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ORIGINAL ARTICLE

Studies on removal of phenol using ionic liquid immobilized polymeric micro-capsules

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Abstract Phenol and phenolic compounds are pollutants of high priority concerns because of their toxicity and contribution to health problems. (Lohumi et al., 2004) The most suitable industrial process for the removal of phenol from aqueous streams is liquid–liquid extraction, which has its own limitations. In order to avoid possible drawbacks, such as persistent emulsification and leaching of extractant in conventional extraction operations, room temperature ionic liquid (RTIL) encapsulated in microcapsules (MC) is used as extractant.

The present study deals with the preparation of RTIL encapsulated microspheres by surfactant free emulsion polymerization under controlled conditions and the microspheres thus synthesized are characterized to ensure the desired particle size, morphology and surface area by using Scanning Electron Microscopy (SEM), FTIR and BET apparatus, respectively.

The effects of process variables such as agitation speed, agitation time, temperature, and shell material and the effect of dispersant were studied to determine the yield and size of microcapsules. This was followed by equilibrium distribution studies. The extractant loading capacity in the microcapsules was also analyzed by solvent extraction using hexane as solvent. Batch Sorption studies were conducted to optimize the process variables in the removal of phenol and the data were validated using various isotherms and kinetic models. Thermodynamic parameters were also established. Regeneration studies were also attempted to ensure the stability and reusability of microcapsules.

1. Introduction

Phenol and its derivatives, as one of the most important organic intermediates, have been widely used for the manufacture of pesticides, rubber, drugs and dyestuffs. As a result, more and more phenol-containing wastewater has been discharged into water bodies. Phenolic compounds are pollutants of high priority concerns because of their toxicity and contribution to health problems (Lohumi et al., 2004; Ram et al., 1990; He and Huang, 1992). Various methods of wastewater treatment, such as cata-

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lytic oxidation, liquid membrane separation, biological degradation and adsorption have been developed (Orshansky and Narkis, 1997; Deiber et al., 1997). Due to the ability of typical adsorbents to adsorb even at high concentrations, the adsorption process has been proved to be one of the most attractive and effective techniques for the separation of pollutants and purification in wastewater treatment (Wang et al., 2004; Fei et al., 2004; Zhai et al., 2003; Cai et al., 2005a, b; Wang, 2004).

In recent years, the polymeric microcapsules (MCs) have been extensively used for the recovery of metal ion pollutants (Araneda et al., 2008) and for drug delivery (Singh et al., 2010; Venkatesan et al., 2009). The MCs correspond to a porous polymeric matrix that contains an encapsulated suitable extracting reagent, room temperature ionic liquids (RTIL), called extractant which is chosen to selectively extract the desired pollutants. RTILs are organic or organo-elemental salts which exist as liquids at room temperature and they perform as ‘‘green solvents’’ due to their negligible volatility, high thermal stability, high electrical conductivity, low nucleophilicity and eco friendliness. The potential advantages of MCs are easy phase separation, large specific interfacial area, minimal use of organic solvent, high selectivity and more stability of extractant.

Optimization of the process variables is needed to achieve the maximum adsorption capacity and removal efficiency. The conventional method of optimizing the process variables requires a very large number of experimental runs which is highly expensive and time consuming. This limitation can be overcome by the statistical design of experiments, which reduces the number of experiments and provides an appropriate model for process optimization. Response surface modeling (RSM) is a useful method to optimize the responses shaped under the influence of process variables (Wang and Fei, 2006; Singh et al., 2011; Wan Ngah et al., 2008; Tao et al., 2009; Jain and Kadirvelu, 2011; Kincl et al., 2005; Singh et al., 2011; Tanyildizi, 2011; Ahmad and Ahmad, 2009; Sahu and Meikap, 2009; Kalavathy et al., 2009; Mohammed and Ahmad, 2010).

The present work deals with the preparation and characterization of RTIL encapsulated MCs under controlled conditions to evaluate the effect of process variables and dispersant in the synthesis of MCs with respect to their yield, size and shell material. The synthesized RTIL encapsulated MCs were used for the removal of phenol from aqueous solution. RSM was used to optimize the process parameters affecting the adsorption such as initial concentration of feed solution, adsorbent dosage, pH of feed solution and temperature.

2. Methodology

2.1. Materials

Gum arabic from acacia tree (Sigma) and Gelatin from porcine skin (Fluka) were used as dispersants for the preparation of microcapsules. Styrene (Alfa Aesar), Divinyl benzene (Alfa Aesar) and ethylene glycol dimethacrylate (Alfa Aesar) were used as monomers. Trioctylphosphineoxide 90% (Cyanex – 923) was the room temperature ionic liquid used as extractant. Benzoyl peroxide (Fluka), as polymerization initiator and toluene as diluent were also used. Phenol, 4-aminoantipyrene, Potassium ferricyanide, Phosphate buffer, 0.5 N ammonium solution, 0.1 N HCl solution, 0.1 M NaOH solution and deionized water were the other chemicals used.

2.2. Preparation of adsorbent

The synthesis of RTIL encapsulated polymer microcapsules was carried out in a batch reactor of 1.0 L capacity. A mixture of 250 mL de-ionized water and 1% of dispersant by weight as continuous phase was placed in the reactor and stirred continuously at a desired agitation speed under inert atmosphere. The organic solutions of styrene and divinylbenzene (1:1 weight ratio), Benzoyl peroxide and RTIL with diluent were used as the dispersed phase. The dispersed phase was added when the temperature of the continuous phase reached the specified temperature and prolonged for 4 h to reach a high conversion of monomers to Polymer MCs. The resulting microcapsules were filtered, repeatedly washed with de-ionized water and then dried at room temperature.

2.3. Characterization of RTIL encapsulated MCs

Synthesized MCs were characterized to determine the specific surface area of the MCs using a surface area analyzer (GeminiV2.00 Micromeritics). The morphological structure and particle size were observed using Scanning Electron Microscopy (Hitachi S3000H). FTIR spectra were recorded using FTIR spectrophotometer (Perkin Elmer, spectrum RXI) to analyze the presence of RTIL within the polymer core shell.

2.4. Adsorption experiments

Batch adsorption studies were conducted to determine the adsorption capacity and percentage removal of phenol using RTIL encapsulated MCs. A specific quantity of RTIL encapsulated MCs was brought in contact with 50 mL of phenol solution of known concentration at a particular pH and agitated in a rotary shaker at 200 rpm. The experiments were carried out by varying MC dosage, initial phenol concentration, contact time, temperature and pH. The samples were withdrawn at predetermined time intervals and analyzed for their phenol content spectrophotometrically at 500 nm using a UV spectrophotometer (JASCO UV Spectrophotometer). The amount of adsorption at equilibrium, q_e (mg/g), and percentage removal (percentage) were calculated using Eq. (1) and Eq. (2).

$$q_e = (C_0 - C_e)V/m \tag{1}$$

$$\text{Percentage removal} = [(C_0 - C_e)/C_0] \times 100 \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/l), m is the weight of adsorbent (g), q_e is the adsorbed quantity or adsorption capacity (mg/g) and V is the volume of solution.

2.5. Regeneration studies

Phenol loaded RTIL encapsulated MCs were regenerated to check the reactivity and stability of extractant. NaOH and $Ba(OH)_2$ were reported (Ozakya, 2006; Rinkus et al., 1997) as the most efficient stripping solutions for Phenol. Desorption studies were carried out by using 50 ml of 0.1 N NaOH solution with the spent adsorbent at a pH of 11 and agitated for 2 h at 200 rpm. After desorption of phenol, the RTIL encapsulated MCs were washed with distilled water until they are neu-