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Removal of benzoic acid from wastewater by pickering emulsion liquid membrane stabilized by magnetic Fe_2O_3 nanoparticles

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ABSTRACT

Emulsion liquid membrane (ELM) is an alternative to the existing separation processes, showing many advantages in terms of efficiency, energy consumption, and operational costs. However, development of an effective method for demulsification after extraction process without changing the oil phase chemistry is still great challenge. In this research magnetic Fe_2O_3 nanoparticles were used to prepare a new Pickering emulsion liquid membrane (PELM) system, in which the internal water and oil emulsion can be simply demulsified by magnetic force. The percentage removal of benzoic acid from aqueous solution by Pickering emulsion liquid membrane was investigated experimentally for various parameters such as, magnetic Fe_2O_3 nanoparticles concentration, internal phase concentration, treatment ratio, and mixing speed of feed solution. These parameters have a strong effect on the percentage removal of benzoic acid. Under improved membrane properties, it was found that the percentage removal of benzoic acid was as high as 99.74%, with emulsion leakage of less than 0.2%.

Keywords: Pickering emulsion liquid membrane; Benzoic acid extraction; Magnetic Fe_2O_3 nanoparticles

1. Introduction

Emulsions are thermodynamically unstable dispersions of two or more immiscible liquids which are kinetically stabilized by an adsorbed film at the liquid–liquid interface. Emulsifying agents are required to prevent the coalescence of emulsion droplets and to obtain a stable emulsion without phase separation. Emulsifiers can be nanometer- and micrometer-sized solid particles that can be adsorbed at the liquid-liquid interface and form an interfacial protective film between the dispersed phase and continuous phase. The emulsions stabilized by solids have been termed Pickering emulsions after Pickering's early work in 1907 [1]. Ramsden reported the stabilization of emulsions by particles early in the 20th century [2], but the research in this field experienced a slow development until the 1980s. In the past years, solid particles as emulsion stabilizers have attracted much attention due to their irreversible adsorption, low cost, and low toxicity [3].

Stabilizers with low molar mass or polymeric surfactants are commonly used but, as recently reviewed by Binks [4], nm sized particles which are partially wetted by both immiscible liquids at a liquid–liquid interface are very effective emulsion stabilizers. This is mainly because nano-particles of the correct wettability are essentially encounter irreversible adsorption at liquid–liquid interfaces, i.e. the energy of adsorption is about 100–10,000 times the thermal energy [4]. While low molar mass surfactants, are reversibly adsorbed because the adsorption energies are close to the thermal energy and hence are less effective as emulsion stabilizers. Recently nanoparticles have been successfully used to stabilize both simple emulsions (i.e. water-in-oil (W/O) and oil-in-water (O/W) types) and multiple emulsions (O/W/O and W/O/W types) [5].

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Commonly used nanoparticles for preparing Pickering emulsions include both spherical particles such as silica [6–9] and polystyrene [10–12] and flake-like particles such as kaolin and clay. Nano-sized iron oxides, among a number of transition metal oxides have been used as Pickering emulsions stabilizers; in addition they have other advantages such as low-cost, environmentally friendliness, and low-toxicity [13]. In many cases, surfactants are usually added to the Pickering emulsions to modify the particle wettability, so that the emulsion type can be changed or the emulsion stability can be enhanced [14].

Emulsion liquid membrane (ELM) has been well studied in separation, extraction and wastewater treatment applications [15–18]. Although ELM is featured by simplicity, high selectivity, rapid extraction and low energy consumption, the commercial application of ELM has been limited due to the instability of the emulsions and the difficulty of their demulsification after extraction [19–23]. In order to recover the internal phase and reuse the oil phase, the internal emulsion must be broken up after extraction. Because most of the emulsions are stabilized by surfactant, the demulsification after extraction is very difficult. Chemical demulsification method is not acceptable because the oil phase cannot be reused after chemical demulsification. Physical demulsification methods, such as electrical, ultrasonication, and thermal treatment, have been reported [24,25]. However the high energy consumption and low efficiency have restricted the commercial applications of ELM technology.

The stabilization of Pickering emulsions depends on the ability of particles to move to the interfacial region, to remain there, and to form an interfacial film that retards coalescence of the droplets [26]. Magnetic Pickering emulsions, which is stabilized by magnetic particles is one of such systems [27–30]. Meanwhile, magnetic emulsion can also be easily demulsified by quickly attracting the emulsifier particles from the droplets interfaces using external magnetic field.

Benzoic acid is one of the oldest chemical preservatives used in food, cosmetics, and drugs. It may be released into the wastewater during its production and use as a chemical intermediate and additive. Benzoic acid was identified to exist in many industrial discharges such as timber 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, and in oil and gas extraction. Benzoic acid among other aromatic compounds is generated as a by product in the commercial production of terephthalic acid in the plastic and textile manufacturing industries and as an intermediate during the synthesis of phenol.

The concentration of benzoic acid was found to range from 10 to 27,500 µg/L in industrial wastewater. 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 [31].

The removal of benzoic acid from wastewater has gained a lot of attention, and several studies have been reported in the literature. Adsorption and catalytic degradation of benzoic acid from an aqueous solution are the most employed methods. 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 Brunauer–Emmett–Teller (BET) surface areas [32–34]. Noncarbon-based adsorbents, including kaolinite and bentonites, have also been developed and found to be 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 [37–39]. 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 and replacement of spent adsorbents, low adsorption capacities of the adsorbent materials, and the need for long contact times which cause a major application problem [36]. To overcome the limitations of the existing methods it is therefore necessary and important to develop new treatment methods. In this context, Pickering emulsion liquid membrane (PELM) could be an attractive alternative to the existing separation processes showing higher efficiency, and lower energy consumption and operational costs.

In this study, a new process of ''Pickering emulsion liquid membrane'' is developed, which used $W_1/O/W_2$ Pickering emulsion to selectively extract benzoic acid from wastewater. Experimentally, magnetic Fe_2O_3 nanoparticles were used as the stabilizer and emulsifier [40,41]. Sodium hydroxide solution (NaOH) was used as the internal aqueous phase (W_1), kerosene as the oil membrane phase for water-in-oil emulsion, and nonionic surfactant sorbitan oleate (Span 80) as surfactant mixed with oil phase. The aqueous feed phase (W_2) was prepared with 500 ppm of benzoic acid with a pH value of 3.57. After emulsification, the emulsion was immediately dispersed into feed phase containing benzoic acid and formed water in oil in water emulsion. Benzoic acid in the aqueous feed phase (W_2) dissolves in the oil membrane phase (O), diffuses across the membrane phase and reacts with a stripping agent, NaOH in the internal aqueous phase (W_1). 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 and high driving force across the membrane phase and hence the extraction process continues until it is completely extracted.

The influence of magnetic Fe_2O_3 nanoparticles concentration, internal phase concentration, treatment ratio, and mixing speed of feed solution on the Pickering emulsion liquid membrane (PELM) extraction performance and stability were studied. Reuse of magnetic particles and oil phase in repeated PELM test was also studied. This work suggests that PELM has great potential as a new class of emulsion liquid membrane for separation and extraction applications in general and for benzoic acid in particular.

2. Materials and methods

2.1. Chemicals

Kerosene of boiling point ranged from 175–325ºC, Span 80 (sorbitan monoolate), sodium hydroxide pellets, and benzoic acid were obtained from Sigma Aldrich (Saint Louis MO 63103, USA). Magnetic Fe_2O_3 nanoparticles with the size range of (20–40 nm) were obtained from Alfa Aesar (Ward Hill, MA 01835, USA). The solutions of sodium hydroxide (NaOH) of desired concentration and benzoic acid of 500 mg/L were prepared by dissolving appropriate weight in de-ionized water.

2.2 Experimental work

A certain quantities of magnetic Fe_2O_3 nanoparticles (0.05, 0.1, 0.15, 0.2, 0.35) % w/w related to internal aqueous phase and Span 80 (2% w/v of the membrane phase) were dispersed into kerosene using a high speed homogenizer, Ultra Turrax IKA-T25. NaOH (0.1–1) mole/L solution was added dropwise to the oil phase, and the mixture was homogenized at 7000 rpm for 10 min. In 800 ml beaker, 40 ml of the prepared PELM (membrane phase and aqueous internal phase) was dispersed into 500 ml of aqueous feed phase at ambient temperature. The contents were stirred by means of RW20 digital overhead stirrer with an agitation speed of (240, 300, and 400) rpm for 15 min. Samples were collected from the agitated solution at various time intervals using a micropipette. Collected samples were then filtered using a nylon syringe filter with nominal pore size of 0.2 µm (Simsii, Inc. USA). The pH was measured by Okton Acron pH meter.

Visual testing for the prepared Pickering emulsions was performed by taking images with the latest Hirox digital microscope model (KH-8700).

The concentration of benzoic acid in the aqueous feed phase decreases with time as reflected by the decrease in electrical conductivity determined by a conductivity meter (Model 3200, Yellow Spring Instrument Co. USA). The relationship between benzoic acid concentration and electrical conductivity was calibrated before the study to find the solute concentration in the feed phase at any time during the process.

The mixture was poured into a separating funnel to separate the lower aqueous feed phase and upper emulsion phase. The upper phase was broken under the magnetic force using a 1T magnet. When the magnetic field is applied to the nano particles, they were separated out and gathered on the wall of the container. As the particles in these emulsions are attracted toward the magnet, they pull on the films surrounding internal phase droplets, resulting in film rupture and demulsification. The collected nano particles were thoroughly washed with acetone and distilled water and were dried under vacuum at 50ºC for 10 h. The recycled particles and oil phase were used for preparing new Pickering emulsion. Fig. 1. shows the schematic diagram of the Pickering emulsion liquid membrane process.

3. Results and discussion

3.1. Membrane stability calculation

Emulsions that are stabilized by magnetic Fe_2O_3 nanoparticles alone are unstable against coalescence, with the bulk oil phase released above. Also, the emulsions possess large drop diameters, suggesting that the hydrophilic particles do not stay at the oil-water interface due to their low attachment energy [14]. The surfactant Span 80 is well-known to form W/O emulsions due to low hydrophilic–lipophilic balance (HLB) value of 4.3. Emulsions with 2% (w/v) Span 80 concentration, were stable with small emulsion droplet size, which comes from the decrease of the oil-water interfacial tension. The long-term stability of emulsions could be greatly improved as a hypothesis of this work by the combination of magnetic Fe_2O_3 nanoparticles with surfactant Span 80 resulting from the formation of a three-dimensional network among the droplets and particles, in which the emulsion droplets would be particularly stable.

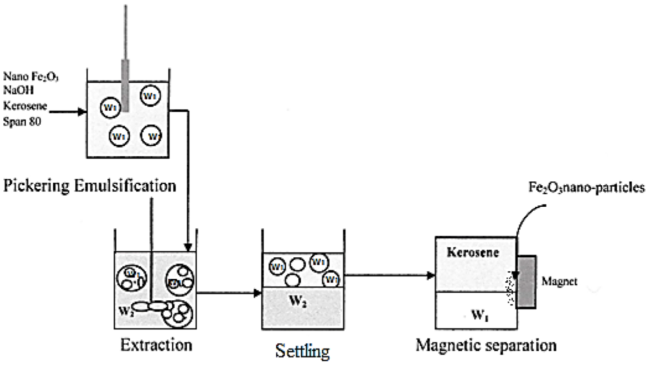

Fig. 1. Schematic diagram of the Pickering emulsion liquid membrane (PELM) process.

In Pickering emulsion liquid membranes stabilized by both surfactant and magnetic Fe_2O_3 nanoparticles; the degree of extraction for benzoic acid into an internal aqueous phase is influenced by the stability of emulsion. This is because membrane breakdown due to instable emulsion causes a decrease in the extraction efficiency and loss of benzoic acid.

A tracer method is usually used to determine the stability of Pickering emulsion liquid membrane. Since the tracer cannot be transported through the membrane phase from the internal phase to the feed phase, the dispersion of tracer substance in the feed phase can be caused only by the membrane breakage [42]. In the present study, sodium hydroxide which was used as the internal phase was also used to find the percentage of emulsion breakage (ε) that is calculated from the following equation:

$$\varepsilon = \frac{V_s}{V_{\text{int}}} \times 100 \tag{1}$$

where (V_S) is the volume of internal phase leaked into the feed phase and (V_{int}) is the initial volume of the internal aqueous phase. The volume V_S is calculated by mass-balance from the feed phase before and after contact as shown in Eq. (2). [43–46]

$$V_s = V_{Ext}\frac{10^{pH_0-14} - 10^{pH-14}}{10^{pH-14} - C_{OH^-}^{\text{int}}} \tag{2}$$

where V_{Ext} is the initial volume of feed phase, C_{OH-}^{int} is the initial concentration of OH^- in the internal phase, pH_0 is the initial pH of the feed phase and pH is the feed phase pH being in contact with the emulsion after a certain time of agitation.

The emulsion leakage can be defined in terms of breakage constant (K_b) as suggested by Goto et al. [47] as follows:

$$\ln(1-\varepsilon) = -K_b t \qquad (3)$$

where t is the time and ε is calculated from Eq. (1).

The Pickering membrane leakage calculated from Eq. (1), and breakage constant value calculated from Eq. (3), were found to be less than 0.2% and 0.1 min^{-1}, respectively, after 15 min of stirring for emulsion with 0.5 mole/L NaOH, 2% (w/v) Span 80, 0.1% (w/w) Fe_2O_3, 300 rpm mixing speed of feed solution, W_1/O: 1/7, and treatment ratio: 1/12. Therefore, an effective treatment of benzoic acid can be achieved at these low membrane leakage/ breakage values [48].

3.2. Effect of magnetic nano-Fe_2O_3 concentration on the extraction of benzoic acid

Benzoic acid in aqueous feed phase diffuses to the O/W_2 interface, then diffuses across the oil membrane to reach the internal W_1/O interface, and reacts with NaOH to form a water insoluble salt as shown in Eq. (4):

$$C_6H_5COOH + NaOH \rightarrow C_6H_5COO^-Na^+ + H_2O \qquad (4)$$

Sodium benzoate cannot diffuse back into the aqueous feed phase through liquid membrane because it is insoluble in the oil membrane phase (kerosene). As a result, benzoic acid is selectively extracted from the feed phase to the internal aqueous phase.

The stability of Pickering emulsion plays an important role in the extraction process as mentioned earlier. Magnetic Fe_2O_3 nanoparticles can form emulsions stable to coalescence because of the protective film formed by the particles at the oil-water interface. The influence of magnetic Fe_2O_3 nanoparticles concentration on the extraction of benzoic acid from 500 ppm feed phase was studied, ranging from (0.05–0.3) % (w/w), related to aqueous internal phase.

The extraction results are presented in graphs as C_t/C_0 vs. time of agitated contact time t. Better extraction was obtained corresponds to lower C_t/C_0. Semi-logarithmic coordinates were used in all figures to dramatize the data at very low solute concentration.

As can be seen from Fig. 2. the highest percentage removal efficiency, defined as $[(1 - C_t/C_0) \times 100]$ was reached at a concentration of magnetic Fe_2O_3 nanoparticles of 0.1 (w/w), and then decreased thereafter. The emulsion becomes more stable with the increasing concentration of magnetic Fe_2O_3 nanoparticles by covering more emulsion droplets interface, resulting in an increase in the separation efficiency. However, with further increasing magnetic Fe_2O_3 nanoparticles concentration beyond full coverage of the emulsion droplets, extra magnetic Fe_2O_3 nanoparticles were dispersed in the aqueous feed phase and some of the particles might form aggregates on W_1/O interface, which affected the stability of emulsion and slowed the transfer process, hence the removal efficiency decreased.

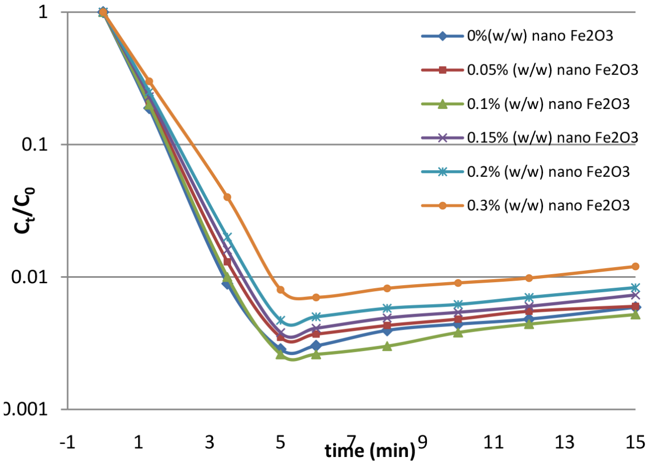

Fig. 2. The effect of magnetic Fe_2O_3 nanoparticles concentration on the extraction of benzoic acid (500 ppm), (0.5 mole/L) NaOH, 2% (w/v) Span 80, mixing speed of feed solution (300 rpm), W_1/O = 1/7, treatment ratio: 1:12, pH of feed solution 3.57.

The droplets of the emulsion stabilized with 0.1% (w/w) Fe_2O_3 are spherical, and their mean size varies from 4 to 20 μm. For emulsion prepared with 0.2% (w/w) Fe_2O_3, the emulsion drops tend to be non-spherical in shape (particularly the larger drops) and aggregated as can be seen from optical microscopy images of emulsions illustrated in Fig. 3.

3.3. Effect of internal phase concentration

The stability of emulsion with varied NaOH concentration in the internal aqueous phase was investigated.

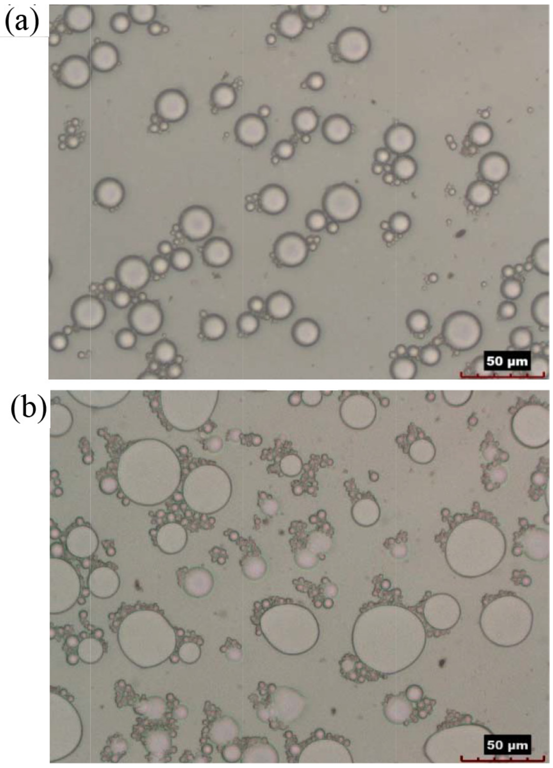

Fig. 3. Optical microscopy images of Pickering emulsions stabilized by (a) 0.1 (w/w), and (b) 0.2% (w/w) magnetic Fe_2O_3 nanoparticles, (0.5 mole/L) NaOH, 2% (v/v) Span 80, emulsification speed (7000 rpm), W_1/O = 1/7.

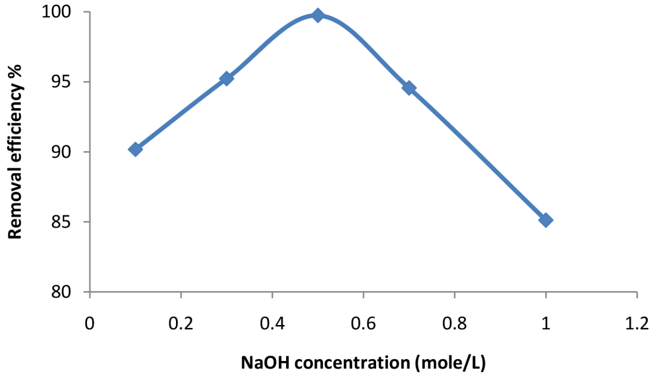

Fig. 4. Removal efficiency [(1 – C_t/C_0) × 100] of emulsion stabilized with different concentration of NaOH, 2% (w/v) Span 80, 0.1% (w/w) Fe_2O_3, mixing speed of feed solution (300 rpm), W_1/O = 1/7, treatment ratio: 1/12, pH of feed solution 3.57.

Under the condition of Fe_2O_3 = 0.1 % (w/w), internal phase: membrane ratio (W_1/O) = 1/7 and surfactant concentration of 2 %(w/v), the emulsion was stable without phase separation over 3 h for NaOH concentration from 0.1 to 0.5 mole/L. However, in the emulsions with 0.7 mole/L and 1 mole/L NaOH, water separation was noticed, indicating the instability of the emulsion.

When the volume ratio of emulsion phase to the aqueous feed phase was fixed at 1/12, the percentage removal showed an increasing tendency first and then decreased with the increasing of NaOH concentration as shown in Fig. 4. As it is known, emulsion stability is the key parameter for a successful ELM process separation. Therefore, the leakage of emulsion would affect the extraction efficiency. Mortaheb et al. [49] stated that a high NaOH concentration will increase the pH of internal phase and osmotic swelling may occur under a high pH difference between the feed phase and the internal phase. When NaOH concentration is low, the emulsion is stable; but, there is no enough NaOH to react with benzoic acid in internal phase because an excess amount of the stoichiometric NaOH is required in order to neutralize the benzoic acid and achieve acid removal rate as high as possible. Hence, the percentage removal increases from 0.1 to 0.5 mole/L with stable emulsion. When NaOH concentration is high, the liquid membrane is unstable and hence the removal efficiency decreases. According to our results, the 0.5 mole/L NaOH concentration in the internal phase which produces the lowest leakage with maximum removal efficiency and therefore it was chosen in this study.

3.4. Effect of treatment ratio

The treatment ratio, defined as the volume ratio of emulsion phase to the aqueous feed solution (E/W_2), has a significant effect on extraction using ELMs. It is known that the rate of mass transfer in ELM systems is directly related to the specific mass transfer area (m^2/m^3). The volume ratio of the emulsion to the feed phase controls the interfacial contact area between the emulsion and feed solutions. It is identical with the solvent to feed ratio in the conventional liquid –liquid extraction. E/W_2 is a measure of the emulsion hold-up in the system. An increase in treatment ratio results in an increase of the emulsion phase holdup and simultaneously an increase in the capacity of the membrane for enhanced permeation of the solute. It also results in an increase in the overall surface area available for mass transfer in the system. An increase in treatment ratio is expected to increase the removal efficiency as can be seen from Fig. 5. The treatment ratio was varied by changing the amount of emulsion added to the feed phase and keeping the volume of the later constant [50]. The effect of the volume ratio of emulsion to feed phase (E/W_2) on the extraction efficiency was studied in the range of 1/8 to 1/14.

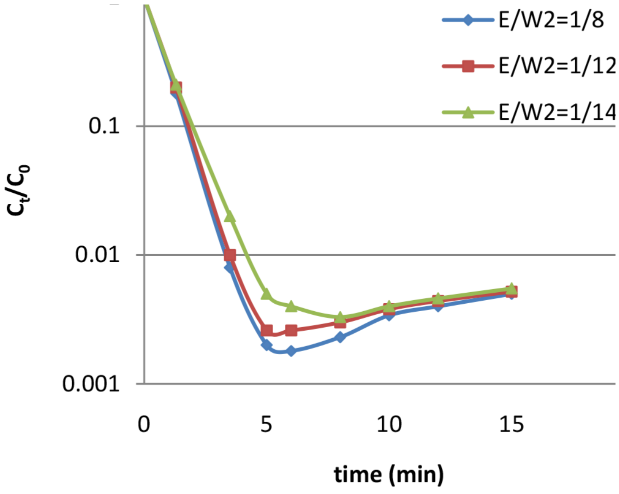

Fig. 5. Effect of volume ratio of emulsion to external phase on the extraction rate, (0.5 mole/L) NaOH, 2% (w/v) Span 80, 0.1% (w/w) Fe_2O_3, mixing speed of feed solution (300 rpm), W_1/O = 1/7, benzoic acid concentration in feed phase: 500 ppm, pH of feed solution 3.57.

The least volume of the emulsion is always desirable to make it less expensive over the conventional solvent extraction processes, as long as there is sufficient internal stripping agent to extract all of the benzoic acid from the feed phase. For that the volume ratio of the emulsion to

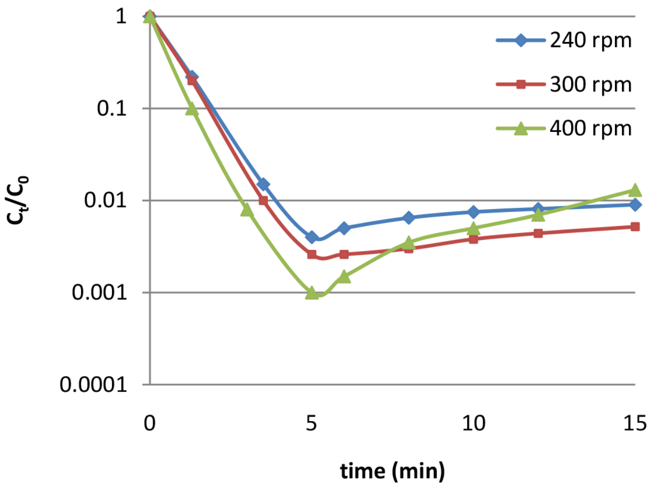

Fig. 6. The effect of mixing speed of feed solution on the extraction of benzoic acid, (0.5 mole/L) NaOH, 2% (w/v) Span 80, 0.1% (w/w) Fe_2O_3, W_1/O = 1/7, treatment ratio: 1/12, benzoic acid concentration in feed phase: 500 ppm, pH of feed solution 3.57.

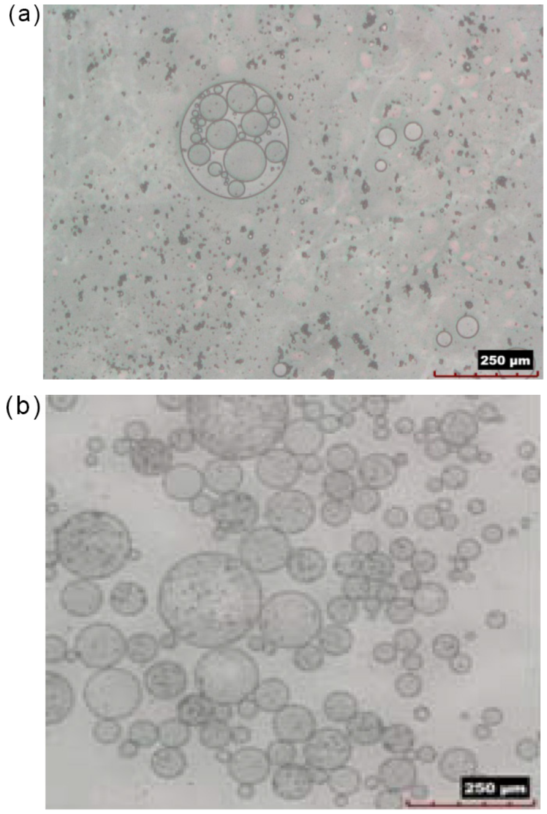

Fig. 7. Optical microscopy images of Pickering emulsions dispersed in benzoic acid solution (500 ppm) with feed mixing speed (a) 300 rpm and (b) 400rpm, 0.5 mole/L NaOH, 2% (w/v) Span 80, 0.1% (w/w) Fe_2O_3, W_1/O = 1/7, treatment ratio: 1/12, pH of feed solution 3.57.

external feed solution of 1/12 was selected as the best treatment ratio.

It was also noticed that the influence of the treatment ratio on the stability was insignificant because less shear imparted into the more dispersed emulsion in the feed phase [51,52].

3.5. Effect of mixing speed of feed solution

The effect of mixing speed of feed solution was studied at 240, 300, and 400 rpm and the obtained results are shown in Fig. 6. For the lower speed (240 rpm), benzoic acid removal efficiency $[(1 - C_t/C_0) \times 100]$ was low because of the formation of larger emulsion globules involving a decrease of mass transfer area. By increasing the mixing speed from 240 to 300 rpm, the shear force, which acts on emulsion globules increases and this makes the globules smaller and increases the area for mass transfer which will increase the removal efficiency. It was also observed that increasing the mixing speed from 300 to 400 rpm increased the rate of transport during the first 5 min. This was due to an increase in the mass transfer coefficient in the aqueous feed phase. Beyond this mixing time the stability of emulsion was reduced due to globules breakage, thereby reducing the removal efficiency.

This suggests that a mixing speed of 300 rpm was recommended as the most appropriate for conducting the extraction experiments of this work.

Fig. 7a and 7b show optical microscopy images of Pickering emulsion liquid membrane dispersed in benzoic acid solution with mixing speeds of 300 and 400 rpm. The size of emulsion globules decreases in size as the mixing speed increases, which agrees well with the findings obtained by Hirato et al. [25].

4. Conclusions

A new Pickering emulsion liquid membrane (PELM) was developed to extract benzoic acid from aqueous solutions. Magnetic Fe_2O_3 nanoparticles in combination with Span 80 were used as the emulsifier to stabilize water in oil effectively. The following results were obtained:

- Optimum membrane properties can yield a stable PELM with a good percentage removal of benzoic acid of 99.74% from aqueous solutions within 5 min and the emulsion leakage can be maintained less than 0.2%.
- The long-term stability of emulsions was greatly improved by the combination of magnetic Fe_2O_3 nanoparticles with surfactant Span 80 resulting from the formation of a three-dimensional network among the droplets and particles, in which the emulsion droplets would be particularly stable.
- The operational conditions in this work that gave an excellent extraction of benzoic acid and stability of the emulsion liquid membrane, were: concentration of surfactant = 2% (w/v), the magnetic Fe_2O_3 nanoparticles = 0.1% (w/w), the internal phase concentration (NaOH) = 0.5 mole/L, the volume ratio of internal phase to organic phase = 1/7, treatment ratio = 1/12, and the agitation speed =300 rpm.
- The removal efficiency increased with the concentration of magnetic Fe_2O_3 nanoparticles and the highest value was reached at 0.1%(w/w), and then decreased thereafter.
- There is a substantial increase in extraction rates with an increase in NaOH concentration in the internal phase. But it had a reverse effect at concentrations beyond 0.5 mole/L, where the liquid membrane is unstable, and the removal efficiency decreases.
- The extraction efficiency $[(1 - C_t/C_0) \times 100]$ increased by increasing the agitation speed. However, the higher mixing speed reduces the stability of emulsion globules, which results in breakage and reduction in the overall extraction. Therefore, a desired agitation speed needs to be defined which 300 rpm in this work was.
- The emulsion was easily broken under external magnetic force. The magnetically controlled systems can easily recover emulsifier, oil phase and find application in a wide range of industrial wastewater treatment process.
- Pickering emulsion liquid membrane (PELM) concept can also be extended to non-magnetic nanoparticles, such as silica nanoparticles [53] in which, the demulsification can be achieved by centrifugation.

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Symbols

C_{OH-}^{int} — initial concentration of OH^- in the internal phase (mole/L)

C_0 — initial concentration of benzoic acid (mg/L or ppm)

C_t — concentration of benzoic acid at the time of measurement (mg/L or ppm)

K_b — breakage constant (min^{-1})

pH — external phase pH (–)

pH_0 — initial pH of the external phase (–)

t — Time (min)

V_{Ext} — initial volume of aqueous feed phase (mL)

V_{int} — initial volume of the internal aqueous phase (mL)

V_S — volume of internal phase leaked into the feed phase (mL)

ε — percentage of emulsion breakage (–)

References

[1] S.U. Pickering, Emulsions, J. Chem. Soc., Trans., 91, (1907) 2001–2021.

[2] W. Ramsden, Separation of solids in the surface-layers of solutions suspensions, Proc. R. Soc., London 72 (1903) 156.

[3] J. Zhou, X. Qiao, B.P. Binks, K. Sun, M. Bai, Y. Li, Y. Liu, Magnetic Pickering emulsions stabilized by Fe_3O_4 nanoparticles, Langmuir, 27 (2011) 3308–3316.

[4] B.P. Binks, Particles as surfactants – similarities and differences, Curr. Opin. Colloid Interface Sci., 7 (2002) 21–41.

[5] R. Aveyard, B.P. Binks, J.H. Clint, Emulsions stabilized solely by colloidal particles, Adv. Colloid Interface Sci., 100 (2003) 503–546.

[6] B.P. Binks, J.A. Rodrigues, Enhanced stabilization of emulsions due to surfactant-induced nanoparticle flocculation, Langmuir, 23 (2007) 1098.

[7] B.P. Binks, C.P. Whitby, Nanoparticle silica-stabilised oil-in-water emulsions: improving emulsion stability, Colloids Surf., A 253 (2005) 105–115.

[8] S. Arditty, C.P Whitby, B.P Binks, V. Schmitt, F. Leal-Calderon, Some general features of limited coalescence in solid-stabilized emulsions, Eur. Phys. J. E, 11 (2003) 273.

[9] B.P. Binks, W. Liu, J.A. Rodrigues, Novel stabilization of emulsions via the heteroaggregation of nanoparticles, Langmuir, 24 (2008) 4443.

[10] J.I. Amalvy, S.P. Armes, B.P. Binks, J.A. Rodrigues, G.F Unali, Use of sterically-stabilised polystyrene latex particles as a pH-responsive particulate emulsifier to prepare surfactant-free oil-in-water emulsions, Chem. Commun., (2003) 1826.

[11] B.P. Binks, S.O. Lumsdon, Pickering emulsions stabilized by monodisperse latex particles: Effects of particle Size, Langmuir, 17 (2001) 4540.

[12] L.L. Dai, S. Tarimala, C.Y. Wu, C.Y. Guttula, J. Wu, The structure and dynamics of microparticles at Pickering emulsion interfaces, Scanning, 30 (2008) 87.

[13] L.G. Torres, R. Iturbe, M.J. Snowden, B.Z. Chowdhry, S.A. Leharne, Preparation of O/W emulsions stabilized by solid particles and their characterization by oscillatory rheology, Colloids Surf., A 302 (2007) 439.

[14] J. Wang, F. Yang, J. Tan, G. Liu, J. Xu, D. Sun, Pickering emulsions stabilized by a lipophilic surfactant and hydrophilic plate like particles, Langmuir, 26(8) (2010) 5397–5404.

[15] B. Gupta, A. Deep, P. Malik, Extraction and recovery of cadmium using Cyanex 923, Hydrometallurgy, 61 (2001) 65–71.

[16] A.A. Nayl, Extraction and separation of Co (II) and Ni (II) from acidic sulfate solutions using Aliquat 336, J. Hazard. Mater., 173 (2010) 223–230.

[17] V. Eyupoglu, R.A. Kumbasar, Extraction of Ni (II) from spent Cr–Ni electroplating bath solutions using LIX 63 and 2BDA as carriers by emulsion liquid membrane technique, J. Ind. Eng. Chem., 21 (2015) 303–310.

[18] L. Gurel, L. Altas, H. Buyukgungor, Removal of lead from wastewater using emulsion liquid membrane technique, Environ. Eng. Sci., 22 (2005) 411–420.

[19] S.H.O. Chaouchi, Extraction of priority pollutant 4-nitrophenol from water by emulsion liquid membrane: emulsion stability, effect of operational conditions and membrane reuse, J. Disper. Sci. Technol., 35 (2014) 1278–1288.

[20] Y.S. Ng, N.S. Jayakumar, M.A. Hashim, Performance evaluation of organic emulsion liquid membrane on phenol removal, J. Hazard. Mater., 184 (2010) 255–260.

[21] Y. Park, A.H.P. Skelland, L.J. Forney, J. Kim, Removal of phenol and substituted phenols by newly developed emulsion liquid membrane process, Water Res., 40 (2006) 1763–1772.

[22] H. Park, T. Chung, Removal of phenol from aqueous solution by liquid emulsion membrane, Korean J. Chem. Eng., 20 (2003) 731–735.

[23] A. Balasubramanian, S. Venkatesan, Removal of phenolic compounds from aqueous solutions by emulsion liquid membrane containing Ionic Liquid $[BMIM]^+[PF6]^-$ in Tributyl phosphate, Desalination, 289 (2012) 27–34.

[24] Y.H. Kim, D.T. Wasan, P.J. Breen, A study of dynamic interfacial mechanisms for demulsification of water-in-oil emulsions, Colloids Surf., A 95 (1995) 235–247.

[25] T. Hirato, K. Koyama, T. Tanaka, Y. Awakura, H. Majima, Demulsification of water-in-oil emulsion by an electrostatic coalescence method, Mater. Trans., 3 (1991) 257–263.

[26] Z. Lin, D. Yu, Y. Li, Study on the magnetic ODSA-in-water Pickering emulsion stabilized by Fe_3O_4 nanoparticle, Colloid Polym. Sci., 293 (2015) 125–134.

[27] Y.J. Kim, Y.D. Liu, Y. Seo, H.J. Choi, Pickering-emulsion-polymerized polystyrene/Fe_2O_3 composite particles and their magnetoresponsive characteristics, Langmuir, 29 (2013) 4959–4965.

[28] Q. Lan, C. Liu, F. Yang, S. Liu, J. Xu, D. Sun, Synthesis of bilayer oleic acid-coated Fe_3O_4 nanoparticles and their application in pH-responsive Pickering emulsions, J. Colloid Interface Sci., 310 (2007) 260–269.

[29] J. Zhou, L.J. Wang, X.Y. Qiao, B.P. Binks, K. Sun, Pickering emulsions stabilized by surface-modified Fe_3O_4 nanoparticles, J. Colloid Interface Sci., 367 (2012) 213–224.

[30] Z. Lin, Z. Zhang, Y. Li, Y. Deng, Magnetic nano-Fe_3O_4 stabilized Pickering emulsion liquid membrane for selective extraction and separation, Chem. Eng. J., 288 (2016) 305–311.

[31] B. Razika, B. Abbes, C. Messaoud, K. Soufi, Phenol and benzoic acid degradation by pseudomonas aeruginosa, J. Water Resour. Protect., 2 (2010) 788–791.

[32] M. Anbia, S. Salehi, Synthesis of polyelectrolyte-modified ordered nanoporous carbon for removal of aromatic organic acids from purified terephthalic acid wastewater, Chem. Eng. Res. Des., 90 (7) (2012) 975–983.

[33] J.M. Chern, Y.W. Chien, Adsorption isotherms of benzoic acid onto activated carbon and breakthrough curves in fixed-bed columns, Ind. Eng. Chem. Res., 40 (2001) 3775–3780.

[34] E. Ayranci, N. Hoda, E. Bayram, Adsorption of benzoic acid onto high specific area activated carbon cloth, J. Colloid Interface Sci., 284 (1) (2005) 83–88.

[35] X. Xin, W. Si, Z. Yao, R. Feng, B. Du, L. Yan, Q. Wei, Adsorption of benzoic acid from aqueous solution by three kinds of modified bentonites, J. Colloid Interface Sci., 359 (2) (2011) 499–504.

[36] J.D. Kubicki, L.M. Schroeter, M.J. Itoh, B.N. Nguyen, S.E. Apitz, Attenuated total reflectance Fourier-Transform spectroscopy of carboxylic acids adsorbed onto mineral surfaces, Geochim. Cosmochim. Acta, 63 (1999) 2709–2725.

[37] T. Velegraki, D. Mantzavinos, Conversion of benzoic acid during TiO_2-mediated photocatalytic degradation in water, Chem. Eng. J., 140 (1–3) (2008) 15–21.

[38] S. Chou, C. Huang, Application of a supported iron oxyhydroxide catalyst in oxidation of benzoic acid by hydrogen peroxide, Chemosphere, 38 (12) (1999) 2719–2731.

[39] A.H.C. Chan, C.K. Chan, J.P. Barford, J.F. Porter, Solar photocatalytic thin film cascade reactor for treatment of benzoic acid containing wastewater, Water Res., 37 (2003) 1125–1135.

[40] K.Y. Yoon, Z.C. Li, B.M. Neilson, W. Lee, C. Huh, S.L. Bryant, C.W. Bielawski, K.P. Johnston, Effect of adsorbed amphiphilic copolymers on the interfacial activity of super paramagnetic nanoclusters and the emulsification of oil in water, Macromolecules, 45 (2012) 5157–5166.

[41] J. Liu, Z. Sun, Y. Deng, Y. Zou, C. Li, X. Guo, L. Xiong, Y. Gao, F. Li, D. Zhao, Highly water-dispersible biocompatible magnetite particles with low cytotoxicity stabilized by citrate groups, Angew. Chem. Int. Ed., 48 (2009) 5875–5879.

[42] Y.H. Wan, X.D. Wang, X.J. Zhang, Treatment of high concentration phenolic waste water by liquid membrane with N503 as mobile carrier, J. Membr. Sci., 135 (1997) 263–270.

[43] M. Chiha, M.H. Samar, O. Hamdaoui, Extraction of chromium (VI) from sulphuric acid aqueous solutions by a liquid surfactant membrane (LSM), Desalination, 194 (2006) 69–80.

[44] M. Chiha, O. Hamdaoui, F. Ahmedchekkat, C. Petrier, Study on ultrasonically assisted emulsification and recovery of copper (II) from wastewater using an emulsion liquid membrane process, Ultrasonics Sonochemistry, 17 (2010) 318–325.

[45] R. Sabry, A. Hafez, A. MaalyKhedr, El-Hassanin, Removal of lead by an emulsion liquid membrane, Part I, Desalination, 212 (2007) 165–175.

[46] A. Dâas, O. Hamdaoui, Extraction of bisphenol A from aqueous solutions by emulsion liquid membrane, J. Membr. Sci., 348 (2010) 360–368.

[47] M. Goto, H. Yamamoto, K. Kondo, F. Nakashio, Effect of new surfactants on zinc extraction with liquid surfactant membranes, J. Membr. Sci., 57 (1991) 161–174.

[48] J. Draxler, R.J. Marr, Emulsion liquid membranes, part I: Phenomenon and industrial application, Chem. Eng. Process. 20 (1986) 319–329.

[49] H.R. Mortaheb, M.H. Amini, F. Sadeghian, B. Mokhtarani, H. Daneshyar, Study on a new surfactant for removal of phenol from wastewater by emulsion liquid membrane, J. Hazard. Mater., 160 (2008) 582–588.

[50] P.S. Kulkarni, V.V. Mahajani, Application of liquid emulsion membrane (LEM) process for enrichment of molybdenum from aqueous solutions, J. Membr. Sci., 201 (2002) 123–13.

[51] M. Djenouhat, O. Hamdaoui, M. Chiha, M.H. Samar, Ultrasonication assisted preparation of water-in-oil emulsions and application to the removal of cationic .dyes from water by emulsion liquid membrane, Part1. Membrane stability, Sep. Purif. Technol., 62 (2008) 636–641.

[52] M. Djenouhat, O. Hamdaoui, M. Chiha, M.H. Samar, Ultrasonication assisted preparation of water-in-oil emulsions and application to the removal of cationic dyes from water by emulsion liquid membrane, Part 2. Permeation and stripping, Sep. Purif. Technol., 63 (2008) 231–238.

[53] B.P. Binks, K.Amro, F. Dyab, D. Paul, I. Fletcher, Novel emulsions of ionic liquids stabilized solely by silica nanoparticles, Chem. Commun., (2003) 2540–2541.