Study on Mg^{2+} removal from ammonium dihydrogen phosphate solution by an emulsion liquid membrane

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Abstract

Mg^{2+} is extracted from ammonium dihydrogen phosphate ($NH_4H_2PO_4$) solution by an emulsion liquid membrane (ELM) using mono-(2-ethylhexyl) 2-ethylhexyl phosphonate (HEHPEHE) as a carrier, sulfonated liquid polybutadiene (LYF) as a surfactant and kerosene as a solvent. To study the extraction efficiency and advantages of the ELM process in the separation of Mg^{2+}, the effects of various operating conditions on the extraction – HEHPEHE volume fraction, reaction temperature, treat ratio (emulsion phase/external phase), phase ratio (membrane phase/internal phase), agitation speed, extraction time, internal phase concentration, surfactant LYF concentration and initial pH of $NH_4H_2PO_4$ solution are experimentally investigated and discussed. The results show that Mg^{2+} in $NH_4H_2PO_4$ solution can be effectively removed by the ELM process. An extraction efficiency of more than 83.1 % is attained at the optimized parameters and superior-grade $NH_4H_2PO_4$ can be obtained by two levels of extraction.

Keywords: wet process phosphoric acid, $NH_4H_2PO_4$ solution, Mg^{2+}, ELM, HEHPEHE.

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$NH_4H_2PO_4$ is used for flame retardant and drip-irrigation fertilization, which needs high pure $NH_4H_2PO_4$. In the past, the high purity of $NH_4H_2PO_4$ is manufactured with thermal-process phosphoric acid. The cost of thermal-process phosphoric acid is very high. The yellow-phosphorus manufacturers are closed one after the other because of the pressure from the energy consumption and environment protection. The cost of yellow phosphorus, as a basic raw material of thermal--process phosphoric acid is becoming higher and higher. Therefore, the low cost of wet process phosphoric acid (WPA) are gradually paid attention to in recent years. However, there are some undesirable impurities (Fe^{3+}, Al^{3+} and Mg^{2+}) in WPA. They will lower the quality of $NH_4H_2PO_4$ products. To get the superior grade $NH_4H_2PO_4$, WPA should be purified.

Improving the pH of the solution, usually between 4–4.5, the most of the metal ions can be removed, but there are still some Mg^{2+} which can cause formation of troublesome water-insoluble substance in the following concentration and crystallization process. The main ingredient of water-insoluble substance is magnesium-containing phosphate. Therefore, Mg^{2+} must be removed before concentrating the neutralized $NH_4H_2PO_4$ solution. Several methods based on solvent extraction [1,2] are used to remove Mg^{2+} industrially, however, in comparison with the solvent extraction process, an ELM process has main advantages such as very high mass transfer rates due to very thin liquid membrane and large interfacial areas between aqueous and organic phases, simultaneous extraction/stripping in one stage and small quantities of expensive extractant.

Since Li first applied an ELM to the separation of hydrocarbons [3], ELMs came to be an effective tool for the purification or separation of various materials, involving the transport of precious metal ions [4–6], rare earth elements [7], drugs [8–12], phenols [13–15], fructose [16–17], and the treatment of seawater [18] and waste water [19–22].

Consequently, in this paper, the ELM process is introduced to extract Mg^{2+} from the $NH_4H_2PO_4$ solution. The aim is to experimentally study the effects of various factors on the extraction efficiency using ELM.

EXPERIMENTAL

Materials

The solvent used in this work is kerosene. HEHPEHE is employed as an extractant produced by Luo Yang Zhong Da Chemical Company (China) (AR grade). The surfactant LYF is synthesized in our laboratory. Pure water is produced by Aquapro making-water machine (ABZ1-1001-P) in our laboratory.

Procedure

External aqueous solution (continuous phase) is prepared by dissolving magnesium sulfate heptahydrate in $NH_4H_2PO_4$ solution. Organic solution is prepared by dissolving HEHPEHE, as a carrier, and LYF as a surfactant in kerosene. Internal aqueous solution is prepared by dissolving hydrochloric acid in deionized

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water. A water-in-oil (W/O) emulsion (dispersed phase) is made by slow addition of the internal aqueous solution to the organic solution at optimal stirring speed (3000 rpm) by means of a motor-driven emulsifier (Shanghai Specimen Model Factory, China). The solution is stirred continuously for 5 min to obtain a white ELM as shown in Figure 1. This high shear-agitator produced high speeds, generating emulsions with small size droplets around 0.5–100 μm. The prepared ELM is added to specific volume of external aqueous solution. The contents are stirred by means of motor-driven at 300 rpm speed for a different transfer time.

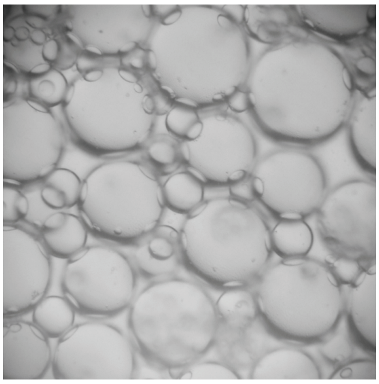

Figure 1. Samples of ELMs examined by a microscopic camera.

Parameters that could affect the extraction process

To study Mg^{2+} removal efficiency and advantages of the ELM process, it is necessary to optimize various parameters that could affect the process. The parameters to be optimized are the HEHPEHE volume fraction, reaction temperature, treat ratio (emulsion phase/external phase), phase ratio (membrane phase/ /internal phase), agitation speed, extraction time, internal phase concentration, surfactant LYF concentration and initial pH of $\text{NH}_4\text{H}_2\text{PO}_4$ solution.

Analysis

The concentration of Mg^{2+} is determined by atomic absorption spectrophotometry (GF3000).

RESULT AND DISCUSSION

In the extraction process, the carrier (HA) reacts with the solute (Mg^{2+}) at the interface between organic and aqueous phases and forms an oil soluble complex according to the following equation:

$$nq\text{Mg}^{2+}_{(a)} + \frac{q(s+2n)}{m}(\text{HA})_{m(o)} \rightarrow$$
$$\rightarrow (\text{Mg}_n\text{A}_{2n} \times s\text{HA})_{q(o)} + 2nq\text{H}^{+}_{(a)} \qquad (1)$$

where m is the aggregation number of HEHPEHE.

At the membrane solution phase - stripping solution interfaces according to the following equation:

$$(\text{Mg}_n\text{A}_{2n} \times s\text{HA})_{q(o)} + 2nq\text{H}^{+}_{(a)} \rightarrow$$
$$\rightarrow nq\text{Mg}^{2+}_{(a)} + q(s+2n)(\text{HA})_{m(o)} \qquad (2)$$

The extraction ratio (E) is defined as followed:

$$E = \frac{M(\text{Mg}^{2+}_{(i)}) - M(\text{Mg}^{2+}_{(r)})}{M(\text{Mg}^{2+}_{(i)})} \times 100 \qquad (3)$$

E represents the efficiency of ELM; $M(\text{Mg}^{2+}_{(i)})$: mole of Mg^{2+} in initial solution, mol; $M(\text{Mg}^{2+}_{(r)})$: mole of Mg^{2+} in the raffinate.

Effect of carrier concentration

It is well known that the efficiency of ELM is directly affected by the concentration of the carrier. In a lower carrier concentration, the interface between the feed solution and membrane is not saturated by the carrier. The increasing of the carrier concentration in ELM will lead to two effects: the viscosity of membrane phase decreases and hence increases the extraction rate. At the same time, the stability of the emulsion will decrease when the carrier concentration is increased to a certain limit [23–26]. On the other hand, an increase in concentration of the carrier in the membrane phase will increase the extraction ability of the membrane phase. The effects of carrier concentration are shown in Figure 2.

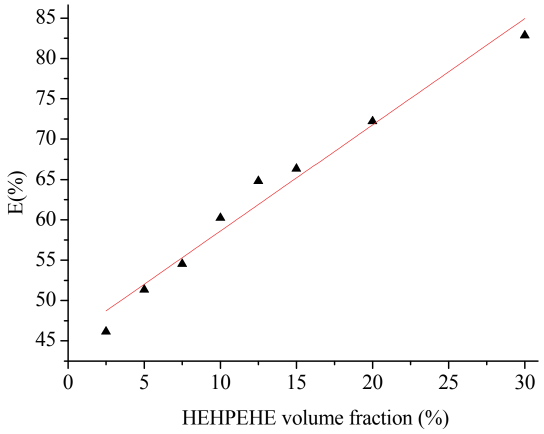

Figure 2. The effects of the HEHPEHE volume fraction (%) on the extraction ratio (E).

Effect of treat ratio (emulsion phase / external phase)

It seems that a large amount of Mg^{2+} and water could be transported into the internal phase at a high treat ratio. In fact, however, the net transport amount of Mg^{2+} is limited by the capacity of the internal phase. As seen from Figure 3, with the decreasing of treat ratio, the extraction ratio (E) decreases gradually. It is well known that HEHPEHE plays an important role in facilitating the Mg^{2+} transport into the internal phase. As the absolute amount of HEHPEHE in the extraction process is decreased, undoubtedly, the transport efficiency of Mg^{2+} also decreases.

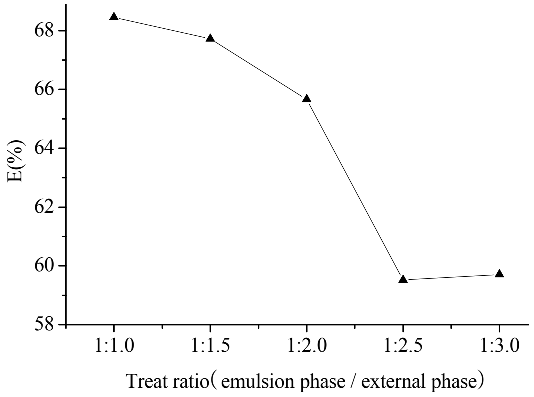

Figure 3. The effects of the treat ratio on the extraction ratio (E).

Effect of phase ratio (membrane phase / internal phase)

In order to form a stable and effective W/O emulsion, the phase ratio must exceed 1:1. With the increase of the phase ratio, the extraction and swelling rates are both strongly improved. The results are shown in Figure 4. This is due to the absolute amount of each component in the membrane phase is raised. It is well known that the HEHPEHE plays an important role in facilitating the Mg^{2+} transport into the internal phase. As the absolute amount of HEPHEHE in the membrane phase is increased, undoubtedly, the transport rate of Mg^{2+} also increases. Meanwhile, it is also demonstrated by Jing Qing Shen [27] that increasing the absolute amount of HEHPEHE and LYF enhances the swelling rate of the membrane because of their hydration properties.

Effect of extraction time

For obtaining the extraction equilibrium time experiments of effect of extraction time on the extraction ratio (E) are carried out. From Figure 5, it can be seen that the extraction equilibrium is achieved in 25 min.

So an extraction time of 25 min is used for all subsequent extraction and stripping experiments.

Effect of agitation speed

As the mixing speed increases, two phenomena occur: 1) the globule size decreases and 2) the breaking rate of the globules increases. A smaller globule size will lead to a larger transfer interfacial area between the feed and the membrane. This increased transfer area allows the extraction to occur at a higher rate, and explains the observations noted above. On the other hand, the higher rate of shear and subsequent higher rate of breakage of globules at the higher agitation speed values, the higher rate of breakage allows more leakage of the solute into the feed phase from the internal phase [28]. Therefore, from the Figure 6, the optimum value for agitation speed is found to be 350 rpm.

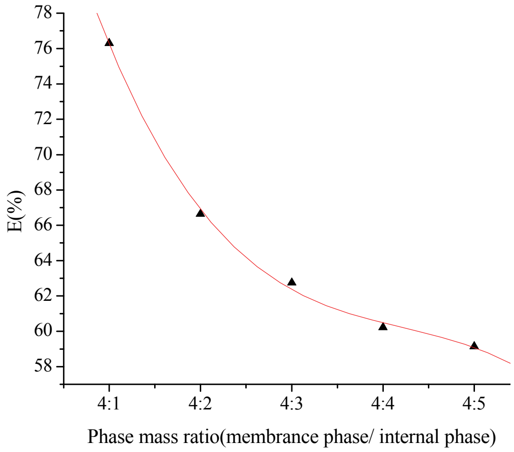

Figure 4. The effects of the phase mass ratio on the extraction ratio (E).

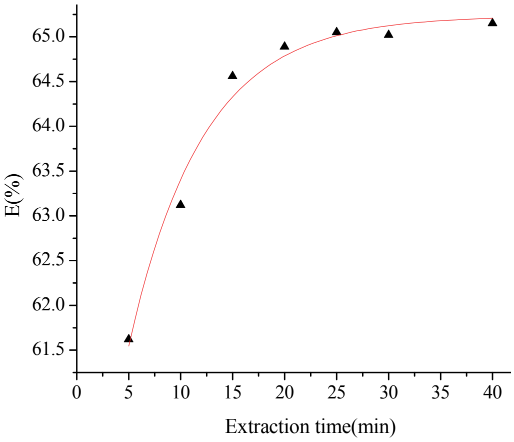

Figure 5. The effects of the extraction time on the extraction ratio (E).

Effect of initial pH of $NH_4H_2PO_4$ solution

The extraction efficiency of Mg^{2+} is obviously affected by the acidity of $NH_4H_2PO_4$ solution. As shown in Figure 7, the extraction efficiency increases with the increase of pH of $NH_4H_2PO_4$ solution. This may be explained as follows.

The strong acidity is favorable to form Mg^{2+}. However, the strong acidity is unfavorable to the ion-exchange reaction between Mg^{2+} and the carrier with an increase of H^+ concentration according to Eq. (1), because the equilibrium is shifted to the left side of the above extraction reaction with an increase in H^+ concentration. The final results are controlled by the competition of these two factors.

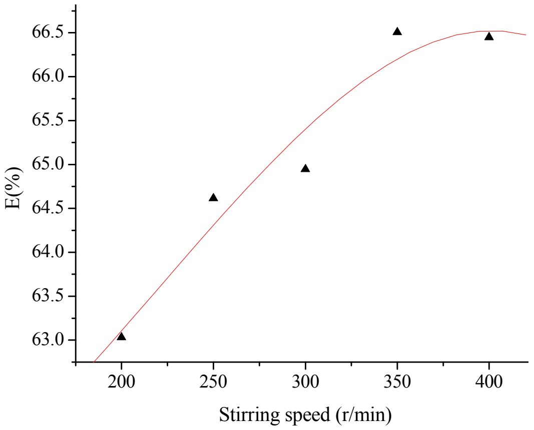

Figure 6. The effects of the agitation speed on the extraction ratio (E).

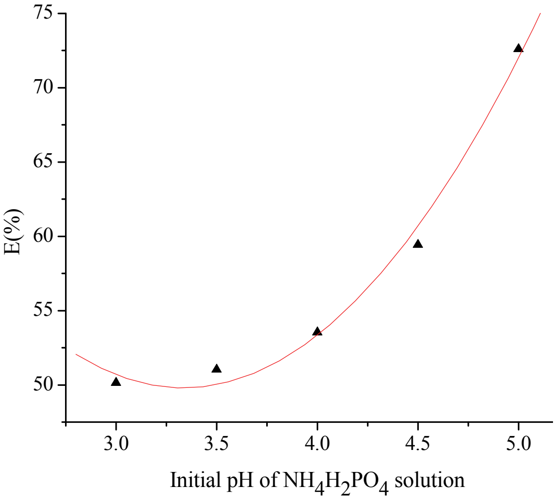

Figure 7. The effects of the initial pH of $NH_4H_2PO_4$ solution on the extraction ratio (E).

Effect of HCl concentration in internal phase

It is quite clear from equation (2) that the transport of Mg^{2+} through the liquid membrane is dependent on the H^+ concentration in the internal phase.

The results shown in Figure 8 indicate that the extraction efficiency decreases with an increase of the concentration of the stripping agents. If the amount of protons increases up to 1.0 and 2.0 M, the Eq. (2) will shift backward and there may be difficulties in dissociating the $MgCl_2$ from MgA_2. This causes the decrease in the efficiency.

Effect of surfactant LYF concentration in membrane

The surfactant concentration in the membrane phase is of crucial importance to any ELM system. While it ensures the stability of the membrane during the extraction, it also changes the viscosity of the membrane phase, so as to change the mass transfer resistance. Figure 8 shows the effects of various LYF concentrations on the extraction ratio (*E*). The figure indicates that the extraction ratio of Mg^{2+} is improved with the increase of LYF concentrations. However, when the LYF concentration increases to certain value about 2.0%, the extraction ratio (*E*) remains almost unchanged. On the other hand, however, an extremely low surfactant concentration cannot stabilize the membrane. As seen from Figure 9, a LYF concentration of 2.0% seems optimal.

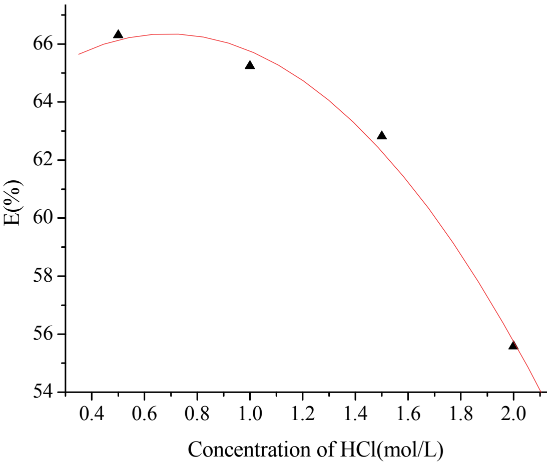

Figure 8. The effects of HCl concentration in feed solution on the extraction ratio (E).

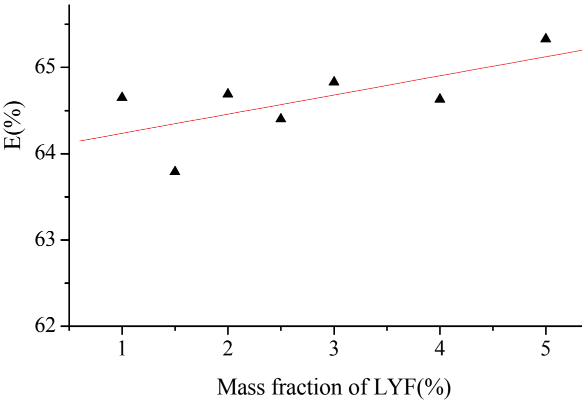

Figure. 9. The effects of the LYF concentration on the extraction ratio (E).

Effect of reaction temperature

The influence of temperature on the transport of Mg^{2+} through the liquid membrane containing HEHPEHE in kerosene is examined at 293, 297, 301, 305, 309 and 313 K.

As can be seen in Figure 10, the extraction efficiency increases as the temperature rises up. From the famous Van't Hoff equation: $d\log D/d(1/T) = -\Delta H/(2.303R) + \text{const}$, ΔH value is 3.67 $kJ \cdot mol^{-1}$, which shows that the extraction of Mg^{2+} with HEHPEHE is endothermic.

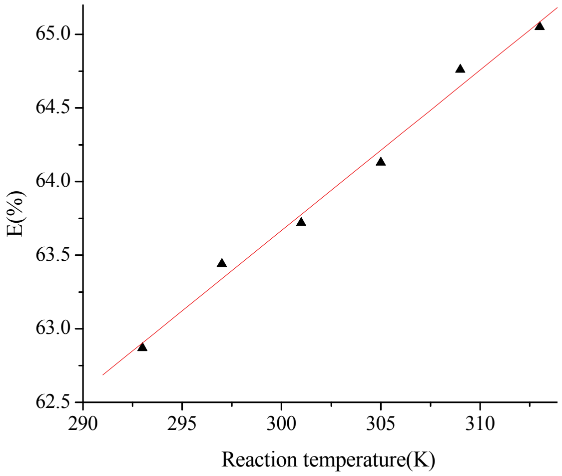

Figure 10. The effects of the reaction temperature on the extraction ratio (E).

Examination

A kind of practical wet-process phosphoric acid is neutralized to pH 4.5 with ammonia and filtered. The neutralized solution is then extracted under the above-mentioned optimal technological conditions. The superior grade $NH_4H_2PO_4$ is produced by the following concentration and crystallization process using the extracted solution. As Table 1 shows, the food grade $NH_4H_2PO_4$ can be obtained.

Table 1. Composition of $NH_4H_2PO_4$ product

Item	N, %	P_2O_5, %	Fe^{3+}, %	Mg^{2+}, %	Al^{3+}, %	Heavy metal Pb, %
Mass fraction	≥12	≥60.5	≤0.0003	≤0.0008	≤0.0002	≤0.0005
Item	As, %	F, %	SO_4^{2-}, %	pH	H_2O, %	Water-insoluble substance, %
Mass fraction	≤0.0050	≤0.0085	≤0.0020	4.5-4.8	≤0.2	≤0.05

CONCLUSION

Based on the results of this research on the removal of Mg^{2+} from $NH_4H_2PO_4$ solution with ELM, the following specific conclusions can be drawn:

1. ELM extraction is an effective method for the removal of Mg^{2+} from $NH_4H_2PO_4$ solution.

2. The optimized parameters are as follows: the HEHPEHE volume fraction: 30%; the reaction temperature: 35 °C; the treat ratio: 1:2; the phase ratio: 4:1; the LYF volume fraction: 1–1.5%, the agitation speed: 300 r/min, the extraction time: 25 min, the internal phase concentration: 0.5 mol/L and the initial pH of $NH_4H_2PO_4$ solution: 4.5.

3. The enthalpy change ΔH of the extraction process is 3.67 kJ·mol^{-1}.

Acknowledgement

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IZVOD

PRIMENA TEČNIH MEMBRANA ZA EKSTRAKCIJU Mg^{2+} IZ RASTVORA AMONIJUM-DIHIDROGENFOSFATA

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(Naučni rad)

Joni Mg^{2+} su izdvojeni iz rastvora amonijum-dihidrogenfosfata ($NH_4H_2PO_4$) primenom tečnih membrana u obliku W/O emulzije (ELM); nosač je mono-(2-etilheksil)-2-etilheksilfosfonat (HEHPEHE), površinski aktivna materija je sulfonovani tecni polibutadien (LYF), a rastvarač je kerozin. Za definisanje efikasnosti ekstrakcije i prednosti ELM procesa pri separaciji Mg^{2+} praćeni su i diskutovani uticaji različitih operacionih uslova, na ekstrakciju HEHPEHE, na primer: reakciona temperatura, odnos teške i lake faze, odnos međupovršine i teške faze, brzina mešanja, vreme ekstrakcije, koncentracija teške faze, koncentracija površinski aktivne materije, i početna pH vrednost rastvora $NH_4H_2PO_4$. Dobijeni rezultati pokazuju da joni Mg^{2+} iz rastvora $NH_4H_2PO_4$ mogu biti efikasno uklonjeni primenom ELM procesa. Pri optimalnim parametrima procesa ostvarena je efikasnost ekstrakcije od 83.1%, a $NH_4H_2PO_4$ visoke čistoće (*superior-grade*) može se dobiti dvostepenom ekstrakcijom.

Ključne reči: Fosforna kiselina-mokri postupak • Rastvor $NH_4H_2PO_4$ • ELM proces • Ekstrakcija Mg^{2+}