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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.

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., 2015) 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

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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 Reddy, 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; Barassi et al., 2009; Fonseca et al., 2010; Kamio et al., 2005; Kiyoyama et al., 2007; Nishihama et al., 2002, 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., 2005) 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; Barassi 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 °C. The initiator was dissolved and premixed with monomers and the