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Removal of phenolic compounds from aqueous solutions by emulsion liquid membrane containing Ionic Liquid $[BMIM]^+[PF_6]^-$ in Tributyl phosphate

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ABSTRACT

An experimental study on removal of phenolic compounds from aqueous solutions using Ionic Liquid Mixed Carrier (ILMC) containing 1-Butyl 3 Methylimidazolium Hexafluorophosphate $[BMIM]^+[PF_6]^-$ dissolved in Tributyl phosphate (TBP) in an Emulsion Liquid Membrane (ELM) was carried out. The effects of various operating parameters such as TBP Concentration, stripping reagent concentration, surfactant concentration, emulsification time, phase volume ratio, treat ratio, stirring speed, external phase pH and $[BMIM]^+[PF_6]^-$ concentration in TBP on removal of phenol has been experimentally investigated. It was found that addition of 0.02% (v/v) of $[BMIM]^+[PF_6]^-$ in membrane phase has enhanced the emulsion stability by 5 times and this was carried out using Rose Bengal dye to visualise the emulsion separation. An FTIR spectrum for TBP, ILMC and membrane phase before and after loading of phenol was generated to indicate their interactions and bonding. By selecting appropriate operating conditions, it was found to remove 99.5% of phenol and more than 90% of chlorophenols from aqueous solutions at the treat ratio of 3.

1. Introduction

Room Temperature Ionic Liquids (RTILs) as “green solvents” are a group of organic salts that exists as liquids at temperatures below 100 °C and it composed solely of anions and cations [1,2]. The cationic parts of some of the ionic liquids are organic-based moieties such as imidazolium, *N*-alkylpyridinium, tetraalkylammonium, and tetraalkylphosphonium ions. The anionic parts can be organic or inorganic, such as halides, nitrate, acetate, hexafluorophosphate, tetrafluroborate, trifluoromethylsulfonate, and bis (trifluoromethanesulfonyl) imide. Most favorable properties of RTILs are insignificant vapor pressure, high thermal stability, high conductivity, low flammability and ability to dissolve a wide range of inorganic and organic compounds. They have been used for several applications in a number of fields in addition to separation processes of organic compounds and metals [1–3].

Phenolic compounds are used widely in many industrial processes, such as petroleum refineries, steel plants, and pharmaceutical, coal conversion, chemical and dye industries. It is highly toxic compound even at low concentrations. US EPA listed phenolic compounds as a priority pollutant with a discharge limit of less than 1 ppm in the treated effluent. However, several industrial effluents contain phenol concentration up to 6900 ppm. Various treatment methods like fenton, ozonation, distillation, liquid–liquid extraction, adsorption, pervaporation, membrane extraction, biological based processes and different kinds of electrochemical methods were currently practiced for phenolic compounds removal [4–17]. In view of high cost of equipment and large volume of toxic solvents, removal of phenolic compounds from wastewater has been intensively studied using the Emulsion Liquid Membrane (ELM) technique. Phenolic compounds removal by ELM has many advantages like high solute transfer flux, high selectivity, minimal usage of toxic organic solvent and it can be regenerated, replacement of conventional organic solvents in ELM with green solvents or carrier like RTILs, single-stage extraction with stripping process and treatment of binary and ternary mixtures in the effluent [18–29]. Liquid membrane process incorporates dispersion of an emulsion containing organic membrane and aqueous internal phase in an aqueous external phase containing a solute. The solute from the external phase permeates into membrane phase and gets react with the stripping reagent present in the internal phase, which is impenetrable in the membrane phase and trapped inside the internal phase. After the extraction, the emulsion phase can be de-emulsified by various techniques for reuse of diluent.

In this study, ELM system was prepared using a new combination of ionic liquid $[BMIM]^+[PF_6]^-$ dissolved in TBP as an Ionic Liquid Mixed Carrier (ILMC) for removal of phenolic compounds (phenol, p-chlorophenol, 2,4 dichlorophenol, 2,4,6 trichlorophenol and pentachlorophenol) from synthetic aqueous solution. There are few literatures available for solvent extraction of phenolic compounds using RTILs [30–34] and TBP [35] but no work was reported with ELM using ILMC as an extractant. Various operating parameters like TBP Concentration, internal phase concentration, surfactant concentration, emulsification time, phase volume ratio (I/M) (internal to membrane phase volume ratio), treat ratio (external to emulsion phase volume ratio), stirring

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speed, external phase pH and ionic liquid $[BMIM]^+[PF_6]^-$ concentration in TBP was examined. The effect of adding ionic liquid $[BMIM]^+[PF_6]^-$ in membrane phase on emulsion stability was studied using Rose Bengal dye to visualise the emulsion separation. An FTIR spectrum for TBP, ILMC, Kerosene, Kerosene with ILMC and membrane phase before and after loading of phenol was generated to study the interaction and binding affinity between the compounds.

2. Materials and methods

2.1. Reagents and analysis

The phenol, p-chlorophenol, 2,4 dichlorophenol, 2,4,6 trichlorophenol and pentachlorophenol, Sodium hydroxide (NaOH) flakes (98%), Sorbitan monooleate (Span 80), kerosene, TBP (99%), 0.1 N Hydrochloric acid (HCl) and Ammonia solution (99%) were obtained from LOBA Chemie (India). Reagents used in 4 Aminoantipyrine procedure (4-AAP) spectrophotometric determination (4-aminoantipyrine, $K_3Fe(CN)_6$, K_2HPO_4, KH_2PO_4, Ammonium hydroxide, and potassium ferricyanide) were of analytical grade supplied by Merck (Germany). Ionic liquid $[BMIM]^+[PF_6]^-$ (99%) was bought from HIMEDIA (India). Sodium phenoxide trihydrate (99%) ($NaOC_6H_5.3H_2O$) and Rose Bengal (Dye content 95%) was obtained from Sigma Aldrich (US). ULTRA TURRAX IKA-T25 (Germany) was used as a high speed homogenizer for emulsion preparation. IKA RW 20 (Germany) overhead stirrer was used for the ELM extraction and Sartorius Basic Meter PB-11 (Germany) was used for measuring pH of the aqueous external phase. Absorbance was measured using UV–Vis Spectrophotometer Shimadzu-UV-2450 (Japan), Hybridization shaker Incubator combi-SV120 (Korea) was used for phenol loading in membrane phase and FTIR spectra were recorded on a Perkin Elmer FTIR Spectrometer-Spectrum RX-I (USA).

2.2. Stock solution preparation

300 ppm of Phenolic compounds (Phenol (6.5pH), p-chlorophenol (6.5pH), 2,4 dichlorophenol (6.3pH), 2,4,6 trichlorophenol (6.1pH), pentachlorophenol (6.2pH)), 1 N NaOH, the reagents for the 4-AAP procedure and 0.5 N Ammonium hydroxide stock solution was prepared by dissolving them into double distilled water respectively.

2.3. Experimental procedure

Initially, emulsion was prepared by emulsifying 0.25 N NaOH aqueous solution of internal phase with an organic phase. The organic phase (membrane phase) consisting of a surfactant Span-80 (4%) and kerosene (96%) as a diluent was used. The internal phase was added drop wise into a beaker containing the organic phase. A phase ratio (I/M) of 1 (v/v) was maintained and homogenized at 8000 rpm for 5 min to obtain a milky-white emulsion. The emulsion was dispersed in the aqueous external phase containing 300 ppm phenolic compounds with treat ratio of 3 by volume and stirred by an overhead stirrer with a speed of 200 rpm. The preparation of emulsion and ELM extraction are shown in Fig. 1. At various time intervals, extracted samples were taken from the beaker and external phase was separated from the emulsion by laboratory centrifuge. The concentration of phenolic compounds in the aqueous external phase was determined by 4-AAP method using UV–Vis Spectrophotometer at a wavelength of 510 nm [36,37]. The leakage can be determined by measuring sodium phenoxide, sodium 4-chlorophenoxide, sodium 2,4-dichlorophenoxide, sodium 2,4,6-trichlorophenoxide, and sodium pentachlorophenoxide concentration in the aqueous external phase directly at a wavelength of 290 [26], 294, 288, 312 and 345 nm respectively to avoid misperception. The concentration of phenolic compounds and sodium phenoxides were found from the absorbance–calibration curves. The percentage removal of phenol and chlorophenols was determined by Eq. (1):

$$\text{Removal of Phenols } (\%) = \left[\frac{(c_0 - c_1)}{c_0}\right] \times 100 \qquad (1)$$

where c_0 is the initial and c_1 is the final concentration of phenols in the external phase.

2.4. Emulsion leakage

Emulsion leakage can be justified by measuring the presence of sodium phenoxides of phenols concentration in the external aqueous phase after ELM extraction [26]. This value was then compared with the total amount of sodium phenoxides of phenols produced by reaction of phenolic compounds with NaOH based on the amount of phenolic compounds removed using mass balance. Phenolic compounds get transported from membrane to the internal phase where it reacts with NaOH to form sodium phenoxides of phenols.

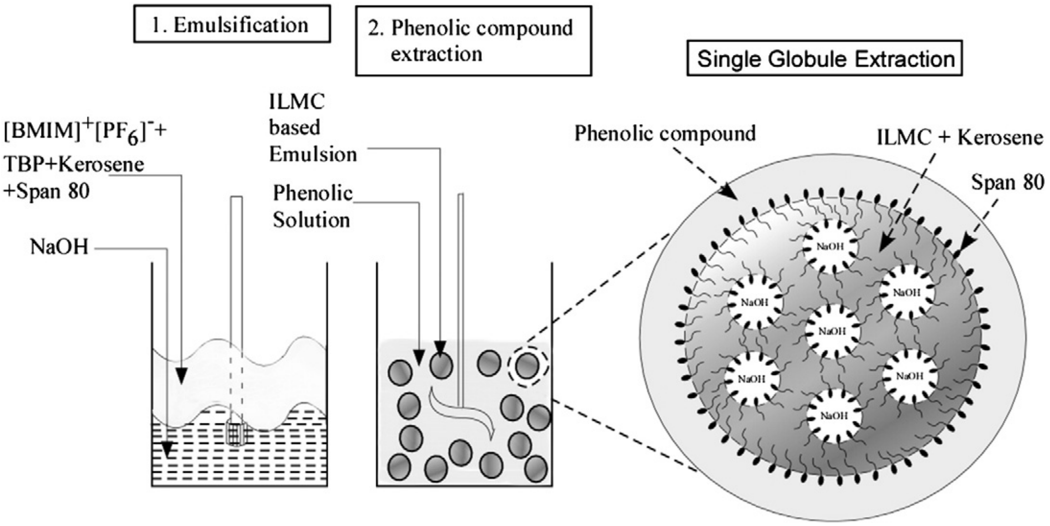

Fig. 1. Schematic diagram of removal of phenolic compounds using ILMC based ELM.