Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Nii, Susumu , Tanaka, Kazuho and Takeuchi, Hiroshi(1995) 'Application of Ferromagnetic Particles to Emulsion Liquid Membranes', Separation Science and Technology, 30: 17, 3253 — 3263
To link to this Article: DOI: 10.1080/01496399508013143
URL: http://dx.doi.org/10.1080/01496399508013143

SEPARATION SCIENCE AND TECHNOLOGY, 30(17), pp. 3253–3263, 1995

Application of Ferromagnetic Particles to Emulsion Liquid Membranes

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ABSTRACT

A study has been undertaken to develop a novel operation mode of emulsion liquid membrane by using ferromagnetic particles. Zinc extraction from aqueous solution with both magnetic oil and water-in-oil (W/O) emulsion drops containing D2EHPA was examined in a spray column under magnetic fields, including behavior of the drop motion. For the W/O drops, more flexible operation was realized by setting up permanent magnets to separate the dispersed phase from the continuous phase. The magnetic drops exhibited unique motions in rotating and alternating magnetic fields, depending on the field strength. It was found that the W/O drops are held in a strong alternating magnetic field and then form a fluid packed bed, whereby the extraction efficiency was significantly improved especially in a counterflow mode, by effective contact between the phases. This finding suggests the potential of a hybrid operation of a moving-bed and a spray column using magnetic W/O drops.

INTRODUCTION

In separation processes using liquid membranes, an emulsion liquid membrane (ELM) has the advantages of larger interfacial area per unit contacting device and high permeation flux over supported or bulk liquid membranes; it is suitable for the removal of waste or the recovery of valuable species such as heavy metal ions (1–3), and organic and amino acids (4–6) from dilute aqueous streams. Although extensive studies have been made, there are still some difficulties for practical application. When the operation is under vigorous mixing conditions, the problem of emulsion stability is crucial (7, 8); a shear stress from the impeller and water permeation through the ELM by osmotic pressure bring about the breakdown of emulsion drops. Column operation is favorable for controlling the residence time distribution of water-in-oil (W/O) emulsion drops; moreover, mild mixing is realized in spray columns. However, the best use of the advantage of ELM cannot be realized owing to a significant mass-transfer resistance through the aqueous boundary film on the external surface of a W/O drop (9, 10).

In a liquid–liquid dispersion system in which an organic solution containing magnetic particles, i.e., a "magnetic fluid," is used as the organic phase, the behavior of drops rising through a continuous aqueous phase can be controlled by the action of a magnetic force. For liquid membrane operation, only a few attempts at applying a magnetic field to an organic liquid containing magnetic particles have been made. Sakai et al. studied the effect of oscillation and vibration of magnetic particles on the transfer rate of a solute across a supported liquid membrane with rotating and alternating magnetic fields (11, 12). Palyska and Chmielewski examined the effect of the concentration of magnetic particles and the liquid membrane thickness on the extraction rate of copper and uranium (13).

In a column operation with W/O emulsion drops containing magnetic particles, there is the possibility of providing unique drop motions, such as fluidization or vibration in the aqueous phase, which are favorable for interphase mass-transfer. Moreover, the phase separation of the emulsion from the continuous aqueous stream can be enhanced by magnetic force. Such advantages make up for the drawbacks in the ELM processes, and they provide the potential for a novel column operation as well. This will be demonstrated in the present study on the extraction of Zn(II) by oil and W/O emulsion drops containing magnetic particles and organophosphoric acid in a column mode.

EXPERIMENTAL

A commercially available magnetic fluid, Marpomagna (FNC-50) from Matsumoto Yushi-Seiyaku Co. (dispersion of magnetite, Fe_3O_4), was diluted with *n*-dodecane, then di(2-ethylhexyl) phosphoric acid (D2EHPA) as an extractant was dissolved in the liquid. The magnetite content of the organic phase was determined as total iron concentration by atomic absorption spectroscopy (AAS). The density of the magnetic oil was measured with a pycnometer. To examine the effect of presence of the magnetite particles on the rate of zinc extraction, a stirred cell with a flat interface was used. The interfacial area of 18.8 cm^2, and two separate stirrers were used for the upper and lower phases. The concentration of Zn(II) in the aqueous phase was also determined by AAS, and its initial extraction rate was obtained from the concentration change with time.

Figure 1 shows a schematic diagram of the experimental apparatus together with two magnetic devices used in the present column operation. The column was made of a glass tube (1.4 cm in diameter, 28 cm in length). The continuous aqueous phase was fed at the upper part of the column, and oil or the W/O emulsion phase was supplied at the bottom of the column through a glass nozzle having the inner diameter of the nozzle face of 0.025 cm.

The dispersed drops rose in the magnetic field and coalesced at the top of the column. Two kinds of magnetic fields were applied at the middle part of the column: a set of permanent magnets on a pulley as a rotating static magnetic field (RS-MF) and a solenoid coil as an alternating magnetic field (A-MF). The magnetic strength in the field was measured at the center of the column on a Gauss meter. The W/O emulsion was prepared by mixing the organic liquid (0.1 M D2EHPA) containing 3 wt% Span 80 as a surfactant and aqueous H_2SO_4 solution at a volume ratio of unity.

Experiments were conducted on the extraction of Zn(II) from a dilute aqueous solution (10 ppm) by the magnetic oil or W/O drops in a counterflow mode. The flow characteristics of the rise drops were observed by a video camera in the upper section of the column just above the magnetic field, and the drop size was determined as the Sauter mean diameter.

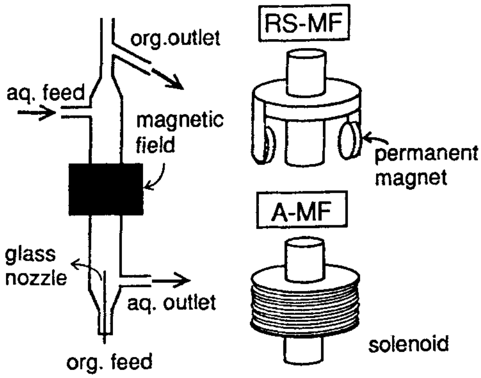

FIG. 1 Schematic drawing of extraction column and magnetic devices used in this work.

RESULTS AND DISCUSSION

Oil–Water System

The density of the magnetic oil (up to 2 wt% Fe) varied from 757 kg/m^3 with *n*-dodecane to 769 kg/m^3 with 2 wt% Fe in the oil, no significant change from *n*-dodecane. Figure 2 shows the effect of the magnetic particles on the extraction rate of Zn(II) with *n*-dodecane solution of D2EHPA in the stirred cell, where both phases were stirred at identical agitator speeds. The extraction rate was slightly lower in the presence of the solid particles; however, the effect on zinc transfer in the magnetic oil phase was not very large. In the present situation the diffusional resistance of Zn(II) through both phases is likely to be dominant in the extraction process.

In column operation under RS-MF, the oil droplets moved upward with a whirling motion, following the rotation of the magnet. Then some of them coalesced, and the resulting larger drops rose quickly in the upper section of the column. Figure 3 shows the drop size distributions represented as the cumulative frequency. Oil drops in the aqueous medium rapidly coalesced when they contacted with each other. Thus, an increase in the magnetic strength leads to a sharp increase in drop size due to the strong attraction of oil drops to the magnet. The formation of larger drops results in a decrease in interfacial area, which is not favorable for the enhancement of mass transfer between the two phases, whereas the whirling motion of small drops is desirable because it provides mild mixing in the column and prolongs the residence time of the drops.

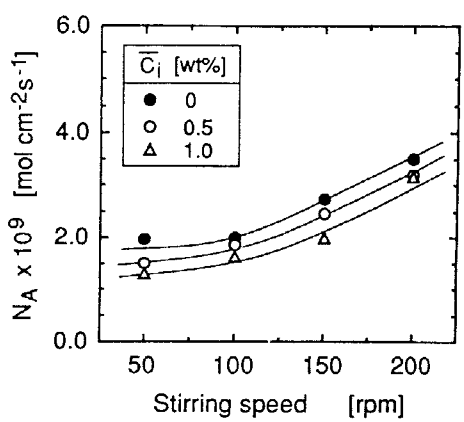

FIG. 2 Effect of the presence of magnetite particles on extraction rate. Aqueous feed: $[Zn^{2+}]$ = 100 ppm, pH 3.2; organic solvent: [D2EHPA] = 0.1 M.

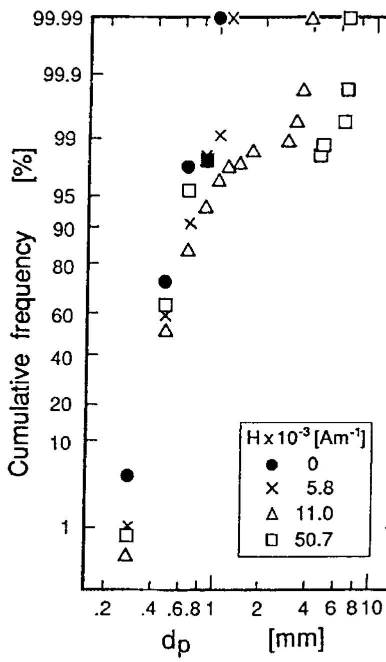

FIG. 3 Effect of RS-MF strength on drop size distribution in magnetic oil system. Q_w = 0.47 cm^3/s, Q_o = 0.07 cm^3/s, n = 52 rpm, and $\overline{C_i}$ = 2 wt%.

The effect of the rotating speed of the magnets on drop size distribution was examined. At a low rotating speed a number of drops are significantly attracted in the direction of the magnet and then coalesce on the column wall. At a the high rotating speed the rising motion of the drops was not influenced by the magnetic strength in the field. In order to achieve an oil drop flow suitable for extraction under RS-MF conditions, there must be an appropriate rotating speed at a given magnetic field in the counter-flow mode.

Solenoid coils provide a uniform magnetic field throughout the cross section of the column. Thus, there is the possibility of holding the magnetic drops in the field or of bringing about fluidization or vibration of the drops, which is related to the velocity and direction of the continuous aqueous flow. This leads to effective contact for mass transfer between the continuous and dispersed drop phases. Figure 4 shows typical results of drop size distributions versus cumulative frequency. There was no change in the drop size at a weaker magnetic strength, and the rise of drops was

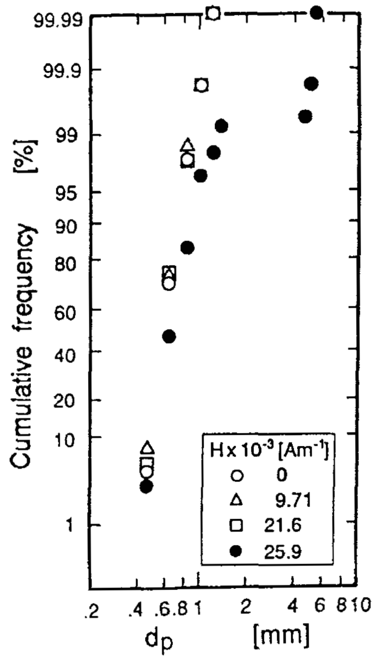

FIG. 4 Effect of A-MF strength on drop size distribution in magnetic oil system. Q_w = 0.47 cm^3/s, Q_o = 0.07 cm^3/s, and $\overline{C_i}$ = 2 wt%.

not affected by the magnetic force. An increase in the magnetic strength caused entrapment of drops and subsequent coalescence in the field.

Figure 5 shows a plot of the percent extraction of Zn(II) against the strength of the RS-MF and A-MF. To illustrate the effect of the magnetic field on extraction, we used experimental conditions that would give a low extraction efficiency: a lower feed pH (2.5–3.5) and dilute concentration (10 ppm). The percent extraction under RS-MF increased slightly with increasing magnetic strength. This may be attributed to mild mixing and an increase in the residence time of the drops, viz., the holdup. In a stronger magnetic field, however, the formation of larger drops caused a lowering of the extraction efficiency. For A-MF, it was found that there is no magnetic field effect on oil drops in the weaker magnetic region. A further increase in the field strength only led to a coalescence of the drops, and thus the extraction efficiency was decreased. In conclusion, the application of A-MF to an oil–water system does not effectively improve extraction of column operation in the counterflow mode.

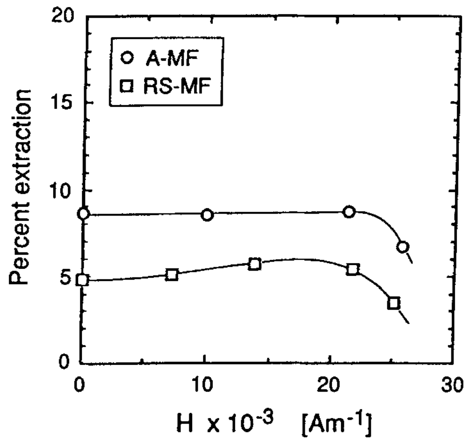

FIG. 5 Effect of field strength on zinc extraction in magnetic oil system. Q_w = 0.47 cm^3/s, Q_o = 0.07 cm^3/s, [D2EHPA] = 0.1 M; aqueous feed: pH 3.0 for A-MF, pH 2.5 for RS-MF.

W/O Emulsion–Water System

In the present (W/O)/W system, coalescence of W/O drops is less significant than in the oil–water system. Thus, there is a problem of separating the emulsion phase from the continuous aqueous phase in the cocurrent flow mode. However, it was found that the emulsion drops coalesce rapidly by forcing flow through a tube on which permanent magnets are mounted. In the counterflow mode, the carry-over of smaller emulsion drops into the aqueous stream was also prevented by attaching a magnet at the outlet of the effluent. These advantages make it possible to realize flexible column operation for magnetic ELM.

Unlike the magnetic oil–water system discussed above, the emulsion drops were found to rise or halt in the magnetic field without coalescence. Figure 6 shows the drop size distributions of W/O emulsion drops under A-MF, indicating that the drop size does not change with the field strength. No formation of larger drops was observed, even with the strongest field in the range covered.

Figure 7 shows the effect of the strength of A-MF on the percent extraction of Zn(II). Although there was no remarkable effect on extraction in the weak magnetic force region, when the field strength was over 22,000 $A \cdot m^{-1}$ the extraction efficiency dramatically increased. Such a behavior is due to a halt of the drops in the magnetic field, whereby a deceleration

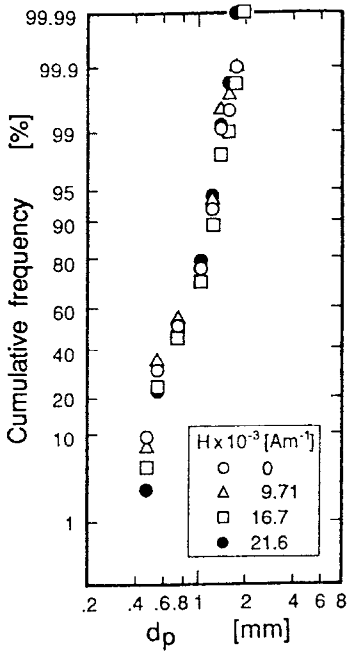

FIG. 6 Effect of A-MF strength on drop size distribution in magnetic (W/O) emulsion system. Q_w = 0.47 cm^3/s, Q_e = 0.10 cm^3/s, and $\overline{C_i}$ = 2 wt%.

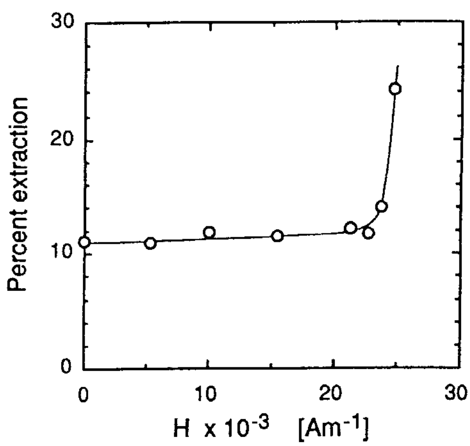

FIG. 7 Effect of magnetic field strength on zinc extraction in (W/O) emulsion system. Q_w = 0.47 cm^3/s, Q_e = 0.07 cm^3/s; aqueous feed: $[Zn^{2+}]$ = 10 ppm, pH 3.4.

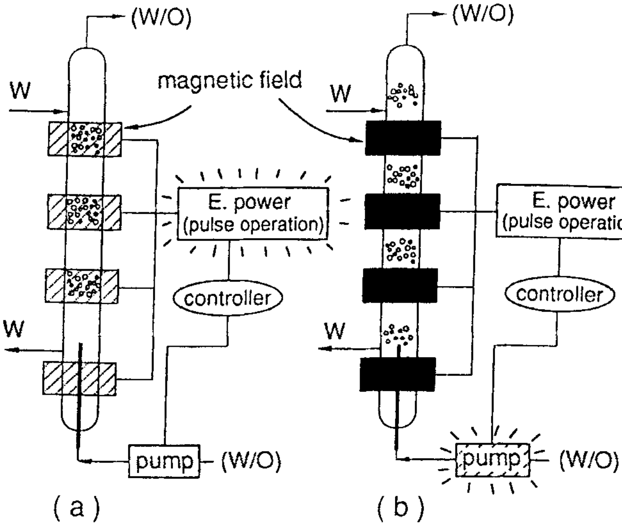

FIG. 8 Schematic diagram of sequential control of hybrid operation of moving bed and spray column.

in the rise of drops balances the continuous aqueous velocity in the reverse direction. It is to be noted that in a strong magnetic field, W/O drops are held without coalescence, and hence a "fluid packed bed" is formed. Bed formation leads to a dramatic increase in the dispersed drop holdup, with the increase depending on the aqueous feed rate. There is also an improvement in the extraction efficiency.

Based on the finding described above, we conclude that a novel operation mode may be realized as a hybrid moving bed of magnetic emulsion drops by adopting a cascade of alternating magnetic fields with a sequential on–off control of electric current and a supply of the W/O emulsion. A conceptual design of the operation mode is illustrated in Figs. 8(a) and 8(b). When an electric current is passed through the solenoids (Fig. 8a), the drops are held in each magnetic field and form multiple beds. When the current is turned off (Fig. 8b), the drops move to the next upper field and fresh drops are supplied to the lowest field. If a pulse current is applied, the drops vibrate in the bed; this motion might give rise to an enhancement of mass-transfer through the liquid boundary film of the continuous phase. Such an operation mode has the possibility of reducing the substantial problems of ELMs. We are now investigating the application of a pulse current.

CONCLUSION

A novel operation mode for an extraction process using magnetic fluid drops and a magnetic field has been proposed. The performance was demonstrated by the extraction of zinc from an aqueous stream by oil and W/O emulsion drops containing D2EHPA. The presence of ferromagnetic particles in the organic phase had no significant effect on extraction behavior in the absence of a magnetic force. Column operation with the W/O emulsion became more flexible through the use of magnets for phase separation from the continuous aqueous phase. When an alternating magnetic field is applied to the column in the counterflow mode, magnetic W/O drops are held in the field and result in the formation of a fluid packed bed which provides an effective contact between the phases. From observations of drop behavior, we propose a hybrid operation of a moving bed and a spray column for ELMs containing magnetic particles in a cascade of alternating magnetic fields.

SYMBOLS

$\overline{C_i}$	total iron concentration in organic phase (wt%)
d_p	diameter of drop (cm)
H	strength of magnetic field ($A \cdot m^{-1}$)
N_A	zinc flux ($mol \cdot cm^{-2} \cdot s^{-1}$)
n	rotating speed (rpm)
Q	flow rate ($cm^3 \cdot s^{-1}$)

Subscripts

e	emulsion
o	oil
w	continuous aqueous phase

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Received by editor March 1, 1995