	0.9994

This model is proposed on the basis of the sorption ability of the microcapsules and is written as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{2}$$

where q_t (mol/g) is the molar amount of metal adsorbed per gram of extractant retained in the microcapsule at any time t (min), q_e (mol/g) the molar amount of metal ions adsorbed at equilibrium condition and k (mol metal/(g extractant s)) represents the rate constant of the sorption model. The driving force of process is obviously $(q_e - q_t)$ which is proportional to the sorption vacant active sites.

Eq. (2) is easily integrated by separating the variables as follows:

$$\frac{dq_t}{(q_e - q_t)^2} = k\,dt \tag{3}$$

For the boundary conditions at $t = 0$, $q_t = 0$ and at $t = t$, $q_t = q_t$, the following expression is achieved:

$$\frac{t}{q_t} = \frac{1}{(kq_e^2)} + \left(\frac{1}{q_e}\right)t \tag{4}$$

Eq. (2) is an expression of the chemical reaction between the metal ion in solution and the extractant immobilized in the microcapsule which does not consider the reversible back-extraction reaction because these reactions do not occur in this stage of the process. It is clear that the sorption capacity of metallic ions by the microcapsules depends on time.

This pseudo-second-order kinetics model to the experimental results of kinetics of extraction of Cd(II) and Cu(II) with the microcapsules loaded with the phosphonic extractant is applied in Figs. 6 and 7 attempting to get a linear fit of data. The experimental values have been plotted according to the Eq. (4) in a series of graphics, where the copolymer composition forming the microspheres has been varied. The rate constants, k, the equilibrium sorption capacity, q_e, and the coefficient of determination, R^2, obtained by linear regression are indicated in Table 3. The adsorption of both metallic ions seem to be controlled by the chemical process according to this pseudo-second-order kinetics model which fits fairly well the experimental data for both metals.

Table 3 also show the dependence of the chemisorption pseudo-second-order kinetics model parameters observed for the extraction of metallic ions with the MCs prepared in this study. It can be observed that both rate constant and the equilibrium sorption capacity resulted to be higher for Cd(II) than that measured for copper ions. This confirms that the acid extractant present a slight but measurable higher extractability towards cadmium ions under this acidic condition. Moreover, it can be appreciated from Table 3 that the best results were determined for microcapsules
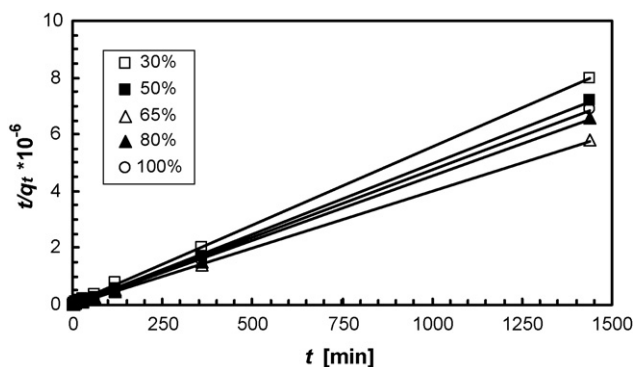

Fig. 6. Kinetics model for the adsorption of Cd(II) onto microcapsules loaded with the alkylphosphonic extractant as a function of EGDMA content in the polymer matrix.
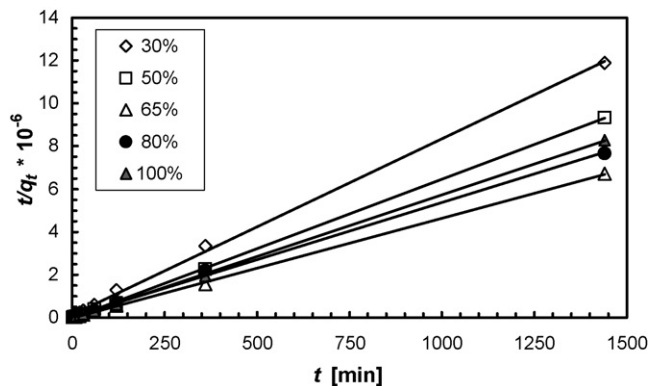

Fig. 7. Kinetics model for the adsorption of Cu(II) onto microcapsules loaded with the alkylphosphonic extractant as a function of EGDMA content in the polymer matrix.

whose polymeric structure was conformed by approximately 60% of EGDMA which ensures a appropriate cross-linking extent of the solid matrix that would help to retain the extractant and the metal-complex and that would prevent a higher leakage of extractant from the microcapsule as their hydrophobicity decreases due to the hydrophilic nature of this monomer.

The use of a cross-linking agent such as ethylene glycol dimethacrylate allows the introduction of a certain degree of reticulation in the structure of the matrix, depending on the initial content of the cross-linker compound, leading to the formation of polymers with a porous three-dimensional network whose structural flexibility makes it possible to obtain microspheres with an improved capacity for diffusion of species through them. Also, the use of monomers such as styrene with a hydrophobic character lower than that of divinylbenzene allows an adequate hydrophilic–hydrophobic balance and degree of swelling of the MCs and favors their wettability, facilitating the adsorption of the metal ions from aqueous solutions.

The results presented in this study show that the use of microencapsulation of commercial extractants in these polymeric matrix constitute an interesting alternative methodology to be employed specially for treating dilute aqueous solution polluted with metallic ions. These microcapsules have a large specific surface area, a very high and improved selectivity with respect to ion-exchange resins and are less expensive since they are prepared following a low cost method using simple and commercially available materials.

The use of microcapsules can be considered a clean technology in separation processes. The application of this MCs system at an industrial level considers the use of a column technology. The simplicity of the reactor and the ease of operation of the columns make it possible to believe that a column packed with MCs can be easily adapted to industrial applications. Hydrophobic interaction between the polymer structure of the MCs and the extractant retained in their structures can be assured, thus avoiding loss of the organic compound from the polymer matrix. Moreover, the typical loss of extractant of SX processing caused by its dissolving or entrainment in the aqueous phase is also avoided since the extractants are immobilized on the polymer structures that make up the microcapsules.

Once the adsorption process has occurred, the final step consists in back-extraction of the metal from the MCs by means of a desorption step by contacting them with a suitable stripping phase consisting of a metal-acceptor solution and where the enrichment of metal is achieved by a continuous increasing of its content in this solution. In the stripping stage, the MCs release the adsorbed metals, where then it will be available for a new adsorption–desorption

cycle. This point is especially important in continuous-columns experiments whose results are currently being analyzed and will be reported shortly.

4. Conclusions

Microcapsules based on copolymers of Styrene (ST) and ethylene glycol dimethacrylate (EGDMA) containing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester as extractant were prepared by *in situ* free radical suspension polymerization method. These microcapsules were utilized in batch adsorption experiments for the removal of Cd(II) and Cu(II) from aqueous solution.

It was found that most of the extractant employed in the synthesis was immobilized within the microcapsules whose structures are spherical and having rough surfaces. Results of experiments accomplished by varying the proportion of both monomers showed that the high production of MCs and the content of extractant retained in their structure were independent of the amount of methacrylate monomer used as crosslinking agent in their synthesis.

Microcapsules whose structure were constituted by 65% EGDMA and 35% ST showed best results with respect to the sorption of both metals. This monomer feed composition resulted in obtaining a polymeric matrix with appropriate degree of cross-linking and a suitable hydrophobic character for the retention of the extractant and the metal-complex formed.

The extraction of metals with the alkylphosphonic compound immobilized in the microcapsules followed the same chemical pattern of behavior of this extractant than that observed in SX processing. This means that the chemical adsorption of metal ions in the microcapsules proceeds by a cation-exchange reaction on the surface of microspheres, which is facilitated by the polarity of the components that participate in it. The chemisorption of both metals onto the microcapsules containing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester follows a pseudo-second-order rate kinetics. PC-88A presented a higher rate constant, k, and a larger equilibrium sorption capacity, q_e, for Cd(II) than for Cu(II) under the acidity condition used in this study.

Results obtained in this study confirm the feasibility of applying the extractant microencapsulation method for the recovery or removal of toxic and valuable metallic ions from dilute aqueous solutions. The information achieved in this study will be of great value in subsequent steps of this research addressed to the employ of continuous columns packed with microcapsules loaded with suitable extractants.

Acknowledgements

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