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Removal of manganese from aqueous solution by emulsion liquid membrane technique

Iman Salahshouri[*, 1], Mohammad Reza Ehsani[2], Mohammad Niroumanesh[1], Sirous Edrisi[3]

[1.] Islamic Azad University, Shahreza branch, Shahreza, Isfahan province, Iran
[2.] Isfahan University of Technology, Isfahan, Iran
[3.] Iran University of Science and Technology, Tehran, Iran
Iman.salahshoori81@gmail.com

Abstract: This paper presents a comprehensive study in recovery of manganese ions from dilute sulfate solution using emulsion liquid membrane (ELM). The liquid membrane was made up from MDEHPA as a carrier, industrial solvent as an organic diluent, sulfuric acid as a stripping solution and Span-80 (sorbitain monooleate) as an emulsifying agent. The selection of the extractant (MDEHPA) and the stripper (H_2SO_4) were on the basis of conventional liquid–liquid extraction studies. The influence of important parameters through the prepared membrane such as hydrogen ion concentration in the external aqueous phase, pH of the acidic leach solution, mixing speed, type and concentration of the stripping solution, extractant and surfactant concentrations, on efficiency of manganese extraction were systematically investigated. Results show that efficiency of manganese extraction was improved by increasing pH, H_2SO_4 (as internal phase) concentration to 0.5M, carrier concentration, surfactant concentration and higher mixing speed. Optimum conditions for manganese recovery were obtained for ELM system.
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1. Introduction

Manganese is a strategic metal because of wide applications in many industries. It is currently being used in ferroalloy or steel industry as (corrosive resistance, hardness, resistance, rolling) , dry cell batteries, chemicals, catalysts, adsorbent, plant fertilizers, animal feed glass, ceramics, paints and for numerous medicinal and chemical purposes (Jacoby, 1983; Zhang and Cheng,2006 ; Lavrukhina and Yukina).

Industrial waste effluents containing manganese are a potential for this valuable metal and recovery of manganese from these streams are interested due to economical and environmental point views (Zhang and Cheng, 2006).

Liquid membranes offer a lot of advantages over conventional separation technologies, such as easy operation, low capital and operating costs, continuous operation, high selectivity, high fluxes, combination of extraction and stripping into a single stage, uphill transport against concentration gradients and small amounts of extractants (Ivakhno and Yurtov, 1908; Noble and Way, 1987; Araki and Tsukube, 1990; Cox, 2006).Emulsion Liquid Membrane (ELM) technique was originally developed for removal of heavy metals and precious metals from aqueous solutions especially when the concentrations of metals are quite low (Duche et al., 2002; Kargari et al. , 2006;Sengupta et al.,2009, Kumbasar, 2009 and 2010; Rajasimman et al., 2009). But due to the inherent instability of the emulsion, their commercialization has been delayed.

Extractant is present in membrane phase and known as carrier. Carrier is promoting solute transfer through the membrane (facilitated transport). The carriers used in coupled metal ion transport may be acidic carriers like –COOH, $–SO_3H$, or chelating groups (LIX agents) as well as basic carriers like amines or quaternary ammonium salts (Othman et al.,2003).The mostly reported organic phosphorus extractants for the extraction of metal ions by ELM are D2EHPA, Cyanex-272, Cyanex-302, LiX 63, LiX 860, Aliquad 366 and etc (Kislik,2010).The extraction of manganese (II) from neutral and weakly acidic solution using D2EHPA based supported and emulsion liquid membranes was reported in the literature (Mohapatra and Kanungo ,1992; Yongtao, 1992; Wodzki and Sionkowski ,1996; Soko et al., 2003).

In this research, removal of manganese from an aqueous solution by emulsion liquid membrane was performed. A mixture of mono and di (2-

ethylhexyl) phosphoric acid (MDEHPA) as the carrier, diluted with an industrial paraffinic solvent were uses for membrane preparation. The results show that the formulated emulsion was sufficiently stable and by determination of the operating conditions, it is capable to use for industrial applications. In the current study, the effect of parameters such as acidic leach solution pH, extractant and surfactant concentrations, mixing speed, type and concentration of stripping solution, phase ratio and treatment ratio on the extraction systems on extracting efficiency and the emulsion membrane stability were studied.

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2. Material and Methods

The Manganese sulfate, sulfuric acid, sodium hydroxide, MDEHPA which is a mixture of 55% di-2-ethyl hexylphosphoric acid ester (D2EHPA) and 45% mono-2-ethyl hexylphosphoric acid ester (M2EHPA) and Span-80 were supplied from Merck Co. An industrial solvent from Laleh Petrochemical Company (Iran) was used as diluent which is containing n-paraffins with aromatics (<100 ppm) having a density of 745.0 kg/m^3 at 25 ºC. Deminaralized water (DM water) was used in experiments had maximum conductivity of 0.2 µS/cm. A Perkin Elmer AA300 was used for determination of Mn ion concentration in the aqueous samples. The pH values of the aqueous solutions were determined by a digital pH meter (Metrohm model 700). Emulsions were homogenized by IKA T25 digital ultra-Turrax homogenizer.

At first for preparing the feed solution, solid manganese sulfate was dissolved in concentrated sulfuric acid and then diluted with DM water to the desired concentration. In order to finding the optimum values for carrier concentration and initial pH of feed solvent extraction experiments were done in batch mode. For this purpose, 20 ml of aqueous solution with a known concentration and pH, stirred with 20 ml organic phase at 25°C in thermostatic bath for 15 min to achieve equilibrium condition.

The W/O/W double emulsion was prepared in two steps: at first, a known volume of internal aqueous phase (from 25 to 100 ml) containing various concentration of sulfuric acid (0.2- 3M) was gradually added to the stirring oil phase at a constant temperature (25 $^{\circ}$C), the resulted W/O emulsion was homogenized by homogenizer at high speed (8000 - 12000 rpm) for different times (10 and 15 min). The oil phase was a mixture of the carrier (5% v/v), and the surfactant (2-5% v/v). The volume fraction of the internal aqueous phase in the primary W/O emulsion (O/A ratio) was varied from 0.25 to 1. In the second step, a known volume of freshly prepared primary W/O emulsion was added to a known volume of external aqueous phase (feed phase), and the mixture was stirred (at different speed) by a Heidolph RZR2020 mixer for 30 minutes at 25ºC. The volume fraction of the primary W/O emulsion in the resulting W/O/W double emulsion (M/F ratio) was 0.1 in all cases.

3. Results and discussions

3.1. Effect of acidic leach solution pH

Because of acidic property of MDEHPA, the pH of stripping solution should be less than the acidic leach solution in ELM process. The pH of the acidic leach solution was changed in the range of 4.5–6.5 using NaOH solution, water and acetic acid–sodium hydroxide buffer solution. The effect of pH on manganese extraction is shown in Fig. 1.

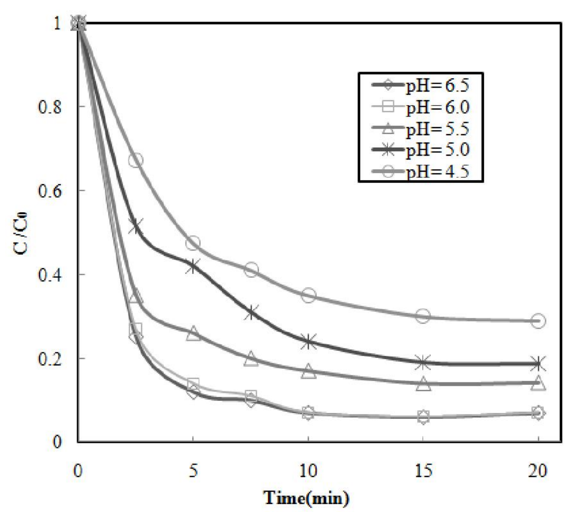

Fig.1. Effect of feed solution pH on the extraction rate of C_o (Span 80: 5%; MDEHPA: 5%; dilute: 90.0%; stripping solution: 25mL 0.5M H_2SO_4; mixing speed: 500 rpm; C_o concentration of feed solution: 1500mg/L; feed solution pH: 4.5–6.5; phase ratio: 25/25; treatment ratio: 1/10.

As shown in Fig. 1, Manganese extraction increased by increasing the pH between 4.5 and 6 but between 6 and 6.5, extraction efficiency of manganese didn't change significantly. This is probably due to the instability of the emulsion at highest pH and deterioration of emulsion stability due to slightly swelling of the emulsion. The poor performance at low pH could be explained by the competition of H^+ ions with the solute due to the release of H^+ ions from extractant to the acidic leach solution. As a result, maximum extraction was achieved at pH 6.0. At this pH value, the swelling of the emulsion was not been observed.

3.2. Effect of stripping solution type

As known from the literature, the main factor of emulsion liquid membrane applicability is stability of emulsion. In addition to mixing speed, extractant concentration and surfactant concentrations, stripping agent type is another important parameter (Kargari et al., 2006) .The selection of suitable stripping solution is considered as a key factor for an effective ELM system. Fig.2 presents the effect of different stripping solutions including HCl, H_2SO_4, and HNO_3 on manganese extraction efficiency.

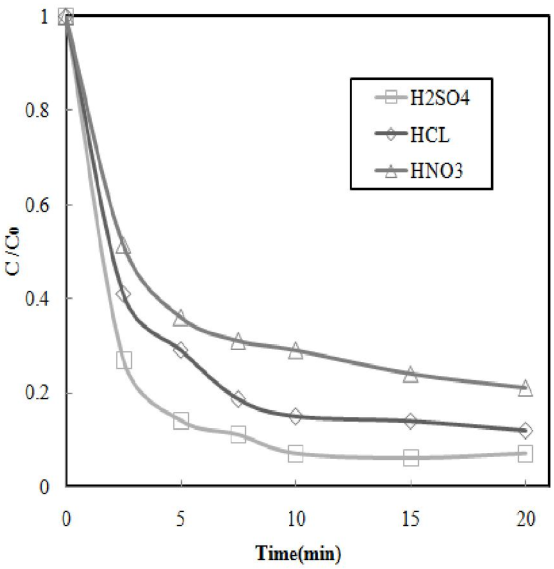

Fig.2. Effect of stripping solution type on the extraction rate of C_o (Span 80: 5%; MDEHPA: 5%; dilute: 90.0%; mixing speed: 500 rpm; C_o concentration of feed solution: 1500mg/L; feed solution pH: 6.0; phase ratio: 25/25; treatment ratio: 1/10.

The results show that stripping solution with H_2SO_4 solution gave higher manganese extraction and more stable emulsion. Therefore, sulfuric acid was selected as the best the stripping solution.

3.3. Influence of internal phase concentration

Internal stripping agent is one of the most important parameter that affects ELM stability and extraction efficiency. The solute extraction rate increases with an increase in the concentration of internal reagent present in the emulsion (Kislik, 2010).

The influence of sulfuric acid concentrations (0.2–0.6M) on the extraction efficiency was investigated. As shown in Fig.3, extraction efficiency increased by increasing sulfuric acid concentration from 0.2 to 0.5 M but decreased from 0.5 to 0.6 M.

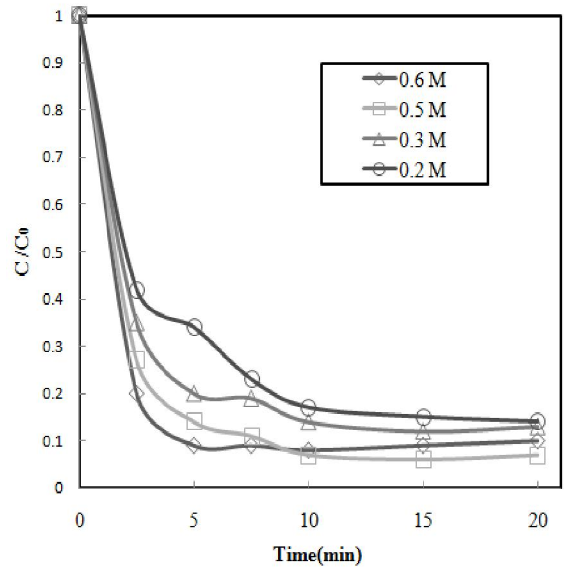

Fig.3. Effect of stripping solution acid concentration on the extraction rate of C_o (Span 80: 5%; MDEHPA: 5%; dilute: 90.0%; mixing speed: 500 rpm; C_o concentration of feed solution: 1500mg/L; feed solution pH: 6.0; phase ratio: 25/25; treatment ratio: 1/10.

The differences of hydrogen ion chemical potentials between the two aqueous phases are the main driving force in the emulsion liquid membrane process. Thus, the extraction efficiency increases with increasing the concentration of H_2SO_4 in the stripping solution from 0.2 to 0.5 M. However, for concentration of 0.6M sulfuric acid, the emulsion swells up due to osmosis phenomenon which leads to the dilution of the internal phase and causing a less effective stripping. This phenomenon is reported by Reis et al, 1993.

3.4. Influence of carrier concentration

By increasing the concentration of carrier two effects should be considered, at first the viscosity of membrane phase declines by increasing the carrier concentration and hence the carrier acts as thinner for the membrane phase. Secondly, increasing the carrier concentration over a certain limit decreases the emulsion stability (Yan and Pal, 2001; Kargari et al., 2006). On the other hand, enhancement of carrier concentration in membrane phase increases the ability of the membrane for extraction.

The effect of extractant concentration on manganese extraction is shown in Fig. 4.

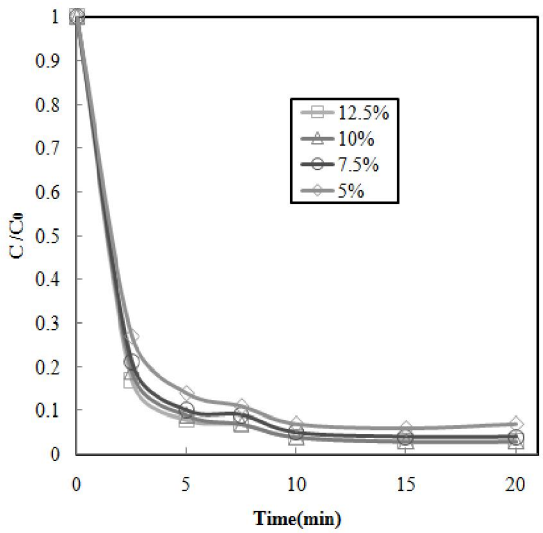

Fig.4. Effect of extractant concentration on the extraction rate of C_o (Span 80: 5%; MDEHPA: 5.0–12.5%; dilute: 82.5–90.0%; %; stripping solution: 25mL 0.5M H_2SO_4; mixing speed: 500 rpm; C_o concentration of feed solution: 1500mg/L; feed solution pH: 6.0; phase ratio: 25/25; treatment ratio: 1/10.

It is evident that extractant concentration has a significant effect on extraction of manganese from acidic leach solutions. Also an increase from 93 to 97% in manganese extraction with an increase in extractant concentration to 10% was observed and then leveled off to 12.5%. It is conceivable that the increase of extractant concentration in the membrane solution and hence at the membrane-acidic leach solution interface enhances the formation of manganese–extractant complexes, resulting in increasing diffusion of manganese from the acidic leach solution to the membrane surface, and increasing the formed complexes through the membrane to the stripping solution. Also a further increase in extractant concentration (from 7.5 to 12.5%) showed negligible increase in the manganese extraction. Therefore, extractant concentration of 7.5% was selected as the best concentration.

3.5. Influence of surfactant concentration

Surfactants are usually organic compounds that are amphipathic, meaning they contain both hydrophilic and hydrophobic groups therefore; they are soluble in organic and water phase. Surfactant must be properly chosen in minimizing the co-transport of water during extraction process. Increasing concentration of surfactant increases the stability of the liquid membrane which leads to the decrease in the breakup rate; hence the extraction degree of metal also increases but an increase in the surfactant concentration decreases the removal efficiency of lead due to mass transfer resistance caused by the surfactant film, therefore there is an optimum concentration for surfactant (Kislik, 2010).By increasing the surfactant concentration, the extraction efficiency increases. This is because of the more stable emulsion formation at high emulsifier concentrations.

Surfactant concentration is an important factor as it directly affects the stability, swelling and break up of ELM. Fig. 5 represents the variation of extraction efficiency of manganese with different concentrations of Span-80.

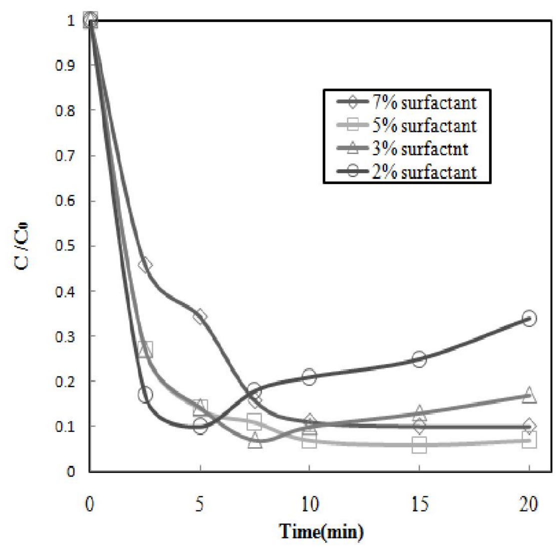

Fig.5. Effect of surfactant concentration on the extraction rate of C_o (Span 80: 2–7%; MDEHPA: 5.0%; dilute: 88.0–93.0%; stripping solution: 25mL 0.5M H_2SO_4; mixing speed: 500 rpm; C_o concentration of feed solution: 1500mg/L; feed solution pH: 6.0; phase ratio: 25/25; treatment ratio: 1/10.

As shown in Fig. 5 that up to 3% of Span-80 concentrations extraction efficiency of manganese increases and then decreases. At lowest surfactant concentration (2%), emulsions break easily leading to poor extraction. This indicates that the break-up of emulsion depends on contributing factor and (Othman et al., 2006) retards the transportation of reactive manganese from membrane phase into receiving phase. At higher surfactant concentration (7%), although the membrane stability increases but mass transfer resistance increases due to presence of more surfactant at aqueous–organic phase interface, resulting in less extraction of Manganese ions to stripping solution; therefore extraction of manganese ions is reduced. Similar results were obtained by Kumbasar, 2008. As a result, manganese extraction is maximum (93%) at 5% concentration of Span-80. Therefore, 5% of Span-80 was selected for the tests to obtain other optimum parameters of ELM system.

3.6. Influence of stirring speed

Stirring speed was found as a key parameter affecting extraction to a large extent. The efficiency of ELM extraction increases with increase in stirring speed. This is due to the fact that with increase of stirring rate during extraction of solute, the sizes of the emulsion droplets become smaller providing more mass transfer area. However, as the stirring rate is increased, the emulsion droplets become more unstable because of the leakage of the internal phase to external phase that adversely affects the solute extraction rate at larger extraction times (Lee and Chan, 1990; Lin and Lang, 1997; Sahoo and Dutta, 1998; Kislik, 2010). It is reasonable that by increase stirring speed the diameter of the internal droplets decreases which increases the mass transfer rate. But when the size of the internal droplets decreases below a critical value, accumulation of the electrostatic charges retards the diffusion of the complex toward the external surface of the internal droplets and consequently the total rate of mass transfer decreases. Effects of mixing speed on the extraction of manganese are shown in Fig. 6.

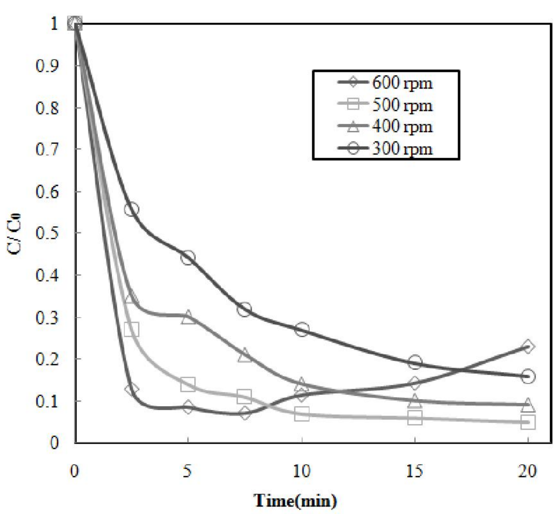

Fig.6. Effect of mixing speed on the extraction rate of C_o (Span 80: 5%; MDEHPA: 5%; dilute: 90.0%; stripping solution: 25mL 0.5M H_2SO_4; mixing speed: 500–700 rpm; C_o concentration of feed solution: 1500mg/L; feed solution pH: 6.0; phase ratio: 25/25; treatment ratio: 1/10.

It was observed that at earlier period of operation, rate of extraction was more at higher mixing speed. This trend was observed during initial 7.5 min. At higher mixing speed, smaller sized emulsion droplets were formed leading to more surface area for mass transfer. But at the same time, higher mixing speed adversely affected the stability of emulsion globules leading to breakage. Therefore extraction efficiency of Manganese decreased in the long run. It was observed from Fig. 6 that maximum extraction (99%) occurred at 20min and with a stirring speed of 500 rpm. Beyond 7.5 min, extraction efficiency decreased with 600 rpm. Maximum extraction at the end of operation was 99% at 500 rpm.

4. Conclusions

Emulsion liquid membrane is a fast and effective method for manganese extraction from aqueous solutions. An ELM system with MDEHPA as carrier and Span-80 as surfactant was prepared for manganese ion extraction from aqueous solution and optimum conditions were obtained. The carrier concentration and stirring speed for emulsification have the minor effect on the membrane stability but concentration of internal phase, surfactant concentration has the most effect on manganese extraction efficiency.The results showed that after 10 min of stirring, about 97% of manganese ions can be recovered from an external aqueous solution containing 1500ppm of manganese ions in 0.5M sulfuric acid medium. The extraction of manganese increased with increasing; the stirring speed of mixing, the carrier concentration in the membrane phase and the stripper concentration (H_2SO_4) in the internal aqueous phase. The optimum conditions were determined experimentally as “surfactant concentration (5%), extractant concentration (7.5 vol %), stripping solution concentration and its type (0.5M H_2SO_4), pH of the feed solution (6.0), mixing speed (500 rpm).

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Corresponding Author:
Iman Salahshouri
Department of Botany Chemical engineering Islamic Azad University
Shahreza, Isfahan province, Iran
E-mail: Iman .salahsoori81@gmail.com

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