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Preparation and characterization of polymeric microspheres for Cr(VI) extraction

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Abstract

Microspheres (MS) from different polymers were prepared using two routes. Route A: process of phase inversion with solutions of polysulfone (PSf) in dichloromethane (DCM) and polyvinylpyrrolidone (PVP) as additive. Different weight ratios of PSf–PVP were used in the MS preparation. Route B: MS were obtained by cross-linking in emulsion using a commercial silicone as raw material. The obtained MS were analysed according to their morphological–structural characteristics and in relation to their Cr(VI) extraction capacity using impregnated MS with Aliquat 336. The results obtained showed that MS prepared with PSf–PVP have both less specific surfaces and relative porosities when the proportion of PVP in the mixture is increased. Extraction tests of ion Cr(VI) indicated that synthesized MS have adequate structural characteristics and interesting adsorptive properties which give rise to impregnating selective extractants. Impregnated microspheres with Aliquat 336 prepared from 2:1 PSf–PVP ratio achieved the highest Cr(VI) extractive performance (92% of Cr extraction for contact time of 60 min) and the best breakthrough point in column tests (up to 10 h in the first cycle).

1. Introduction

Solvent extraction and ion exchange are among the most widely used techniques of recovery and separation of metal ions. Both techniques have limitations when applied to aqueous effluent treatment. Extraction by solvents requires multistage cycles of extraction and back-extraction to attain a favourable separation. Another drawback is the use of organic solvent because it can contaminate the aqueous phase due to its own solubility in water. On the other hand, 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 (SIRs).

Polymeric resins are impregnated with a selective ion extractant to be separated. The advantage of this system is that it can be used either in batch or column process. In the latter case, it can be used in a continuous process with columns in counter-current flow and the solid phase can be easily separated. With respect to this type of processes, Kabay et al. investigated Cd(II) and Cu(II) extraction with SIRs with bis(2,4,4-trymethylpentyl)monothiophosphinic acid as extractant [1] and Cr(VI) extraction using Aliquat 336 [2]. Akita and Takeuchi [3,4] investigated Co(II) and Zn(II) extraction using a macro-molecular resin with D2EHPA or EHPNA. Draa et al. [5] reported the extraction of Pb(II) by XAD7-impregnated resins with organophosphorous extractants (DEHPA, IONQUEST 801, CYANEX 272).

Recently, Kamio et al. [6] have reported the use of microcapsules (MC) containing organophosphorous compounds which were prepared in situ by the polymerisation method. Through this technique, MC of different materials according to monomers used in the preparation can be obtained. The system studied was the extraction of Ga(III) and In(III) with D2EHPA, EHPNA and DISPA. In this work, the stability of encapsulated

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and impregnated EHPNA was also analysed. It was found that for pH values of aqueous solution higher than 4, Ga(III) ion was mostly extracted. The same researchers [7] reported the separation of these ions by MC containing EHPNA in packed columns.

Yang et al. [8] prepared polysulfone (PSf) microcapsules containing 2-ethylhexylphosphoric acid (D2EHPA) by solvent evaporation method and the extraction equilibrium and kinetics characteristics for Cu(II) recovery were studied. The extraction experiments spent less than 10 min to reach equilibrium and a percentage of about 0.6 was achieved in the microcapsule extraction process when the initial metal ions concentration was 10 ppm. In other work, Yang et al. [9] reported the preparation of polystyrene microcapsules containing Aliquat 336 using the solvent evaporation method. The separation of Cr(VI)/Cd(II) and Cr(VI)/Zn(II) in a column packed with MC was studied. Both Cd(II) and Zn(II) were obtained from the aqueous effluent solution with high purity and Cr(VI) inside microcapsules.

This work attempts to obtain microspheres with different morphology properties from commercial polymers such as PSf, polyvinylpyrrolidone (PVP) and silicone. The efficacy of these MS will be analysed in relation to their capacity of impregnation with an extractant and their extractive efficiency. The metal ion-extractant system studied is Cr(VI) with Aliquat 336. This extractant is an effective compound to remove Cr(VI) from industrial effluents and is widely used in liquid–liquid extraction process [10–15].

2. Experimental

2.1. Reagents

The silicone resin was stocked by Anaerobicos S.A. (Siloc^{TM}), Polysulfone P-3500 was provided by Amoco, polyvinylpyrrolidone K30 and sodium dodecyl sulfate were provided by Fluka and Aliquat 336 was supplied by Cognis. Agar–agar powder, dichloromethane, potassium dichromate, chromium standard for AA (titrisol), NaOH and NaCl were provided by Merck.

2.2. Preparation of microspheres

MS were prepared following two different procedures or routes:

Route A: Precursor polymeric solution consists of a mixture of different ratios of PSf and PVP. PSf is a linear polymer soluble in (CH_2Cl_2) solvent and insoluble in water while PVP is a polymer soluble in solvent as well as in water. In this route, MS formation occurs by phase inversion process of PSf polymer, while the presence of PVP favours the generation of cavities or pores in MS structure. PSf–PVP mixture was varied according to the following weight ratios—1:1, 2:1 and 1:3.
Route B: A silicone solution in CH_2Cl_2 was used. In this case, MS formation process is due to polymer cross-linking in emulsion.

Table 1
Composition and viscosity of polymer solutions

	Polymer, wt%	PVP, wt%	DCM, wt%	η, cp
PSf–PVP (1:1)	11.62	11.62	76.75	950
PSf–PVP (2:1)	12.34	6.17	81.49	940
PSf–PVP (1:3)	7.55	22.65	69.80	450
Silicone	20.00	–	80.00	250

Viscosities (η) of polymeric solutions were measured with a Brookfield viscometer Model DV-III. Compositions of each reagent in the mixture, and viscosity values of the polymeric solutions are given in Table 1.

The experimental methodology of MS synthesis is similar for both routes and it is based on the following outline: in a 1 dm^3 vessel, 0.8 dm^3 distilled water with 2% agar–agar and 2% sodium dodecyl sulfate were added. The polymeric solution was added drop by drop to the aqueous phase under a continuous mixing with a blade stirrer (800 rpm). After the last drop was added, emulsion temperature was gradually increased up to 50 °C. Finally, MS were filtered, washed with distilled water and air-dried at room temperature.

2.3. Microsphere impregnation with extractant

MS samples were impregnated in solution of Aliquat 336, a selective extractant of ion Cr(VI). Impregnation was carried out by the following methodology: 0.33 g of MS was laid in contact with 1 g Aliquat 336 for 24 h. Impregnated MS (IMS) were separated by filtration from the excess of extractant solution and washed three times with distilled water, dried and weighed. The total amount of Aliquat incorporated to MS (%W) was determined by the relative change of weight before and after MS impregnation.

The content of Aliquat in the MS (%ACt) after the Cr(VI) extraction process was determined by the relative change of weight before and after solvent extraction using heptane as Aliquat solvent according with Yang et al. [9].

2.4. Microsphere characterization

2.4.1. Optic microscopy (OM)
Images were carried out by an optic system NanoScope OMV-PAL which took images in a digital format. They were analysed with ScanPro image program to obtain statistic values of MS size distribution.

2.4.2. Mercury porosimetry
Hg penetration test was carried out using an Autopore III 9410 porosimeter (Micromeritics Instrument Co.), working from 0 to 414 MPa, corresponding to pore sizes from 300 to 0.003 μm. To calculate pore sizes, a 180° angle of contact of Hg with polymers was assumed.

2.4.3. Contact angle measurements
To determine the contact angle θ of polymeric materials used in the manufacturing of MS, dense films of silicone and polysulfone were prepared from their dissolutions in CH_2Cl_2. The

contact angles between water and the dense film surfaces were measured with a 1501 Micromeritics contact anglometer.

2.4.4. Extraction and stripping tests with Cr(VI)

Extraction and stripping batch tests at 298 K were carried out. Extraction procedure consisted in placing 0.3 g of IMS in contact with 80 cm^3 of 40 ppm Cr(VI) ion aqueous solution for 24 h. After that, the IMS with added Cr(VI) were washed with pure water and used in the stripping tests. The Cr(VI) back-extraction experiments were performed laying the washed IMS in contact with a 0.1 M solution of NaOH and 1 M NaCl. During extraction-stripping tests, solutions in contact with IMS were constantly stirred at 100 rpm and samples of aqueous solutions were taken at different intervals of time. The Cr(VI) concentration was determined by atomic adsorption spectrometry using a Varian 50AA spectrometer.

2.4.5. Column operation

In the column chromatography study, 1 g of IMS was packed into a column of 4.8 mm of diameter and 130 mm in height. The aqueous feed solution containing 40 ppm of Cr(VI) at pH 4 with a flow rate of 0.6 ml/min was tested. The stripping tests were performed with a solution of 0.1 M NaOH and 1 M NaCl.

3. Results and discussion

3.1. Optic microscopy analysis

Fig. 1(a–c) shows images of MS prepared from PSf–PVP. MS images indicate that they have nearly spherical shape with
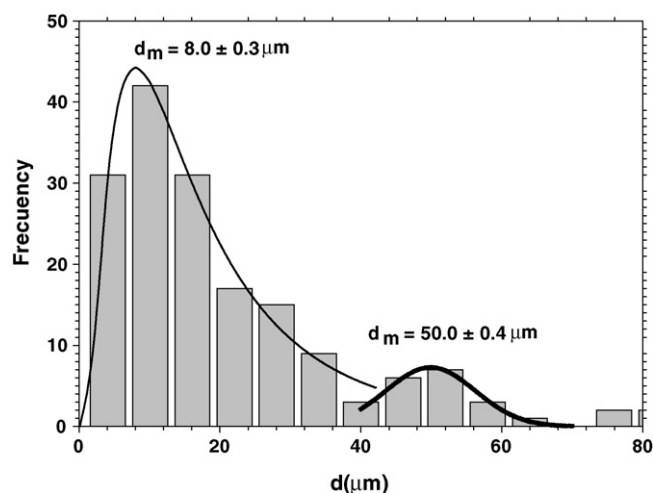

Fig. 2. Particle size distribution for MS of PSf–PVP (1:3).

different diameter size ranging from 2 to 600 μm. In general, these MS are linked to one another forming mainly three types of small agglomerates: rosary or chain-like, cluster conformation and crown type (a larger microsphere surrounded by smaller ones).

The analysis of MS size distribution indicates that there exists a bimodal distribution for those MS prepared with a 1:3 ratio in PSf–PVP, tri-modal for 1:3 ratio in PSf–PVP, while for 2:1 ratio of PSf–PVP, the distribution was mono-modal. Values of diameters obtained in the maximum point of distribution curves are listed in Table 2. In Fig. 2, the diameter size distribution corre-
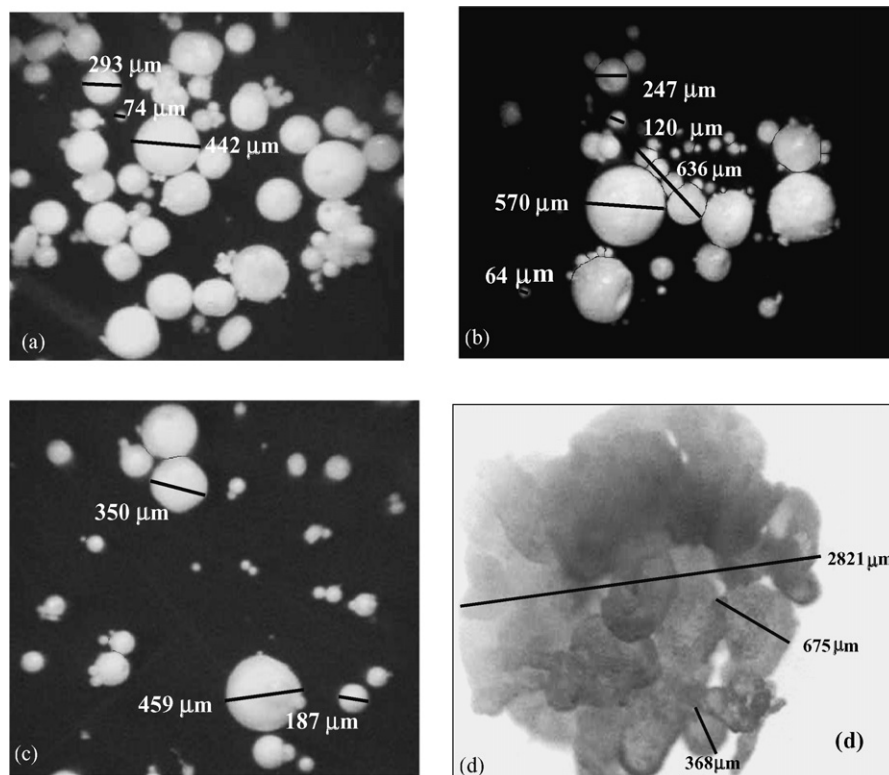

Fig. 1. Optical microscopy images of MS: (a) PSf–PVP (1:1), (b) PSf–PVP (1:3), (c) PSf–PVP (2:1) and (d) silicone.

Table 2
Microsphere diameters obtained by optical microscopy

Materials	PSf–PVP (1:3)	PSf–PVP (1:1)	PSf–PVP (2:1)	Silicone
Sphere diameter, μm				
Principal peak	8 ± 0.3	15 ± 3	3.8 ± 0.6	>3000
Secondary peak	50 ± 0.4	89 ± 4	–	–
Tertiary peak	–	230 ± 30	–	–

sponding to MS synthesized from PSf–PVP (1:3) is represented. The results obtained for MS of PSf–PVP indicate that the polymer forming the structure (PSf) controls the size of spheres. This must be so because, being PSf insoluble in water there is a lack of stability when the organic solution is incorporated to the aqueous solution, generating nucleus of polymer-rich phase up to a maximum concentration of precipitation. Once that concentration is reached, new nucleuses are formed. Increasing PSf concentration, there is a higher availability of polymer to reach precipitation concentration with smaller miscele radius which causes a decrease on MS diameter sizes.

MS prepared from silicone (Fig. 1d) presented a gel-type continuous structure with a non-defined geometric configuration, forming agglomerates of very big sizes (>3000 μm) formed by spheroid nodules closely linked each other. Although sizes of nodules ranging from 80 to 400 μm could be seen, due to their high cross-linking the nodule size distribution could not be analysed.

3.2. Porosimetry of Hg

Fig. 3 and Table 3 show the results obtained by porosimetry of Hg. Distributions of pore size range between 0.004 and 20 μm. Several researchers have reported the effect of the aggregate of PVP in polymeric membrane preparation [16–23]. The addition of a third component to the casting solution can either induce or suppress formation of macrovoids in asymmetric membranes. PVP effect on membrane structure is strongly dependent on a large number of factors, such as solvent characteristics, polymer molecular weight, and concentration of membrane forming polymer. It has generally been observed that an increase in PVP/PSF relationship produces an increase of polymeric solution viscosity which leads to morphologies with a lower content of macrovoids, and therefore a more densified solid polymeric structure. The different behaviours have been explained by thermodynamic and rheological considerations [24–29]. According
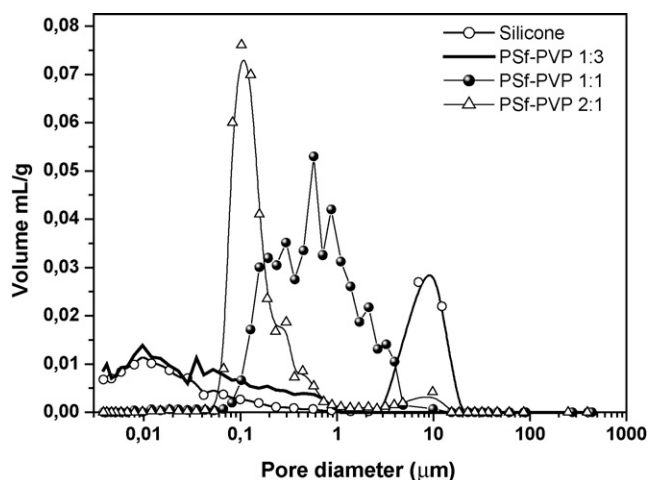

Fig. 3. Pore size distribution of microspheres from Hg porosimetry technique.

to the work reported by Han and Nam [25], PVP is widely used in a casting solution in the phase inversion polysulfone membrane, because the good miscibility in PSf–solvent solution and high solubility in water. This allows to assume that the PVP in the casting solution is leached by the water phase during the phase inversion process. The results (Fig. 3; Table 3) show that MS obtained with PSf–PVP (1:1) solution have a distribution of pore size ranging between 0.1 and 8 μm, whereas in those obtained with PSf–PVP (2:1 and 1:3) solutions distributions are displaced to values of smaller pore size. Despite other authors' general trend, our results indicate that a decrease of casting solution viscosity (Table 1) favours the formation of MS with structures having higher apparent densities and smaller pore sizes (Table 3). This might be due to the fact that during MS preparation, DCM organic solvent is slowly evaporated causing the non-solvent and surfactant to diffuse more rapidly inside the polymer-rich phase. Thus, the structure is rapidly frozen avoiding fluctuation of high concentrations which produce pores of higher sizes.

Table 3
MS morphological properties by mercury porosimetry technique

Microsphere	PSf–PVP (2:1)	PSf–PVP (1:1)	PSf–PVP (1:3)	Silicone
Total intrusion volume, ml/g	0.3566	0.4855	0.2147	0.1841
Total pore area, m^2/g	11.474	5.998	70.895	58.938
Median pore diameter (volume), μm	0.1243	0.5633	0.0189	0.0185
Median pore diameter (area), μm	0.1031	0.1901	0.0059	0.0060
Average pore diameter (4 V/A), μm	0.1243	0.3238	0.0121	0.0125
Bulk density, g/ml	0.4124	0.3626	0.6179	0.5363
Apparent (skeletal) density, g/ml	0.4835	0.4400	0.7124	0.5951
Porosity, %	14.7057	17.6023	13.2668	9.8733

Table 4
Extractant impregnation (%W) and content (%ACt) in MS

	%W	%ACt
PSf–PVP (1:1)	46	9
PSf–PVP (2:1)	15	13
PSf–PVP (1:3)	2.5	2
Silicone	13	11

Table 3 shows that total volume of intruded Hg and MS porosity values have the following trend: PSf–PVP (1:1) > PSf–PVP (2:1) > PSf–PVP (1:3) > silicone. This indicates that MS prepared from PSf–PVP (1:1) would have a higher volumetric capacity to store the extractant.

3.3. Assays of extraction and stripping

The results indicate that mass (W) of Aliquat incorporated to MS prepared with PSf–PVP is related qualitatively to the pore volume determined by Hg intrusion. Thus, PSf–PVP (1:1) has a mass increase of $W = 46$ wt%; PSf–PVP (2:1), $W = 15$ wt%; and PSf–PVP (1:3), $W = 2.5$ wt% (Table 4). The 15% impregnation value found for silicone MS contrasts with the lower volume value of intruded Hg in relation to MS of PSf–PVP (2:1) and PSf–PVP (1:3). The reason for this can be that silicone has more hydrophobic characteristics than PSf, favouring a higher affinity and interaction with hydrocarbon chains (carbon C6–C10) present in the Aliquat extractant. The degree of hydrophobicity of both materials can be related to their angle of contact θ [30,31]. Measurement tests of contact angle with water gave values of $\theta = 112°$ for silicone and $\theta = 78°$ for PSf. The higher angle of contact of silicone indicates a higher repulsion between its surface and water and therefore, a higher hydrophobicity. These results would indicate a higher absorption and impregnation of Aliquat in MS of silicone with an average pore size lower than that found for PSf. On the other hand, if the distribution of pore sizes is analysed (Fig. 3), it can be observed that MS of silicone present a significant fraction of volume with pore sizes relatively large – between 9 and 10 μm – which would favour the extractant impregnation.

Fig. 4 shows extraction values achieved with MS, represented as percentage of Cr(VI) extracted (%E) as function of operation time, being

$$\%E = \frac{C_i - C_t}{C_i} \times 100 \qquad (1)$$

where C_i is the initial Cr(VI) concentration in aqueous solution and C_t is the Cr(VI) concentration in the aqueous solution at extraction time t.

If results of MS prepared from different PSf–PVP ratios are compared, ratio 2:1 presented the higher extraction performance with $E = 92\%$ for contact time of 60 min, and $E = 98\%$ in equilibrium conditions ($t \geq 90$ min). For MS of PSf–PVP with ratios 1:1 and 1:3, the extraction was 58 and 60%, respectively, for a contact time of 90 min. In both MS, a contact time higher than 700 min was necessary to reach equilibrium conditions ($E \approx 98\%$). MS of silicone reached their extraction equilibrium conditions after 90 min of contact ($E \approx 92\%$). A more detailed
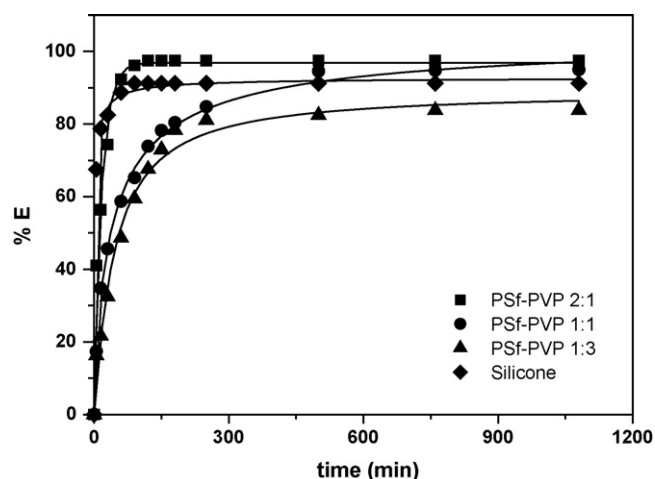

Fig. 4. Cr(VI) extraction (%E) vs. time for the prepared IMS.

work related with the extraction kinetic has been done by the authors [32].

The higher efficiency of MS of PSf–PVP (2:1) compared to those of PSf–PVP (1:1) can be attributed to different pore structures. Although PSf–PVP (1:1) has a higher impregnated volume of extractant, it also has a wide distribution of pore sizes ($d_p \approx 0.1$–8 μm). This fact would produce a leaching of extractant by aqueous solution in those pores of higher size. The presence of turbidity in aqueous solutions at the beginning of extraction assays with MS of PSf–PVP (1:1) seems to confirm a partial leaching of extractant. This result was confirmed by the Aliquat content after extraction (%ACt = 9, Table 4), that is, 80% of Aliquat was leaked from ME into the aqueous solution. On the contrary, MS of PSf–PVP (2:1) have a porous structure with a narrow pore size distribution centred to pores of smaller sizes ($d_p \approx 0.09$–0.3 μm), which would decrease the extractant leaching by the aqueous solution. The value of %ACt = 13 for MS of PSf–PVP (2:1) agree with this assumption.

The lower performance presented by MS of PSf–PVP (1:3) compared to those of PSf–PVP (2:1) could be explained by a low impregnation of MS due to their smaller pores which makes the extractant more difficult to access to the inside of them. Therefore, for the same material, the impregnation and permanence of Aliquat are strongly determined by pore size and actually by MS morphology. MS prepared with silicone showed a similar performance to those of PSf–PVP (2:1), with an extractant content of 11%. This behaviour can be attributed to both silicone MS impregnation capacity and hydrophobic affinity between the extractant and silicone which reduces the effect of leaching.

Fig. 5 shows data of stripping tests, represented as percentage of Cr(VI) recovered (%R) from MS as function of operation time, using a solution of NaOH of 0.1 M and NaCl of 1 M, %R is given by

$$\%R = \frac{C_{t,s}}{C_i} \times 100 \qquad (2)$$

where $C_{t,s}$ is the Cr(VI) concentration at time t in the stripping solution and C_i is the initial Cr(VI) concentration in the feed solution.
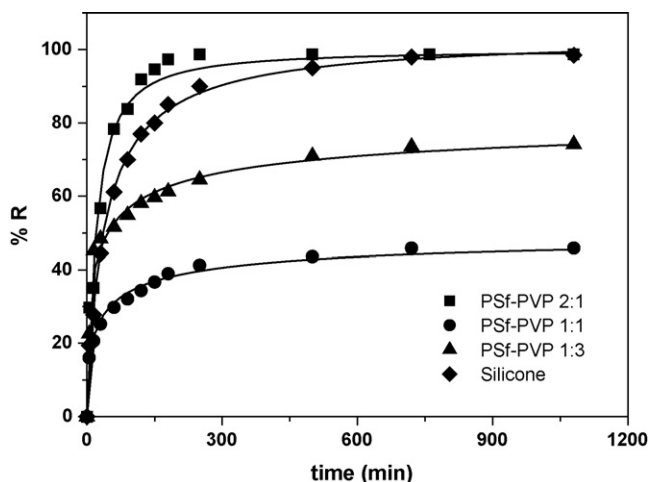
Fig. 5. Cr(VI) recovery (%R) vs. time for the prepared IMS.

A similar behaviour is observed with respect to extraction tests, in which a higher efficacy is obtained with MS of PSf–PVP (2:1) (92% of Cr(VI) recovered after 120 min). With the same contact time, MS of silicone, PSf–PVP (1:3) and PSf–PVP (1:1) reach a Cr(VI) recovery of 75, 49 and 34%, respectively. It should be noted that after reaching equilibrium, the system remains inalterable up to 24 h.

3.4. Column tests and MS stability

In data analysis of column tests, the extraction time at which the feed Cr(VI) concentration reached the value of 0.5 ppm was selected as the breakthrough point. This concentration value is the maximum concentration allowed by the National Regulation of Argentina [33] on water characteristics for direct discharge into municipal wastewater treatment plants. The MS stability was tested in column working with three consecutive cycles, where each cycle was performed as a single Cr(VI) extraction-stripping process. For clarity of comparison, only the results of the first cycle for all synthesized MS are shown in Fig. 6, and Fig. 7 shows data of three cycles for PSf–PVP (2:1) and silicone microspheres. The breakthrough point values are given in Table 5. These results indicate that, although interesting breakthrough points are obtained, the Cr(VI) extraction performance decrease after each cycle. In the case of PSf–PVP (2:1), a decrease in the breakthrough point from 10 h and 24 min (first cycle) to 7 h and 30 min (third cycle) was obtained. Cr(VI) concentration higher than 0.5 ppm was found in the second cycle for

Table 5
Breakthrough points (h) (at 0.5 ppm Cr(VI)) in column operation

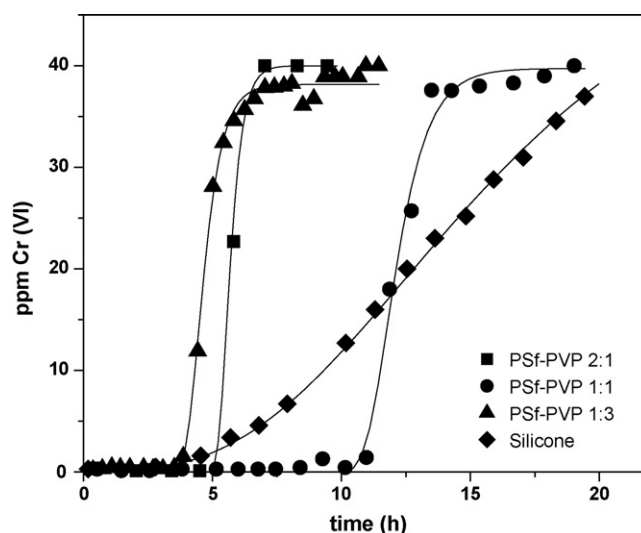| Microspheres	Breakthrough point (h)		
	Cycles		
	1	2	3
Silicone	3.12	1.60	–
PSf–PVP (2:1)	10.40	8.14	7.50
PSf–PVP (1:1)	5.02	–	–
PSf–PVP (1:3)	3.75	–	–

Fig. 6. Breakthrough curves of Cr(VI) in the first cycle from column tests packed with IMS.
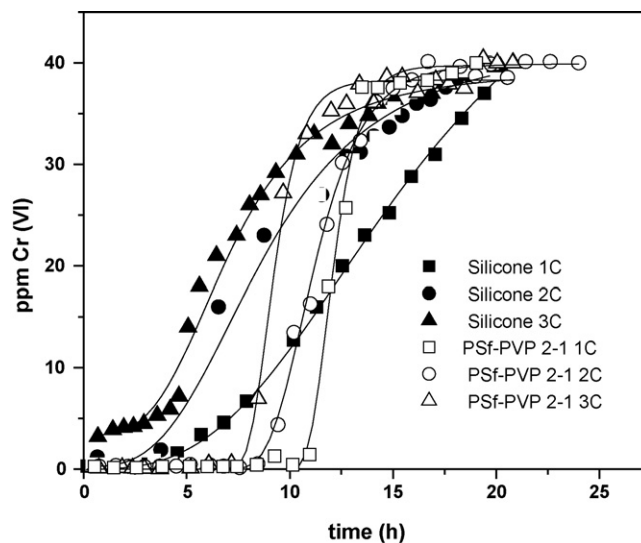

Fig. 7. Breakthrough curves of Cr(VI) in three cycles from column tests packed with IMS of PSf–PVP (2:1) and silicone.

MS of PSf–PVP (1:1 and 1:3) and in the third cycle for silicone MS.

4. Conclusions

Microspheres from both silicone and mixtures with different ratios of PSf–PVP applied to processes of metal ion extraction were synthesized by two methods. MS of silicone were prepared from polymer cross-linking in emulsion, while MS of PSf were obtained by the phase inversion process. Through this type of preparation, MS could be structurally modified. Observations by microscopy show that those MS prepared with PSf–PVP (2:1) presented spheres shape with smaller sizes with a mono-modal distribution centred in $d_e \approx 3.8\ \mu m$. The highest extractive performance of Cr(VI) was obtained from MS of PSf–PVP (2:1) (98% of extraction at 90 min) and silicone MS (92% of extrac-

tion at 90 min). This can be attributed to MS structural and extractant–polymer interaction characteristics which lead to a high stability of the extractant impregnated in pores and a higher availability of extractant per mass unit of MS during the process of extraction. Column operation studies shown that MS of PSf–PVP (2:1) has the best extraction performance with breakthrough points of 10 h and 24 min, 8 h and 8 min and 7 h and 30 min for the first, second and third cycle, respectively. These results indicate that MS of PSf–PVP (2:1) have structural and chemical characteristics appropriate to be used during long time as impregnate microspheres for Cr(VI) extraction from wastewater solutions.

Acknowledgements

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