Journal of Water Process Engineering 13 (2016) 79–87

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

Investigating the performance of ELM systems in separating organic pollutants from industrial wastewater

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ARTICLE INFO

Article history:
Received 2 May 2016
Received in revised form 26 June 2016
Accepted 6 August 2016

Keywords:
Emulsion liquid membrane
Benzoic acid extraction
Ionic liquids

ABSTRACT

Emulsion liquid membrane (ELM) is one of the processes widely used in industrial separation process. Extraction of benzoic acid from aqueous solutions by an emulsion type liquid membrane was investigated. The influence of two emulsion composition variables, namely the surfactant concentration, and organic phase to internal stripping phase ratio(V_O/V_I), as well as three process parameters, emulsion to external feed phase ratio (V_E/V_F), mixing speed of feed solution, and extraction time on the rates of extraction of benzoic acid, was experimentally studied. The emulsion liquid membrane consists of kerosene as solvent, Span 80 as surfactant, and NaOH as internal stripping phase. The role of a hydrophobic ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[BMIM]^+[NTf_2]^-$ in increasing the stability of the emulsion membrane was also studied. The stability of emulsion containing 0.2% (v/v) of $[BMIM]^+[NTf_2]^-$ has significantly increased in comparison with that without ionic liquid. Approximately 99.7% of benzoic acid was extracted after only 5 min of contact with tested mixtures under the most favorable operating conditions.

1. Introduction

Wastewater is a potential source of organic solutes, which may be toxic and cause serious problems to environment. Most of traditional methods of purification such as, distillation, liquid extraction, electro – oxidation, and adsorption are still in use; however, industries are looking for competing alternative technologies to remove and recovery of organic and inorganic matters which may overcome some of the inherent disadvantages of the traditional processes [1].

Emulsion liquid membranes (ELM) first invented by Li with the purpose of increasing the interfacial area for extraction to shorten the diffusion path [2]. Emulsion liquid membranes have been used for the removal of several solutes from either aqueous or organic solutions, including biological and medical applications. In this technology, solutes are not only removed but also concentrated; extraction and stripping are carried out in a single step. ELMs are relatively low cost and independent on equilibrium consideration; in addition, they can be prepared using simple materials and equipment [3]. Emulsion liquid membranes are, in fact, double emulsions, water/oil/water (W/OW) systems or oil/water/oil (O/W/O) systems. The oil phase (membrane) acts as a selective barrier and separates the encapsulated internal droplets in the emulsion from the external continuous phase. Typically, the encapsulated internal tiny droplets in the emulsion have 1–10 μm diameter. The emulsion when dispersed in the feed break up into small globules of about 0.1–2 mm in diameter. The solute is selectively transported from the external continuous phase to the internal encapsulated droplets. At the end of an extraction operation the emulsion is separated from the continuous phase by settling and the encapsulated phase can be recovered by breaking the emulsion [4].

The ELM technique has shown potential for the removal and recovery of different metal ions [5–7] and hydrocarbons [2] from wastewater, where conventional methods provide lower separation efficiency. The diffusivity of most molecules through the organic liquid phase is much higher than through polymer membranes because it is thin and permits selective transport of molecules [1].

Resistance of the individual globules to coalescence determines the stability of W/O/W emulsions which is known as one of the most serious problems in the application of the emulsion liquid membrane to industrial separation. The instability of the emulsion can be caused by repeated coalescence of the internal droplets on the interface, creaming due to density difference, Ostwald Ripening and flocculation. Several techniques have been proposed to improve emulsion stability, and these include the use of aliphatic solvent

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http://dx.doi.org/10.1016/j.jwpe.2016.08.001
2214-7144/

Nomenclature

C	Solute concentration in the feed phase permeating across a given area of the membrane/unit time
C_0	Initial concentration of benzoic acid (ppm)
C_t	Concentration of benzoic acid at the time of measurement (ppm)
D	Diffusion coefficient of permeating specie through the membrane (m^{-1} min^{-1})
D'	Effective permeation rate constant (min^{-1})
D_{AB}	Diffusion coefficient (cm^2/s)
M	Molecular weight of solvent (kg/kg mol)
t	Time (min)
T	Temperature (k)
V_A	Solute molar volume (m^3/kg mol)
V_E/V_F	Treat ratio volume of emulsion to volume of feed ratio (−)
V_O/V_I	Volume of organic phase to volume of internal phase ratio (−)
Δc	Concentration difference of the permeating species on either side of the membrane (ppm)
Δx	Membrane thickness through which permeation takes place (m)
μ	Viscosity of solvent (kg/m s)
Ψ	Solvent association factor (−)

instead of aromatic solvent [8], aliphatic solvent with long carbon chain [9], high surfactant concentration [10], high membrane viscosity [9,11], the use of co-surfactants [12], adding polymer to the organic phase or non-Newtonian conversion of the membrane phase [13], the use of Janus particles as stabilizers in emulsion polymerization [14] and the use of functionalized silica particles for high internal phase emulsion [15]. Nevertheless, every remedy has its own tradeoffs.

Room temperature ionic liquids (RTILs) are a group of low melting point salts that consist of organic cations and organic/inorganic anions. They have negligible vapor pressure, inflammability, thermal stability even at high temperatures, and application based adjustable miscibility/immiscibility in chemical processes [16–21]. These unique properties serve them as an option to replace the volatile organic solvents for removal process of an organic pollutant. Ionic liquids possess a very negligible vapor pressure that has enabled them to be used as a "green solvent" in synthesis [19,20,22–24], separation and purification [25–30], and electrochemical applications [31].

Goyal et al. showed that the stability of a W/O emulsion with kerosene as solvent was improved by incorporating the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[BMIM]^+[NTf_2]^-$ in the membrane phase as a stabilizer. They showed that by the addition of 3 wt% $[BMIM]^+[NTf_2]^-$ the stability of the W/O emulsion could enhanced from a few minutes up to 7 h. $[BMIM]^+[NTf_2]^-$ will therefore be used in this research in combination with Span 80, due to its low viscosity (5 mPa s) compared to other ionic liquids, which facilitates the homogenous dispersion in ELM. It is also hydrophobic, has a low toxicity and a low density [32].

Benzoic acid is one of the oldest chemical preservatives used in food, cosmetics, and drugs. It may be released into wastewater during its production and use as a chemical intermediate and additive. Benzoic acid was found in discharges of the following industrial products, leather tanning, iron and steel manufacturing, petroleum refining, nonferrous metals, paint and ink, printing and publishing, ore mining, inorganic chemicals, pulp and paper, rubber processing, soaps and detergents, auto and other laundries, pesticides manufacture, photographic industries, pharmaceuticals, oil and gas extraction. Benzoic acid, among other aromatic compounds is as a byproduct in the commercial production of tetraphthalic acid in the plastic and textile manufacturing industries and as an intermediate during the synthesis of phenol [33].

The concentration of benzoic acid was found to range from 10 to 27,500 μg/L in the ground water. The World Health Organization (WHO) recommends a maximum endurable human intake of benzoic acid is 5 mg/kg of body weight per day. Some countries have discontinued the use of benzoic acid as a food additive; even in trace amounts [34].

The removal of benzoic acid from wastewater has gained a lot of attention, and several researches have been reported to be effective for benzoic acid removal. Adsorption, and catalytic degradation of benzoic acid from an aqueous solution are the most applied. Conventionally, carbon-based adsorbents, including granular activated carbon or activated carbon fibers, have been shown to be effective for the removal of benzoic acid because of their large surface areas. Noncarbon- based adsorbents, including bentonites and kaolinite, have also been developed and found effective for the treatment of wastewater polluted with benzoic acid [35,36]. Other treatment methods such as electrochemical or catalytic oxidation and photochemical degradation have also been used for the control of benzoic acid in wastewater [37–43]. Although adsorption is the most widely applied method for the removal of benzoic acid from wastewater, it may have disadvantages such as high cost of regeneration of replacement of spent adsorbents, low adsorption capacities of adsorbent materials, and long contact times which cause a major application problem [35]. To overcome the limitations of existing methods, it is therefore necessary and important to develop new treatment methods. In this context, emulsion liquid membrane (ELM) may be an attractive alternative.

The extraction of benzoic acid from an aqueous phase by ELMs is represented in Fig. 1. Benzoic acid in the external feed phase dissolves in the oil membrane phase, diffuses across the membrane phase and reacts with a stripping agent, NaOH in the internal aqueous phase. The transferred benzoic acid is converted into sodium benzoate which is not soluble in the membrane phase; therefore, it is trapped in the internal stripping phase. The zero concentration of benzoic acid in the internal stripping phase results in high concentration gradient across the membrane phase and the extraction process continues until it is completely extracted. In addition, the capacity of the internal phase can be increased by employing excess amount of NaOH as a stripping agent [44].

Span 80 is used as surfactant for the ELM formulation and Span is the commercial name for sorbitan fatty acid esters, which are nonionic surfactants. Span 80 is a sorbitan monoolete and classified as environmentally friendly, as it is sugar based and produced from renewable sources and is also biodegradable [45].

In this work, the factors affecting the extraction efficiency of ELM system for the removal of benzoic acid from wastewater was studied. In addition experiments were performed to determine the effect of using a hydrophobic ionic liquid $[BMIM]^+[NTf_2]^-$ on enhancing the stability of ELM.

2. Materials and methods

2.1. Chemicals

Kerosene of boiling point ranged from 175 to 325 °C, Span 80 (sorbitan monoolate), sodium hydroxide pellets, hydrochloric acid, benzoic acid, and ionic liquids $[BMIM]^+[NTf_2]^-$ were obtained from Sigma Aldrich (USA). The structural formula of the ionic liquid is illustrated in Fig. 2 and the physical properties are given in Table 1. The solutions of sodium hydroxide (NaOH) of desired concentra-