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Full Length Research Paper

Study on Mg^{2+} removal from ammonium dihydrogen phosphate solution by a novel emulsification extraction process

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The emulsification extraction process (EEP) is a novel method for separating solutes from aqueous solution, and for its high extraction ratio, the EEP presents huge potential for extraction from dilute solution. In this paper, the EEP is successfully generated with mixing solutions containing aqueous and organic phases at high speed. The extraction of Mg^{2+} from ammonium dihydrogen phosphate ($NH_4H_2PO_4$) solution is studied by using kerosene as a solvent, di(2-ethylhexyl)phosphoric acid (D2EHPA) as an extractant. To study the extraction ratio and advantages of the EEP process in the removal of Mg^{2+}, various parameters - D2EHPA volume fraction, reaction temperature, phase volume ratio, initial pH of $NH_4H_2PO_4$ solution, stirring speed, stirring time were studied and optimized. The results show that Mg^{2+} in $NH_4H_2PO_4$ solution can be effectively removed by EEP process. An extraction ratio of more than 90.1% is attained at the optimized parameters and superior-grade $NH_4H_2PO_4$ (MAP) can be obtained by two levels of extraction.

Key words: Emulsification extraction process, di(2-ethylhexyl)phosphoric acid, $NH_4H_2PO_4$, Mg^{2+}.

INTRODUCTION

MAP, which is the common name of $NH_4H_2PO_4$ is used as flame retardant and drip-irrigation fertilization, which needs highly pure MAP mainly manufactured with thermal-process phosphoric acid in the past. The cost of thermal-process phosphoric acid is very high. The yellow-phosphorus manufacturers are closed 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. So the low cost of wet-process phosphoric acid (WPA) is gradually being paid attention in recent years. However, there are some undesirable impurities (Fe^{3+}, Al^{3+}, Mg^{2+}) in WPA. They will lower the quality of MAP products.

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To get the superior grade MAP, WPA should be purified. Improving the pH of the solution, usually between 4 to 4.5, can remove most of the metal ions, but there still are some Mg^{2+} which can cause formation of troublesome water-insoluble substance in the following concentration and crystallization process. The main ingredients of water-insoluble substance are magnesium-containing phosphate. Therefore, the Mg^{2+} must be removed, before concentrating the neutralized MAP solution. Several methods based on solvent extraction (McCullough, 1976; Lo et al., 1983; Bradford, 1977; Kenneth et al., 1972; Miki et al., 1997; Mohammad et al., 1997; Hannachi et al., 2007; Wang et al., 2000) are used to remove Mg^{2+} in phosphorus chemical industry; however, conventional solvent extraction suffers from two disadvantages. It needs a mixing-setting stage, and it requires a high phase volume ratio of solvent/water below which extraction is poor.

Furthermore, because of the nature of the mixing, sometimes there is the undesirable possibility of the formation of a third colloidal phase which is difficult to eliminate. Faced with these problems, a novel technique of EEP can solve them efficiently. The idea of EEP (the emulsification extraction pocess) originated from the emulsification phenomena which is often produced in conventional solvent extraction process. However, it is well known that the emulsification can form an enormous interfacial area as in Figure 1, which can lower the phase volume ratio of solvent/water and where a transfer of solute from one phase to another can occur very rapidly with a minimum energy requirement and shorten the equilibrium time of extraction process. So, how to make full use of the advantages of emulsification phenomena is considered in this work. In this study, the removal of Mg^{2+} from ammonium dihydrogen phosphate with EEP is investigated. The aim of this work is to experimentally study the effects of various factors on the extraction ratio using EEP.

MATERIALS AND METHODS

Materials and equipment

The solvent used in this work is kerosene. D2EHPA is employed as an extractant produced by Luo yang Zhongda Chemical Company (China) (AR grade). Pure water is produced by Aquapro making-water machine (ABZ1-1001-P) in our laboratory. Emulsification generator using a high-speed stirrer (JRJ-300-I) produced by Shanghai Specimen and Model Factory (China).

Parameters that could affect the EEP process

To study Mg^{2+} removal efficiency and advantages of the EEP (the emulsification extraction process) process, it is necessary to optimize various parameters that could affect the process. The parameters to be optimized are the D2EHPA volume content, the reaction temperature, the phase volume ratio, the stirring speed, the stirring time, the phase volume ratio and the initial pH of $NH_4H_2PO_4$ solution.

Extraction experiment conditions

Solvent: kerosene, D2EHPA volume content: 50%, phase ratio (aqueous/organic) = 5:1, stirring speed: 4500 r/min, initial Mg^{2+} concentration: 600 mg/L, initial pH of ammonium dihydrogen phosphate: 4.5, stirring time: 60 s, reaction temperature: 55℃.

Analysis

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

RESULTS AND DISCUSSION

Extraction ratio (E) is defined as follows:

$$E = \frac{M_{(i)}^{Mg^{2+}} - M_{(r)}^{Mg^{2+}}}{M_{(i)}^{Mg^{2+}}} \times 100\% \qquad (1)$$

E represents the efficiency of EEP; $M_{(i)}^{Mg^{2+}}$: Mole of Mg^{2+} in initial solution, mol;

$M_{(r)}^{Mg^{2+}}$: Mole of Mg^{2+} in the raffinate, mol.

Effect of D2EHPA volume fraction (%)

Increasing D2EHPA concentration in solvent phase will increase the amount of extractant, so the numbers of free extractant taking participate in the extraction reaction will also increase. However, when the D2EHPA concentration increases to a certain value, the extraction ratio (E) remains almost unchanged, because the extraction reaction reaches equilibrium. Therefore, the extraction ratio (E) increases as shown in Figure 2.

Effect of phase ratio

The phase ratio (aqueous/organic) has a significant effect on extraction ratio (E) and entrainment. This effect is studied by changing the phase ratio (aqueous/organic) from 5:1 to 1:1. The results presented in Figure 3 clearly show that, a phase ratio of 1:1 gives the best extraction of Mg^{2+}. The reason (Wang et al., 2000) for this is that, for the fixed Mg^{2+} concentration in solution, increasing phase ratio in extraction process will enhance the amount of solvent and extractant.

Effect of stirring time

The extraction of Mg^{2+} by emulsification extraction and solvent extraction are presented in Figure 4. Figure 4 indicates that the extraction ratio (E) of Mg^{2+} is improved with the increase of stirring time. The equilibrium time for the emulsification extraction of Mg^{2+} is observed to be 100 to 120 s, which is far less than the solvent extraction equilibrium time of about 30 min. What is more surprising is that, the extraction ratio (E) of Mg^{2+} by emulsification extraction is higher than solvent extraction. This is because EEP (the emulsification extraction process) make the reaction of Mg^{2+} with D2EHPA more complete than solvent extraction. Therefore, this means that the equilibrium time for emulsification extraction needs 120 s to ensure completion.

Effect of initial pH of ammonium dihydrogen phosphate solution

The results of the experiments are shown in Figure 5.

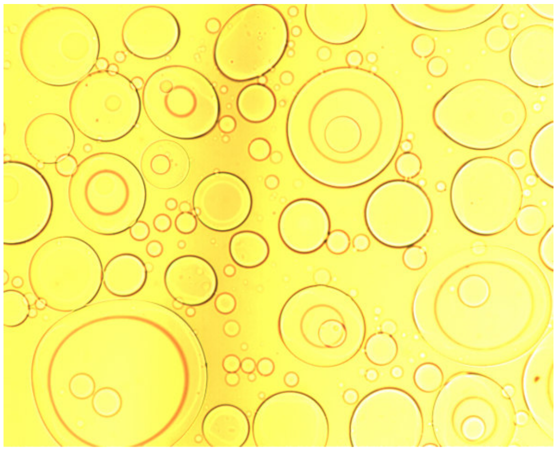

Figure 1. Samples of emulsion liquid are examined by a microscopic camera.

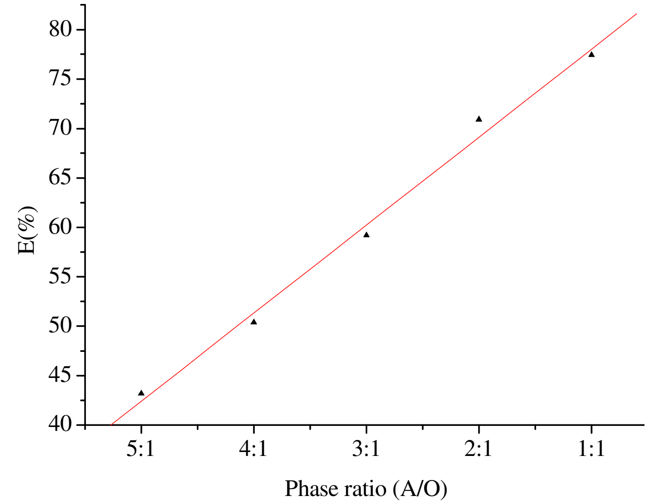

Figure 3. The extraction ratio (E) versus the phase ratio (A/O).

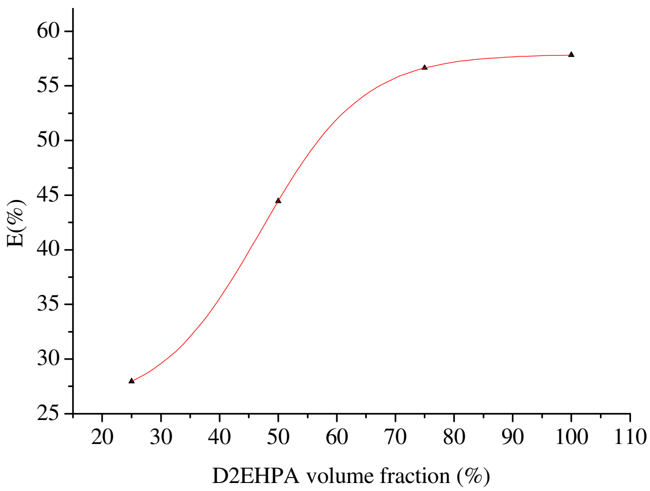

Figure 2. The extraction ratio (E) versus the D2EHPA volume fraction (%).

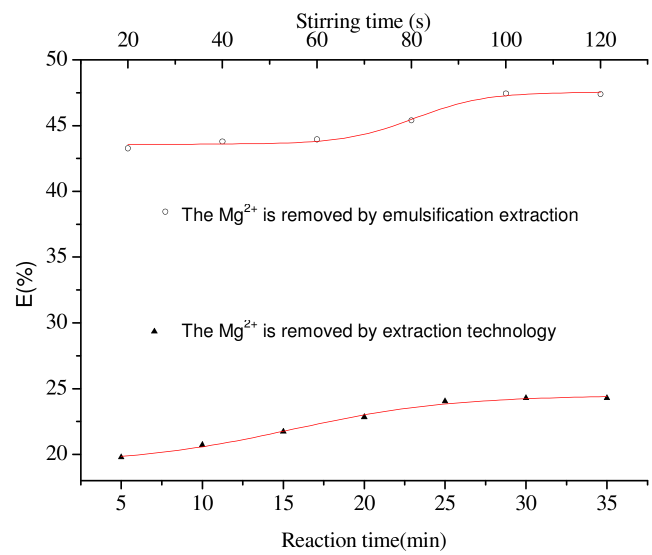

Figure 4. The extraction ratio (E) versus the stirring time.

The extraction of Mg^{2+} reach a maximum at the pH 4.5 where the formation of an ion-pair in ammonium dihydrogen phosphate media is favorable. It was observed that, with a further increase in pH to 5.0, Mg^{2+} extraction decreases gradually. At higher pH, there is a possibility of hydrolysis of the Mg^{2+} ion-pair complex. The lower values obtained at higher acid concentrations (pH<3.5) are due to competition between the extractable Mg^{2+} and $H_2PO_4^-$ which predominates in ammonium dihydrogen phosphate media at low pH.

Effect of reaction temperature

From Figure 6, the extraction ratio (E) increases as the temperature rises up, which shows that the extraction of Mg^{2+} with D2EHPA is endothermic.

Effect of stirring speed

As the stiring speed increases, a smaller globule size will lead to a larger transfer interfacial area between the feed and the solvent phase. This increased transfer area allows the extraction to occur at a higher rate. However, Figure 7 shows that the emulsification speed does not affect the extraction ratio (E) too much when the stiring speed reaches 4500 r/min. Therefore, the optimum value for stiring speed is found to be 4500 r/min.

Examination

A kind of practical wet-process phosphoric acid is

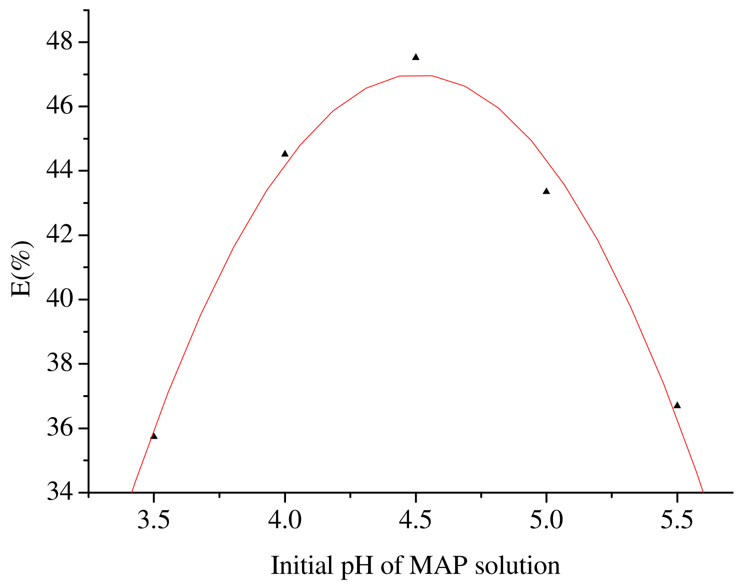

Figure 5. The extraction ratio (E) versus the initial pH of ammonium dihydrogen phosphate solution.

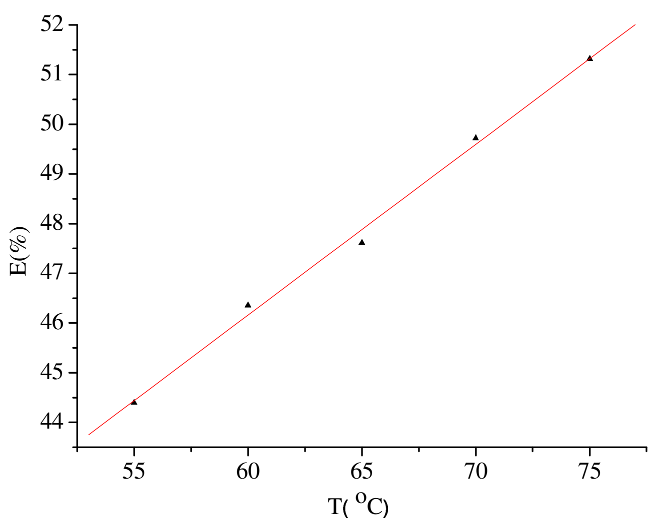

Figure 6. The extraction ratio (E) versus the reaction temperature.

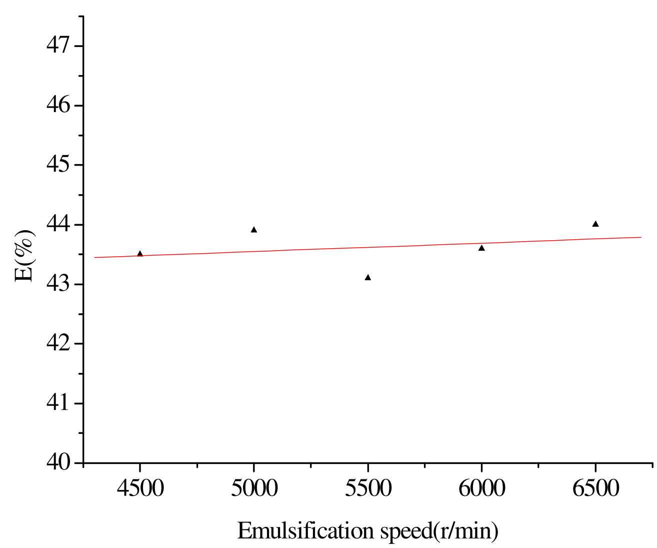

Figure 7. The extraction ratio (E) versus the emulsification speed.

neutralized to pH=4.5 with ammonia and filtered. The neutralized solution is then extracted under the aforementioned optimal technology conditions. The superior grade MAP is produced by the following concentration and crystallization process using the extracted solution. As Table 1 shows, the food grade MAP can be obtained.

Conclusion

Based on the results of this research on the removal of Mg^{2+} from ammonium dihydrogen phosphate solution with EEP (the emulsification extraction process), the following specific conclusions can be drawn:

1. EEP treatment can be a more effective method for the removal of Mg^{2+} from ammonium dihydrogen phosphate solution than solvent extraction.
2. The optimized parameters affecting the process are as follows: The D2EHPA volume fraction: 75%, the stirring time: 100s, the reaction temperature: 65℃; the phase volume ratio: 1:1; the stirring speed: 4500 r/min, and the initial pH of $NH_4H_2PO_4$ solution: 4.5.

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	≤0.0010	≤0.0002	≤0.0005
Item	**As (%)**	**F^- (%)**	**SO_4^{2-} (%)**	**pH**	**H_2O (%)**	**Water-insoluble substance (%)**
Mass fraction	≤0.0090	≤0.0085	≤0.0020	4.5-4.8	≤0.2	≤0.05

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