Microencapsulation of TOMAC by Suspension Polymerisation: Process Optimisation

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Abstract

The optimisation process for the synthesis of microcapsules containing trioctylmethylammonium chloride (TOMAC), a selective extractant agent for the removal of mercury from wastewaters, by the suspension copolymerisation of styrene (St) and divinylbenzene (DVB) was studied. The influence of the diluent, mass ratio of the suspending agents (arabic gum –AG– and polivinylalcohol –PVA–), TOMAC:diluent volume ratio and weight percentage of DVB respect to the monomers mixture (% DVB) on the encapsulation process and the physical properties of the resulting microcapsules were investigated.

It was found that using heptane as diluent led to non-spherical microcapsules with poor reaction yield and conversion of the monomers. Nevertheless, when toluene was used these properties were improved. Furthermore, for a TOMAC:toluene ratio of 1:3 spherical beads were obtained. The combined use of the suspending agents was more appropriate than using them separately, due to the latex product and the low conversion of the monomers for AG and PVA, respectively. The increase of the % DVB from 18.8 to 50 % enhanced the mechanical resistance of the polymeric shell, increasing the reaction yield up to an 84.7 % and maintaining the TOMAC encapsulation (36.0 %) and the sphericity of the microcapsules. The obtained particle size (40 µm) indicated that the main application of this material will be in fluidised beds or in perfectly mixed reactors. On the basis of the experimental results, a AG:PVA mass ratio of 1:1, a TOMAC:toluene volume ratio of 1:3 and 50 % DVB were established as the best conditions to produce this kind of microcapsules, enabling its reproduction on a pilot scale plant. In addition, the high values of the distribution coefficient for mercury removal confirm the success of this optimisation process.

Keywords: microencapsulation, suspension polymerization, TOMAC (Aliquat 336), extraction, mercury.

1. Introduction

The environmental persistence and easy bioaccumulation of mercury make it be considered as one of the most toxic contaminants at global scale. Mercury is introduced in the food chain through the transformation into methylmercury in aquatic environments which is accumulated in fishes and can finally affect the human health. Thus, the water treatment for the mercury removal is a vital research field which is also promoted by the new European regulations regarding this concern (Commission of the European Communities, 2010).

Nowadays, the main industrial processes for heavy metal uptake from water are the solvent extraction (Mane et al., 2012) and the ion exchange resins (Dabrowski et al., 2004). However, both techniques present important disadvantages that limit their final application. On the one hand, part of the extractant agent used in the solvent extraction technique moves from the organic media to the water phase and therefore, additional purification steps are required. On the other hand, conventional ion exchangers exhibit low selectivity and slow kinetics. In order to overcome these disadvantages, our research group is working in the development of microcapsules containing extractant agents with high mercury selectivity which combine the advantages of both technologies trying to solve the above commented problems. The existence of a large interfacial area, high selectivity, reduced use of organic solvents and easy separation of metal-loaded microcapsules are some of the advantages of this alternative.

Many different extractant agents have been applied for the removal of mercury from wastewaters such as tri-n-octylphosphine oxide (TOPO), tri-n-butylphosphate (TBP), di-n-hexylsulfide (DHS), O,O’-dimethyl-O-(3-methyl-4-nitrophenyl)phosphorotioate (DMTP), O,O’-diisopropyl-S-benzylthiophosphate (DPBTP) (Shigetomi et al., 1983), trioctylamine (TOA) (Chakrabarty et al., 2010), trioctyl methyl ammonium chloride (TOMAC) (Cattrall and Daud, 1979; Fábrega and Mansur, 2007; Lothongkum et al., 2011), panicillamine (Kõszegi-Szalai and Paál, 1999), di(2-ethylhexyl)phosphoric acid (DEHPA) (Gupta et al., 2011) and thiosubstituted organophosphoric acids extractants such as the commercial Cyanex 471X, 932 or 301 (Francis and Reedy, 2003; Francis et al., 2000; Meera et al., 2001). Among all of them, TOMAC stands out due to its superior mercury extraction ability in systems with low mercury concentrations between 0.005 and 0.250 mg L^{-1} (Lothongkum et al., 2011).

The microencapsulation of extractant agents for the removal of water pollutants is attracting the researchers' attention over the last two decades (Ni et al., 1994). Depending on the extractant agent and the final application, different microencapsulation techniques and shells have been used. The most common techniques described in literature for the microencapsulation of extractant agents are interfacial polymerisation (Laguecir et al., 2002; Ni et al., 1994), suspension polymerisation (Araneda et al., 2008; Barasi et al., 2009; Fonseca et al., 2010; Kamio et al., 2005; Kiyoyama et al., 2007; Nishihama et al., 2002 and 2004; Sánchez-Silva et al., 2011), solvent evaporation (Ozcan et al., 2010; Yang et al., 2004, 2005) and gelation (Outokesh et al., 2006, Wu et al., 2008; Zhang et al., 2011). Among the microcapsules shells, polydivinylbenzene –DVB– (Kamio et al., 2005; Kiyoyama et al., 2007) and poly(styrene-co-divinylbenzene) –P(St-DVB)– (Alcázar et al., 2011; Fonseca et al., 2010; Nishihama et al., 2002, 2004; Valenzuela et al., 2006) are usually employed, since P(St-DVB) is the most common material used in the manufacturing of commercial ion exchange resins. It is also common the use of polystyrene –PSt– (Yang et al., 2005), poly(styrene-co-ethylene glycol dimetacrylate) –P(St-EGDMA)– (Araneda et al., 2008; Barasi et al., 2009), polyurea (Ni et al., 1994), polyamides (Laguecir et al., 2002) and sodium alginate (Outokesh et al., 2006; Wu et al., 2008).

According to the reviewed literature, the use of the suspension polymerisation of P(St-DVB) is one of the best alternatives for the encapsulation of extractant agents. The easy heat removal and temperature control, the negligible viscosity increase, the easy handling and isolation of the obtained product, the low levels of impurities in the polymer product and the low-cost of the process, can be remarked as the main advantages of this encapsulation technique compared to other polymerization methods (Yuan et al., 1991). Regarding the microencapsulation of TOMAC, which as commented above is the most efficient extractant agent for the removal of mercury, Nishihama et al. (2004) reported the feasibility of using P(St-DVB) as shell by means of suspension polymerisation with 2,2'-azobis(isobutyronitrile) (AIBN) as initiator and arabic gum as stabiliser. Microcapsules with a particle size of 30-150 μm and a loading capacity for Cr(VI) of 0.054 mmol g^{-1} were obtained by these authors; nonetheless, the microencapsulation process was not optimised.

As is well known, a suspension-like polymerisation process for microencapsulation involves two phases: a continuous one composed by the reaction media (usually water) and a suspending agent; and a discontinuous one containing the monomers, initiator and the active agent to be encapsulated. The success of the suspension polymerisation technique and the final properties of the microcapsules strongly depend on the mobility between the components, compatibility between the polymers and monomers, hydrophilicities and the monomer ratios (Stubbs and Sundberg, 2008). Moreover, porogen agents or diluents are also added in order to create porous microcapsules through which the pollutants can diffuse and reach the extractant agent.

Hence, the aim of this research work is to carry out the optimisation of the microcapsule synthesis, finding the proper recipe, diluent, diluent:extractant and suspending agent mass ratios, and % DVB in order to accomplish the proper microcapsules properties (morphology, particle size, particle size distribution, extractant agent content and mechanical stability). In the same way, whereas the conversion of the monomers, the yield of the reaction and the encapsulation efficiency will be improved, the generated wastewater pollutant potential will be minimised. Additionally, by using the proper recipe, the microcapsules will be synthesised at pilot plant scale using a reactor of 10 L, having geometrical analogy with that used at lab scale. Finally, the ability for the selective removal of mercury will be determined in order to confirm that the steps followed are also suitable for the development of a material with the best characteristics for mercury uptake.

2. Materials and methods

2.1. Materials

The monomers, styrene (99 wt.%, Sigma-Aldrich Chemical Co.) and divinylbenzene of technical grade (containing 80 % DVB isomers, Fluka Chemical Co., Ltd.), were purified by washing with aqueous sodium hydroxide solution and using calcium chloride as a desiccant. TOMAC (≥93 wt.%, mixture of octyl $–C_8–$ and decyl $–C_{10}–$ chains, being C_8 dominant; Fluka Chemical Co., Ltd.) was used as the extractant agent. Benzoyl peroxide (97 wt.%, Fluka Chemical Co., Ltd.) (98 wt.%, Aldrich Chemical Co.) was used as the initiator. Arabic gum of reagent grade (Sigma-Aldrich Chemical Co.) and polyvinylalcohol (10-98, Mw 61.000 g mol^{-1}) of analytical grade, supplied by Fluka Chemical Co., Ltd.; were used as stabilisers. Heptane and toluene of analytical grade (BDH Prolabo, VWR Co.) were used as inert diluents.

Water with a conductivity of 1 μS cm^{-1} was purified by distillation and subsequent deionisation using ion exchange resins (Milli-Q water). Nitrogen was high-purity grade (99.999 %).

An aqueous solution containing 0.010 mg L^{-1} of mercury at pH = 1 was prepared by dissolving mercury (II) chloride (≥99 wt.%, Panreac Chemical Co.) in Milli-Q water. Its pH value was adjusted with hydrochloric acid (≥37 wt.%, Sigma-Aldrich Chemical Co.).

2.2. Methods

Microcapsules from P(St-DVB) containing TOMAC were obtained by suspension-like polymerisation technique in a 0.5 L jacketed glass reactor (Mervilab) (Madrid, Spain) equipped with a nitrogen gas inlet tube, a reflux condenser, a digital control of stirring and a thermostatic bath (Ultraterm-200, SELECTA) (Abrera, Spain) to hold the reactor at the desired conditions. The synthesis process involves two phases: a continuous phase containing water and the suspending agent or suspending agents and a discontinuous phase containing the monomers, the diluent, the initiator and TOMAC. Materials were prepared in order to encapsulate by ~30 wt.% of extractant agent following the method and the optimum recipe described in a previous study (Alcázar et al., 2011). The continuous phase was transferred to the glass reactor fixing the agitation at 400 rpm to ensure a good dispersion of the organic phase and the temperature at 80 ºC. The initiator was dissolved and premixed with monomers and the extractant agent at 50 ºC and 250 rpm employing a hot plate stirrer Agimatic-ED (of the trading house SELECTA) (Abrera, Spain). Then, the discontinuous phase was added to the continuous one. The polymerisation process was carried out for 5 h under a nitrogen atmosphere maintaining 400 rpm as the agitation rate by means of a six-bladed Rushton turbine stirrer power by an overhead stirrer Heidolph RZR 2021 model (Schwabach, Germany). The product was purified by repeated washing with water and finally dried at room temperature for 24 h.

Distribution coefficients for mercury were determined as follows: 0.1 L of the metallic solution of pH = 1 and 0.010 mg L^{-1} of mercury were added to each flask in which 0.5 g of wet microcapsules were loaded. The suspension formed by the solid material and the solution was vigorously agitated at 1000 rpm with a multipoint magnetic stirrer and the temperature was kept constant at 25 ºC using a thermostatic bath (Tectron 3473200, commercial SELECTA), until equilibrium was achieved (24 h). At the end of this period, the content of mercury in the liquid phase were analysed as described in section 2.3.5.

The solid phase concentration in equilibrium with the liquid phase was obtained by the mass balance equation:

$$q^* = [(C_0 - C^*)\ V]/W \tag{1}$$

where q^* = amount of mercury in the microcapsule (mg $g^{-1}_{\text{dry microcapsules}}$), C_0 and C^* = initial and equilibrium concentrations of mercury in the liquid phase (mg L^{-1}), respectively; V = initial volume (L) and W = weight of dry solid (g).

2.3. Characterization

2.3.1. Environmental Scanning Electron Microscopy (ESEM)

The morphology and surface features of the microcapsules were observed by using a Quanta 250 (FEI Company) with a wolfram filament operating at a working potential of 12.5 kV. A Gaseous Secondary Electron Detector (GSED) and a Large Field Detector (LFD) were employed. The electron beam resolution at this vacuum mode is 2.0-3.0 nm at 30 kV.

2.3.2. Thermogravimetric Analyses (TGA)

The thermal stability and extractant agent content of the synthesised microcapsules were obtained by using a TA instruments SDT Q600 Simultaneous DSC-TGA from room temperature to 700 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. This equipment presents a calorimetric accuracy/precision of ±2 % (based on metal standards) and a balance sensitivity of 0.1 μg.

2.3.3. Particle size and particle size distribution

The average particle size of the microcapsules in number ($dpn_{0.5}$) and volume ($dpv_{0.5}$) as well as the particle size distribution (PSD) were determined by Low Angle Laser Light Scattering (LALLS) using a Mastersizer Hydro 2000 equipped with a Scirocco 2000 unit that works with air as dispersing agent. $dpn_{0.5}$ and $dpv_{0.5}$ represent 50 % of beads whose mean numeric and volumetric diameter, respectively, is less than this value. Each sample was analysed at least three times to ensure reliable measurements with a precision of 1 %.

2.3.4. Total organic carbon (TOC) and chemical oxygen demand (COD)

The polluting potential of the waste liquid obtained after the polymerisation process was measured by TOC and COD analyses. The TOC levels were determined by high temperature catalytic oxidation (HTCO) method, using a commercial Shimadzu TOC 5000 analyser, with a standard deviation (SD) of ±320 mg L^{-1}. The analyses of COD were carried out using the Hach COD reactor where samples were digested at 148 ºC during 2 h and a Hach DR/2000 spectrophotometer was used to measure the optical density of the recovered solution at 620 nm. An experimental error of ±0.002 mg L^{-1} is associated to this spectrophotometer, which performs itself the measurements three times.

2.3.5. Process parameters optimisation

The conversion of the monomers (X_m), yield of the reaction (η_r) and encapsulation efficiency (EE) were determined following the below equations:

$$X_m\,(\%) = MC\text{-}TOMAC \cdot (1 - TOMAC_{TGA}) \,/\, (St+DVB)_{feed} \cdot 100 \qquad (2)$$

$$\eta_r\,(\%) = MC\text{-}TOMAC \,/\, (TOMAC_{feed} + (St+DVB)_{feed}) \cdot 100 \qquad (3)$$

$$EE\,(\%) = TOMAC_{TGA} \cdot MC\text{-}TOMAC \,/\, TOMAC_{feed} \cdot 100 \qquad (4)$$

where $MC\text{-}TOMAC$ is the total amount of microcapsules synthesised in each reaction (g); $TOMAC_{feed}$ and $(St+DVB)_{feed}$ are the amount of the extractant and monomers fed to the reactor (g), respectively; $TOMAC_{TGA}$ is the percentage of TOMAC encapsulated, determined from the TG analyses (wt.%).

2.3.6. Concentration of mercury in the aqueous phase

Mercury content in the liquid phase was measured using a Cold Vapour Atomic Fluorescence Spectrophotometer (Millennium Merlin, PS Analytical) (sensitivity of 1 ng L^{-1} and three repetitions of the measurements).

3. Results and discussion

The set of experiments shown in Table 1 were carried out with the aim of optimising the process and obtaining the microcapsules with the desired characteristics.

Table 1 – Experiments conducted in the optimisation of MC-TOMAC synthesis.

Exp.	**Scale**	**Diluent**	**AG:PVA (w:w)**	**TOMAC:diluent (v:v)**	**% DVB (wt.%)***
1	laboratory	heptane	1:1	1:1	18.8
2		toluene			
3			0:1		
4			1:1	1:0	
5				1:3	
6					50.0
7	pilot plant				

*** wt.% respect to the monomers mixture**

Table 2 summarises the properties of the microcapsules ($dpn_{0.5}$, $dpv_{0.5}$, content of TOMAC, X_m, η_r and *EE*) and the polluting potential of wastewaters (COD and TOC) resulting from each experiment.

Table 2 – Characteristics of the microcapsules and the pollution indicators of the wastewaters for each experiment.

Exp.	**$dpn_{0.5}$ (µm)**	**$dpv_{0.5}$ (µm)**	**$TOMAC_{TGA}$ (wt.%)**	**X_m (%)**	**η_r (%)**	***EE* (%)**	**COD (mg L^{-1})**	**TOC (mg L^{-1})**
1	18.81±1.48	758.11±1.57	52.70	14.17	20.62	34.87	47300	14050

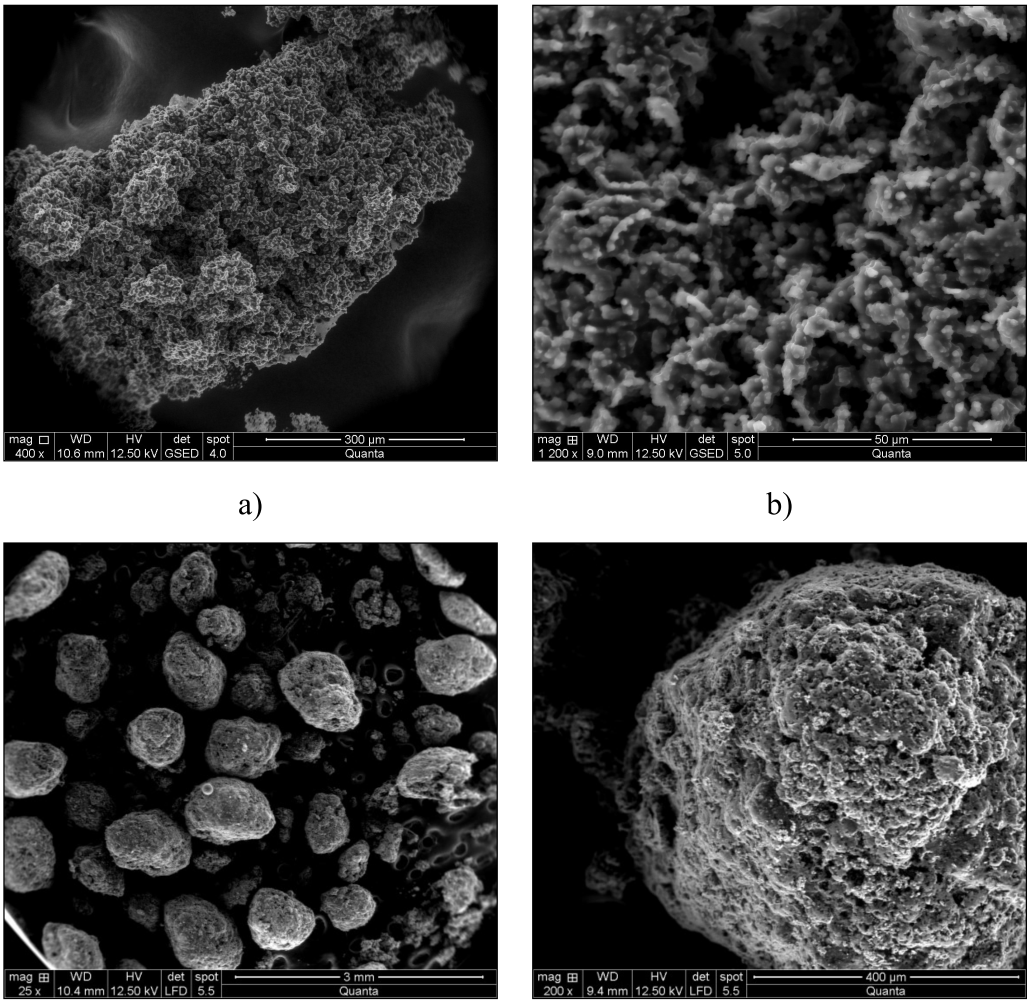
2	99.06±13.92	867.94±37.41	35.82	56.32	60.42	69.47	45900	13750
3	608.29±21.51	936.56±11.49	40.84	41.09	47.66	62.05	52200	13020
4	-	-	46.05	39.62	51.43	79.02	49100	14290
5	96.47±0.04	180.03±2.92	34.85	71.33	75.35	84.25	37100	12230
6	2.79±0.01	41.71±0.91	36.00	79.80	84.70	95.10	45200	12460
7	5.80±0.24	9.63±0.06	37.70	75.95	81.87	93.96	45000	12300

Note: dpn$_{0.5}$ and dpv$_{0.5}$ represent mean±SD (*n* = 3).

3.1. Selection of the diluent

Heptane and toluene are usually employed in the synthesis of ion exchange resins as porogens (Barreto de Oliveira, et al., 2005; García-Diego et al., 2005; Kiatkamjornwong et al., 2001) and also in the conventional liquid-liquid extraction processes to form the organic liquid membrane (Hu et al., 2014; Xu et al., 2014). Thus, both diluents would be good candidates for the synthesis of this kind of microcapsules. Furthermore, toluene has been used in prior studies for the synthesis of microcapsules containing DEHPA with successful results (Alcázar et al., 2011).

Experiments 1 and 2 were performed under the same conditions but for the diluent type in order to select the most proper one for this application. Fig. 1 shows the morphology of MC-TOMAC synthesised using heptane (Fig. 1a and 1b) and toluene (Fig. 1c and 1d). As can been observed, these materials presented a particle size larger than 300 μm and were constituted by the agglomeration of smaller particles, giving them a roughness and a non-spherical appearance. Thus, they presented a bimodal PSD in number and volume. Nonetheless, dpn$_{0.5}$ and dpv$_{0.5}$ were slightly larger for microcapsules obtained with the aromatic solvent.



a) b)

c) d)

Fig. 1 – ESEM micrographs of MC-TOMAC synthesised using heptane (Exp. 1): a) general view, b) high magnification; and toluene (Exp. 2): c) general view, d) high magnification. TOMAC:diluent (v:v) = 1:1, GA:PVA (w:w) = 1:1, 18.8 wt.% DVB.

Regarding the content of extractant encapsulated, in Fig. 2 TG and DTG curves for the P(St-DVB) polymer, pure TOMAC and the synthesised microcapsules using toluene are illustrated. As can be noted, TG plot for pure TOMAC indicates that this compound evaporates between 69.6 and 298.3 ºC, showing two non-defined peaks which can be attributed to the mixture of C_8 and C_{10} chains that are present in its formulation. On the other hand, the P(St-DVB) is stable within this temperature range and decomposes between 300.0 and 461.6 ºC. Thus, the first degradation step of the MC-TOMAC can be related with $TOMAC_{TGA}$, 35.82 wt.%.

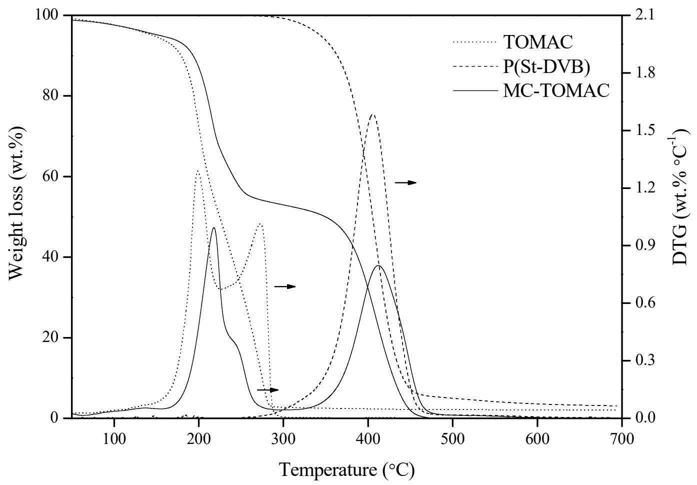


Fig. 2 – TG and DTG curves for pure TOMAC, P(St-DVB) and MC-TOMAC synthesised using toluene.

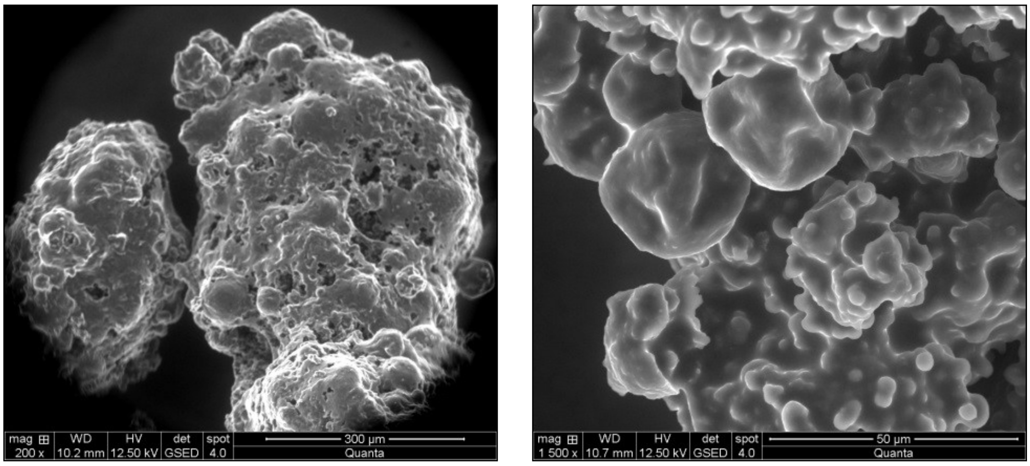
The encapsulation efficiency achieved in experiment 2 was twice as high as that obtained for microcapsules synthesised using heptane although $TOMAC_{TGA}$ diminished by 32.04 %. This is due to an increase in the yield of the reaction, which was almost three times higher. This also justifies the larger conversion of the monomers into the polymeric shell (4 times higher) and thus, an improvement in the mechanical properties. The greater yield sought was confirmed by the lower contamination of the wastewaters, whose COD and TOC values decreased by 3 and 2 %, respectively.

Taking into account the results reflected in Table 2 and despite the non-spherical morphology of the material, toluene was selected as the most suitable diluent for the synthesis of MC-TOMAC.

3.2. Effect of the mass ratio of the suspending agents

The influence of arabic gum (AG) and polyvinylalcohol (PVA) as suspending agents was explained in a previous work in which microcapsules containing DEHPA were synthesised (Alcázar et al., 2011), demonstrating that AG and PVA had opposite effects on the morphology of the particles. A mass ratio AG:PVA of 1:0 led to smaller microcapsules and a lesser percent of non-spherical microcapsules respect to that for a ratio 1:1, meanwhile for a AG:PVA of 0:1, greater average particle sizes and higher content of amorphous material were obtained. Thus, in this research work additional mass ratios of 1:0 and 0:1 AG:PVA were tested.

When AG was employed as the only suspending agent a latex was obtained, which would lead to sizeable pressure drop values in a conventional ion exchange column and difficult handling in fluidised beds or in perfectly mixed reactors. Therefore, this material was rejected for further considerations and analyses and not included in Tables 2 and 3. For a AG:PVA of 0:1 (Exp. 3), non-spherical large microcapsules (dp > 600 μm) with a rough surface were obtained, as can be observed in Fig. 3. With regard to the rest of the process and product properties of this experiment 3 (Table 2), the content of the extractant encapsulated was 14.00 % greater than that achieved for a AG:PVA ratio of 1:1 (Exp. 2). This increase is due to the lower conversion of the monomers (27.05 % lower) and the yield of the reaction, which diminished by 21.11 %, so that the encapsulation efficiency diminished by 10.70 %. As a result, comparing the COD values, it is observed that the pollution of the wastewater rose by 13.33 %.



a) b)

Fig. 3 – ESEM photographs of MC-TOMAC obtained for a AG:PVA mass ration of 0:1 (Exp. 3): a) general view, b) high magnification. TOMAC:toluene (v:v) = 1:1, 18.8 wt.% DVB.

These results confirm PVA as a suspending agent that promotes the production of non-spherical material with great particle size and a low yield of the reaction. Thus, a mass ratio 1:1 was selected for the synthesis of MC-TOMAC. Nonetheless, further modifications in the recipe were performed in order to produce a spherical material for its ion exchange applications.

3.3. Selection of the volume ratio TOMAC to diluent

The effect of diluents in the synthesis of commercial ion exchange resins is very well defined in literature since they act as porogens in the polymerisation reaction, changing their internal structure. However, this effect has not been described yet in the synthesis of complexing microcapsules.

Two different volume ratios of TOMAC to toluene were analysed: 1:0 and 1:3 (Exp. 4 and 5, respectively); apart from the one previously studied in Exp. 2 (1:1).

The material achieved in the absence of toluene was not mechanical stable and thus, not considered for further purposes. On the other hand, for the volume ratio 1:3, the surface of the microcapsules was softer and their morphology was spherical according to the ESEM analyses shown in Fig. 4, obtaining beads with a particle size close to 200 µm. Furthermore, number and volume PSD depicted in Fig. 5, indicates the uniformity of the product due to the unimodal distributions and the close $dpn_{0.5}$ and $dpv_{0.5}$ values (96.47±0.04 and 180.03±2.92 µm, respectively).

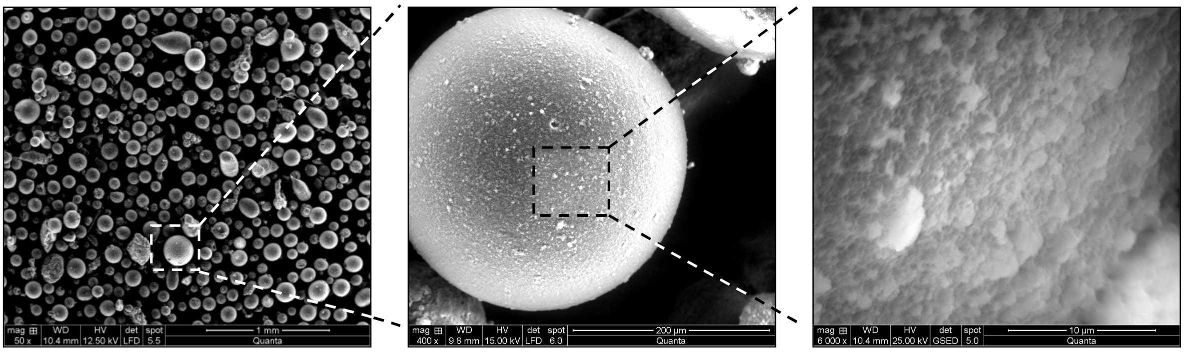


Fig. 4 – ESEM photographs of MC-TOMAC and magnifications for a TOMAC:toluene volume ratio of 1:3 (Exp. 5). GA:PVA (w:w) = 1:1, 18.8 wt.% DVB.

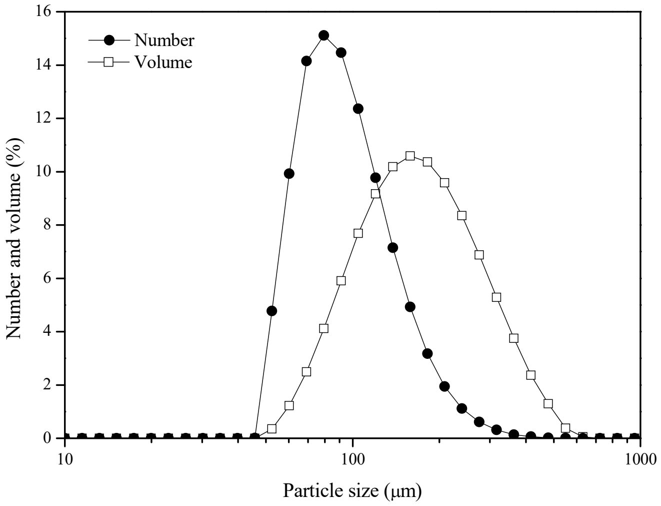


Fig. 5 – PSD in number and volume of MC-TOMAC for a TOMAC:toluene volume ratio of 1:3 (Exp. 5). GA:PVA (w:w) = 1:1, 18.8 wt.% DVB.

The effect of the volume ratio TOMAC:toluene on the whole process can be illustrated in Fig. 6. According to it, the higher the amount of toluene employed in the reaction, the lower the content of TOMAC encapsulated. This fact was due to the rise of the conversion of the monomers, as it was demonstrated by the increase in the yield (up to 75.35 %) and by the diminution of the pollution parameters (up to 37100 mg L^{-1} for COD and 12230 mg L^{-1} for TOC). Meanwhile, when toluene was not used, the encapsulation efficiency was larger than that achieved for the experiment with the highest amount of the diluent. This fact could be due to the low conversion of the monomers and the great amount of extractant encapsulated. For this reason COD and TOC values were up to ~7 % (49100 mg L^{-1}) and ~4 % (14290 mg L^{-1}) higher, respectively, than those for 1:1 volume ratio, causing a low increase in the waste pollution.

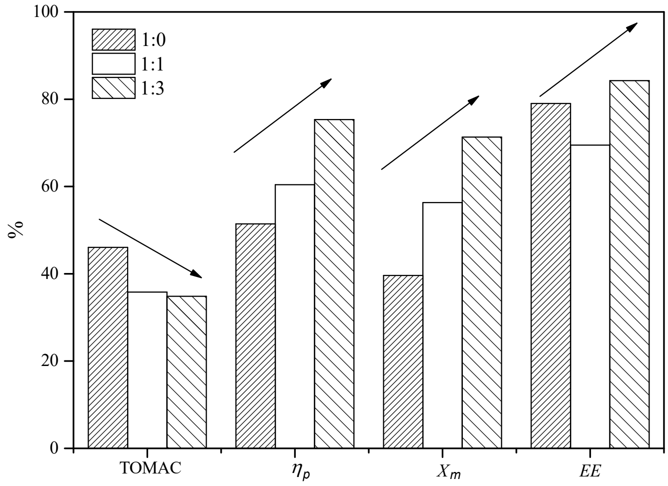


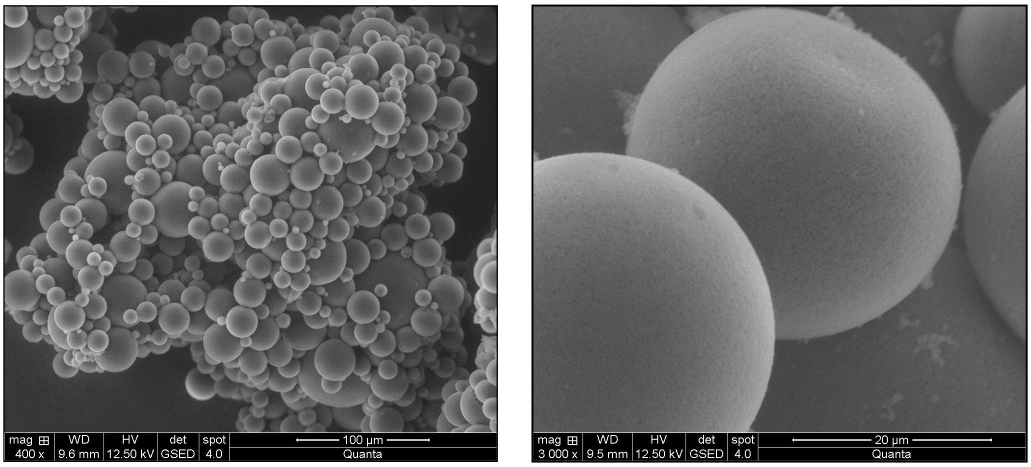
Fig. 6 – Comparison of the characterisation parameters for the studied TOMAC:toluene ratios for a AG:PVA of 1:1. 18.8 wt.% DVB.

Taking into account the aforementioned results, it was selected the volume ratio TOMAC:toluene of 1:3 as the most suitable for the synthesis of MC-TOMAC. Nevertheless, it was necessary to improve the mechanical properties of the material and the conversion of the monomers; since in the case of microcapsules, the presence of the extractant in the polymer matrix reduces its mechanical resistance. To this end, the percentage of DVB respect to the monomers mixture was increased due to the improvement in the physical stability achieved when the crosslinking density is risen (Zaganiaris, 2009).

3.4. Selection of the percentage of DVB respect to the monomers mixture

DVB is a crosslinker widely used in the synthesis of ion exchange resins due to its capacity to improve the chemical and mechanical properties of the synthesised particles. Typical values of this crosslinker from 18 up to 60 wt.% (respect to the monomers mixture) for macroporous resins are found in literature (Fritz and Gjerde, 2009; Harland, 1994). Considering this fact, the % DVB was risen from 18.8 % up to 50 % (Exp. 6).

Fig. 7 shows MC-TOMAC synthesised under these conditions. It can be observed that these microcapsules have a spherical morphology and a smooth surface, with particle sizes larger than 20 µm.



a) b)

Fig. 7 – ESEM photographs of MC-TOMAC obtained for a 50 % DVB (Exp. 6): a) general view, b) high magnification. TOMAC:toluene (v:v) = 1:1, GA:PVA (w:w) = 1:1.

PSD in number was bimodal (Fig. 8), being the average particle size lower than 40 µm (Table 2), too tiny for its application in fixed-bed columns but, in the range of the values found in literature by Barassi et al. (2009), Nishihama et al. (2004) and Yang et al. (2005) for microcapsules containing TOMAC. This depletion in the particle size respect to that shown by those materials obtained for 18.8 % DVB could be due to the high reactivity of DVB. In suspension polymerisation, the reaction occurs exclusively in the organic phase droplets, which behave as a mini-bulk reactor. Therefore, as DVB it is consumed more rapidly than St (Ding et al., 1992) the identification point of the particles is reached sooner and consequently, at lower sizes.

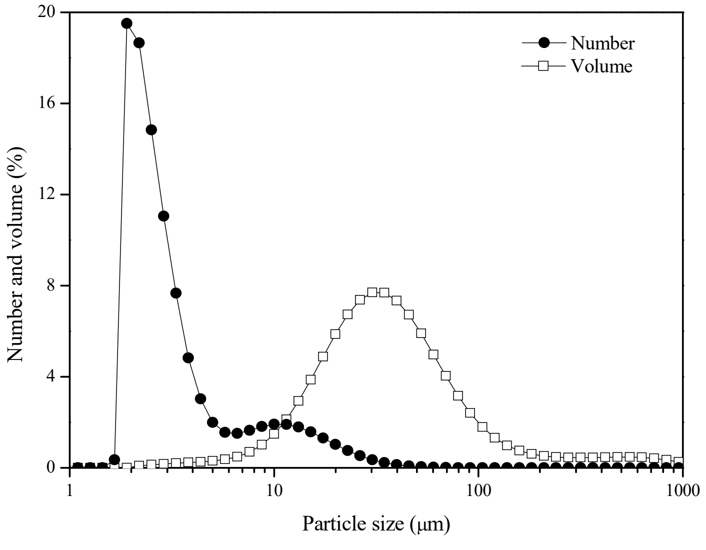


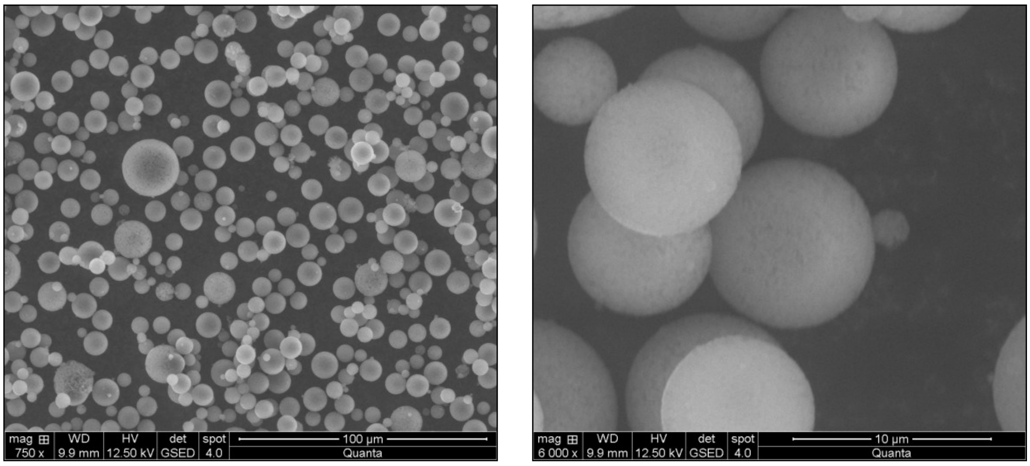
Fig. 8 – PSD in number and volume of MC-TOMAC produced for a 50 % DVB (Exp. 6). TOMAC:toluene (v:v) = 1:1, GA:PVA (w:w) = 1:1.

When a higher content of DVB was utilised in the production of MC-TOMAC, as it was expected, the conversion of the monomers grew up to 79.80 %. That increase did not affect the percentage of TOMAC encapsulated, which kept constant. Thus, the yield of the reaction and the encapsulation efficiency rose by 12.40 and 12.90 %, respectively. Consequently, pollution parameters diminished by 5.12 % for COD and 1.06 % for TOC.

Although microcapsules synthesised with a 50 % DVB had a particle size below that presented by commercial resins, they showed a spherical morphology and good properties such as high yield of the reaction (close to 85 %), great encapsulation efficiency (95 %) and a content of the extractant higher than the theoretical value. Therefore, this formulation was selected as the most suitable to carry out the synthesis of microcapsules containing TOMAC as extractant agent within P(St-DVB) shells, being its main application in fluidised beds or in perfectly mixed reactors.

3.5. Production of the microcapsules at pilot plant scale

Once the recipe was selected, the production of the microcapsules on a larger scale was conducted so as to check the robustness of the formulation (Exp. 7). The material was synthesised in a pilot scale plant with a 10 L reactor and stirrer, both geometrically proportional to those used in the laboratory scale experiments. Likewise, the dimensions of the Rushton turbine impeller were based on the standard stirrer configuration reported by McCabe et al. (1991) for continuous stirred tank reactors. Assuming that the energy dissipation rate is uniformly distributed in the turbulence field in both scales, the agitation rate in pilot plants should be lower than that used in laboratory scale in order to obtain a product that exhibits a similar particle size distribution. Nevertheless, the stirring rate calculated from Kolmogorov microscale expression, determined by Sánchez-Silva et al. (2010) for microcapsules containing paraffin, was too small to ensure a good dispersion of the organic phase and therefore, a higher value (450 rpm) was employed in the scale-up reaction. This fact gave rise to a decrease of the mean particle diameter of the material since, the greater the agitation rate the smaller the particle size. A larger power input per unit of volume provided by the stirrer for the reaction medium will result in higher breakdown of the droplets in the suspension, less coalescence and, therefore, smaller particle size (Zhang et al., 2004).



a) b)

Fig. 9 – ESEM photographs of MC-TOMAC obtained for a 50 % DVB in a 10 L reactor (Exp. 7): a) general view, b) high magnification. TOMAC:toluene (v:v) = 1:1, GA:PVA (w:w) = 1:1.

On the other hand, the content of TOMAC encapsulated, process parameters and pollution indicators were similar to the laboratory scale data (Exp. 6). Furthermore, spherical beads with smooth surface were obtained as well, as can be observed in Fig. 9. Thus, it was possible to scale up the production of microcapsules containing TOMAC as extractant agent owing to the robustness of the formulation. In spite of this fact, further experiments should be carried out so as to determine the agitation rate needed in pilot scale to obtain the same particle size of the laboratory scale."

In order to know the structure and porosity of the microcapsules, a SEM micrograph of a single-particle cross section was made and it is shown in Figure 10.

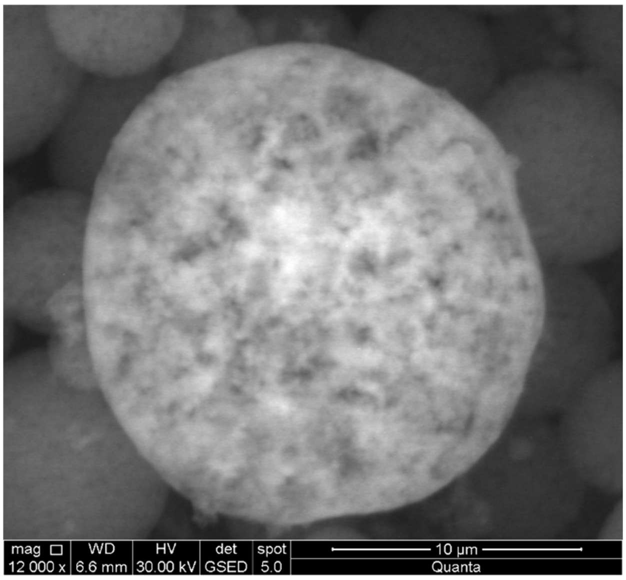


Fig. 10– ESEM photograph of a single-particle cross section obtained for a 50 % DVB in a 10 L reactor (Exp. 7): TOMAC:toluene (v:v) = 1:1, GA:PVA (w:w) = 1:1.

As can be seen, the structure of MC-TOMAC is matrix type, being the extractant agent trapped into the porous of the polymer. Besides, as expected this resin is completely macroporous attending to the value of used crosslinker perecentage respect to the monomers mixture (50 DVB wt.%) which is within the corresponding value for commercial macroporous resins (18 to 60 wt.%). The large porous size of this material suggests a faster diffusion of the pollutants from the bulk solution to the active sites of the microcapsules and also, favours the accessibility of these active sites by the counterions. In that way, a large porosity is a guarantee of the usability of the full capacity of the MC-TOMAC.

3.6. Distribution coefficient for mercury

As has been mentioned previously, TOMAC presents a high selectivity for mercury, especially in a range between 0.005 and 0.250 mg L^{-1} (Lothongkum et al., 2011) and pH = 1 (Fábrega and Mansur, 2007), since at high Cl^{-} concentrations and pH values lower than 6, the predominant species are $HgCl_3^{-}$ and $HgCl_4^{2-}$ (Fábrega and Mansur, 2007; Kataoka and Yoshida, 1988; Miretzky et al., 2005), which are preferentially extracted by amine salts (Gupta and Mukherjee, 1990).

Thus, the determination of the distribution coefficient for each of the synthesised materials, under the conditions described in section 2.2, permits to confirm that the steps followed in the optimisation process are correct. This parameter was calculated from equation (5) and the obtained values are presented in Table 3.

$$D = [MR_n]_{MC} / [M^{n+}]_{aq} \tag{5}$$

where D denotes the distribution coefficient for each material (mg g^{-1}/mg mL^{-1}), $[MR_n]_{MC}$ and $[M^{n+}]_{aq}$ are equivalent to q^* and C^*, respectively.

Table 3 – Distribution coefficient for the microcapsules synthesised in each experiments.

Exp.	D (mg g^{-1}/mg mL^{-1})	Exp.	D (mg g^{-1}/mg mL^{-1})
1	$7.23\cdot10^4$	5	$6.41\cdot10^5$
2	$4.90\cdot10^5$	6	$9.98\cdot10^6$
3	$1.16\cdot10^5$	7	$2.10\cdot10^7$
4	$1.46\cdot10^5$		

Bearing in mind the results shown in Tables 2 and 3, it can be concluded that microcapsules with spherical shape (experiments 5-7) had the greatest values of D ($>6\cdot10^5$ mg g^{-1}/mg mL^{-1}), X_m (>68 %) and η_r (>75 %), and the lowest contents of TOMAC (~36 wt.%). Additionally, results of the experiments 6 and 7 confirm the robustness of the formulation as D for scale up microcapsules is almost the same as that of the laboratory scale.

In contrast, those materials synthesised in experiments 1, 3 and 4, which presented the smallest X_m and η_r values (<40 % and <52 %, respectively), showed the highest amount of TOMAC encapsulated (>41 wt.%) but the lowest distribution coefficients ($<5\cdot10^5$ mg g^{-1}/mg mL^{-1}). Furthermore, the employment of toluene (experiment 2) in the synthesis instead of heptane (experiment 1) as diluent improved this parameter in almost one order of magnitude. Thus, the structure and morphology of the microcapsules have a larger influence on their ability to remove metals than the amount of extractant itself.

4. Conclusions

The extractant agent TOMAC was successfully encapsulated within a polymeric shell from P(St-DVB) by suspension-like polymerisation technique.

Despite toluene is more toxic than heptane, it seemed to a better diluent for the synthesis of MC-TOMAC due to the greater yield of the reaction.

Single suspending agents AG and PVA led to a difficult handling latex and a poor conversion of the monomers, respectively. Consequently, the mixture AG:PVA 1:1 was the proper mass ratio for stabilising the organic droplets in the suspension.

The higher the content of toluene in the organic phase, the greater the yield of the reaction; being 75.35 % for a volume ratio TOMAC to toluene of 1:3. Furthermore, the achieved material was spherical and thus, this volume ratio was selected as the best option for the synthesis of the microcapsules.

Regarding the percentage of the crosslinker, 50 % of DVB respect to the monomers mixture provided a macroporous material with good mechanical properties maintaining the sphericity of the beads. Moreover, a yield of the reaction close to 85 %, a great encapsulation efficiency (95 %) and a content of the extractant higher than the theoretical value (36 wt.%) were obtained. Therefore, owing to the robustness of the formulation it was possible to scale up the production.

According to these results, it is possible to encapsulate an anionic extractant such as TOMAC using the same recipe proposed in a previous study, where the cationic extractant DEHPA was encapsulated, but increasing the percentage of the crosslinker.

Finally, distribution coefficient values showed that the developed material is suitable for mercury uptake, being this parameter improved with the use of toluene as diluent. Bearing in mind the low particle size obtained (~40 μm), the main application of this material will be in fluidised beds or in perfectly mixed reactors.

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