Removal of Fluorine from Wet-Process Phosphoric Acid Using a Solvent Extraction Technique with Tributyl Phosphate and Silicon Oil

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ABSTRACT: The deep removal of fluorine from wet-process phosphoric acid is currently a very serious issue. In this paper, an efficient liquid−liquid separation method based on a bubble membrane was developed to solve this problem. Tributyl phosphate (TBP) and silicon oil (SIO) were used as the organic phase. The effects of the component proportion in the organic phase (TBP/SIO v/v), organic to aqueous phase ratio (O/A), pH, temperature, and reaction time on the extraction ratio were investigated. The extraction ratio of fluorine was 98.4% when using only one stage with the following conditions: 90 °C, pH −0.46, volume ratio (TBP/SIO v/v) of 7:3, phase ratio (O/A) of 1:5, stirring speed of 200 rpm, and reaction time of 50 min. Fourier-transform infrared spectroscopy and inverted fluorescence microscopy were used to investigate the reaction mechanism and reaction kinetics. In addition, the scrubbing and stripping process was investigated. When a 2 mol/L sodium hydroxide solution ([NaOH]) was used as the stripping agent with a phase ratio (O/A) of 1:10, a stirring speed of 200 rpm, and a reaction time of 30 min, a maximum stripping ratio of 90.1% was obtained.

1. INTRODUCTION

Because of the increasing demand for phosphoric acid, Chinese factories produce more than 8 million tons of phosphates every year. Currently, there are two primary methods of manufacturing phosphoric acid: the thermal process, the product of which is called thermal process phosphoric acid (TPA), and the wet process, the product of which is called wet-process phosphoric acid (WPA).1 Because of its advantages over the thermal process of lower cost, lower energy consumption, and reduced pollutant generation, the wet process is the preferred method, and more than 90% of Chinese factories produce phosphoric acid with this method.2−7 However, the main disadvantage of WPA is that during its manufacturing process, there are many impurities present, among which fluorine is one of the major impurities.8−10 Five main methods have been used to remove fluorine from WPA. They are precipitation, steam stripping, cooling and crystallization, vacuum concentration, and solvent extraction.11−13 Solvent extraction is among the most popular method because of its low cost, high productivity, and high recyclability.14−17

Historically, precipitation was the most popular method for removing fluorine from WPA, and then steam stripping and vacuum concentration took the place of precipitation, as they were more effective in fluorine removal.18 Solvent extraction was used in certain countries, such as the United States of America and Canada, before it was introduced in China.19,20 Recently, there have been many reports investigating the solvent extraction of fluorine from WPA. Hutchins, Lembrikov et al., Amin et al., and Wang chose alcohol, phenol, amine, alkane, and ether solvents as extractants to remove fluorine from WPA.6,9,21,22 Compared to the phenol and alkane derivatives, the ether, amine, and alcohol derivatives provided higher fluorine extraction rates, which could reach 80−90% under the optimum conditions when using two- or three-stage countercurrent extractions. To date, most reports on the solvent extraction of fluorine from WPA, such as the report by Feki et al., have investigated how to efficiently extract...
phosphoric acid while indirectly extracting fluorine.\textsuperscript{23–26} However, few researchers have investigated direct ways of separating fluorine from WPA. Moreover, the methods that previous researchers used were complicated, expensive, and inefficient. Developing a more efficient, less-expensive and simpler method to solve these problems is thus necessary.

Hence, an efficient extraction method based on a bubble membrane that meets the above requirements is developed in this study, and it is substantially different from conventional liquid–liquid extraction techniques. Compared to conventional liquid–liquid extraction processes, in which chemical reactions between the functional groups in the organic phase and fluorine occur, this bubble membrane method mainly removes fluorine by controlling the reaction conditions, such as the pH and temperature, according to the physical characteristics of fluorine. Finally, the fluorine ions in the form of small HF bubbles enter the organic phase through the interfacial liquid membrane.\textsuperscript{27} Compared with other methods, this method offers not only better separation efficiency but also broader applicability, and it is particularly instructive.

2. RESULTS AND DISCUSSION

2.1. Separation Reaction. 2.1.1. Effects of pH and Temperature. Experiments were carried out in a high-acidity and high-temperature environment. The pH and temperature substantially affected the extraction ratio of fluorine (% E), so they were the first influencing factors to be investigated. First, pH levels ranging from 1.21 to −2.1 were tested to investigate their impact on the % E. The pH was adjusted by adding 75% sulfuric acid (vol %). The other reaction conditions were set as follows: temperature of 50 °C, tributyl phosphine (TBP) to silicon oil (SIO) volume ratio (TBP/SIO v/v) of 1:1, organic phase to aqueous phase ratio (O/A) of 1:5, stirring speed of 200 rpm, and reaction time of 1 h. Figure 1a shows that % E increased from 5.4 to 66.7% as the pH decreased and reached its maximum value of 66.7% at a pH of −2.1. However, when the pH was less than −0.46, the increases in % E became quite small, from 63.6 to 66.7%. The results suggest that a lower pH provides a better % E, and −0.46 was chosen as the reaction pH. These results may be explained by the reaction of hydrogen ions with fluoride ions to form HF and the combination of TBP with HF through hydrogen bond formation, thereby causing the fluorine ions in the aqueous phase to distribute into the organic phase.\textsuperscript{15}

Second, temperatures ranging from 15 to 100 °C were tested to investigate their impact on the % E. The other reaction conditions were set as follows: pH −0.46, volume ratio (TBP/SIO v/v) of 1:1, phase ratio (O/A) of 1:5, stirring speed of 200 rpm, and reaction time of 1 h. As shown in Figure 1a, % E increased from 38.4 to 95.7% with increasing temperature and reached its maximum value of 95.7% at 100 °C. However, when the temperature exceeds 75 °C, the increase in % E gradually slows because temperature has an important effect on the thermodynamics of the reaction process. With increasing temperature, the thermal motion of the ions increases, and the number of free fluorine ions increases. High temperature also facilitates the separation of the organic and aqueous phases. As the temperature increases, the surface tension and viscosity decrease, thereby weakening the diffusion resistance.\textsuperscript{27} Hence, % E increases rapidly during the first stage. Then, as the organic layer reaches saturation, the maximum loading of fluorine in the organic phase is quickly reached. During this stage, the mass transfer resistance becomes stronger, and the increase in % E slows.\textsuperscript{27} In addition, according to the Clausius–Clapeyron equation, the Gibbs enthalpy change (∆H) was calculated to be 21.63 kJ/mol, which indicated that the extraction of fluorine was an endothermic process.\textsuperscript{16} In conclusion, a higher temperature and a higher acidity improve the extraction ratio of fluorine.

2.1.2. Effects of the Volume Ratio of TBP to SIO and the Ratio of Organic to Aqueous Phases. First, constant reaction conditions, namely, a temperature of 90 °C maintained with a water bath, pH −0.46, a phase ratio (O/A) of 1:5, a stirring speed of 200 rpm, and a reaction time of 1 h, were used. TBP and SIO were each used separately as the organic phase to extract fluorine. The % E values obtained with TBP and SIO were 57.6 and 74.8%, respectively. Then, TBP was combined with SIO to generate mixed organic phases. The volume ratio (TBP/SIO v/v) was varied from 1:9 to 9:1, and the other reaction conditions were maintained as described above. Figure 1b shows that % E increased from 64.7 to 98.2% as the volume ratio (TBP/SIO v/v) increased from 1:9 to 7:3. However, when the volume ratio (TBP/SIO v/v) was increased beyond 7:3, the % E decreased from 98.2 to 92.1% because when the volume ratio (TBP/SIO v/v) was 7:3, TBP and SIO were in the optimal ratio for complexation and offer the best synergistic effect on fluorine ion separation.\textsuperscript{11} To maximize the separation rate and minimize waste, the loading capacity of the organic phase for fluorine ions had to be maximized, and the amounts of reagents consumed had to be minimized.\textsuperscript{27} Thus, 7:3 was chosen as the best volume ratio (TBP/SIO v/v).

Second, experiments were conducted using phase ratios (O/A) from 1:1 to 1:10. The other reaction conditions were the same and were as follows: the temperature was maintained at 90 °C using a water bath, the pH was −0.46, the volume ratio (TBP/SIO v/v) was 7:3, the stirring speed was 200 rpm, and the reaction time was 1 h. As shown in Figure 1b, % E decreased slightly as the phase ratio (O/A) decreased. When the phase ratio (O/A) was 1:1, % E reached its maximum value of 98.4%. Even when the phase ratio (O/A) was 1:10, % E reached 80.6% because the contact area between the organic and aqueous phases decreases with decreasing phase ratio (O/A). This change has a direct and negative influence on the interaction between the organic reagents and the fluorine ions. The loading of fluorine ions was relatively lower at a 1:10 phase ratio than at a 1:1 phase ratio. In addition, the mass transfer resistance becomes stronger as the phase ratio decreases. All of these factors are able to negatively affect the separation rate and lead to a decrease in % E.\textsuperscript{27} Based on the above results, 7:3 is the best volume ratio of TBP to SIO, and a
lower organic to aqueous phase ratio will result in a lower fluorate extraction rate.

2.1.3. Effect of the Reaction Time and the Determination of $\Delta$ $p$H. With the temperature maintained at 90 °C with a water bath, the pH at −0.46, the volume ratio (TBP/SIO v/v) at 7:3, the phase ratio (O/A) at 1:5, and the stirring speed at 200 rpm, experiments with reaction times ranging from 10 to 120 min were performed to investigate the effects of the reaction time on the % E. At the same time, the $\Delta$pH was measured, and this value was determined as the pH of the aqueous phase at a certain reaction time minus the pH of the feed solution.

As shown in Figure 2a, % E increases from 56.7 to 98.4% with increasing reaction time, and the $\Delta$pH increases to a maximum value of 0.10 at 120 min. When the reaction time was 30 min, the % E rapidly increased to 94.1%. Then, the growth in % E slowed until it reached a maximum of 98.4% at 120 min. This trend was attributed to the high number of free fluorate ions in solution and to the interactions between the organic reagents and the fluorate ions, which were so strong that % E initially increased quickly. Later, as the reaction progresses, the free fluorate content in the aqueous layer decreases, and at the same time, the potential additional loading of fluorate decreases. The interactions between the organic reagents and the fluorate ions became weaker: however, the mass transfer resistance was stronger, and the separation system reached equilibrium. Hence, during the last stage, % E remains almost constant with increasing reaction time. These results suggest that the extraction ratio of fluorate increases with increasing reaction time.

Regarding the increase in $\Delta$pH, the pH of the aqueous phase increased as the reaction progressed, possibly because hydrogen ions enter the organic phase and initiate an unknown chemical reaction. The hydrogen ions may react with other ions in solution to form larger species that will then enter the organic phase; this kind of process is physical adsorption. Additional validation experiments and discussions about this speculation are presented in the following sections (Sections 2.1.6 and 2.1.7). As shown in Figure 1a, a higher acidity will improve the % E. These results suggest that hydrogen ions are involved in the extraction process and help improve % E.

2.1.4. Selectivity of the Separation System. Because of their commercial values, fluorate is considered an impurity in the wet process, whereas phosphoric acid is the target product. The ideal separation result would be a high yield of phosphoric acid and a low yield of fluorate. Some comparative experiments were conducted to investigate the selectivity of the separation system for fluorate ions over phosphoric acid in the feed solution under the developed reaction conditions (temperature maintained at 90 °C with a water bath, pH of −0.46, volume ratio (TBP/SIO v/v) of 7:3, phase ratio (O/A) of 1:5, stirring speed of 200 rpm, and reaction time of 50 min). In terms of the results shown in Figure 2b, the separation system has a removal rate of 98.3% for fluorate ions and a removal rate of 2.1% for phosphoric acid. This method not only has successfully realized the objective of efficiently extracting fluorate from WPA but also has almost no effect on the phosphoric acid in WPA. These results confirm that this separation system has a high selectivity.

2.1.5. Equilibrium of the Separation System. Through the above experiments, almost all of the reaction parameters for the separation system were optimized. Some additional experiments were conducted to investigate the separation system’s equilibrium under the ideal reaction conditions: the temperature was maintained at 90 °C using a water bath, the pH was −0.46, the volume ratio (TBP/SIO v/v) was 7:3, the phase ratio (O/A) was 1:5, the stirring speed was 200 rpm, and the reaction time was 50 min. The fluorate ion distribution isotherm was obtained from the final experimental data. The McCabe-Thiele diagram, as shown in Figure 3, indicates that at a phase ratio (O/A) of 1:5, the extraction rate of fluorate can reach only 98.4% one stage; two stages are theoretically needed to completely remove the fluorate ions from the aqueous phase.

Figure 2. (a) Effects of reaction time on % E and the variation in the pH of the aqueous phase. (b) Extraction rate of the separation system for fluorate and phosphoric acid.

Figure 3. McCabe-Thiele diagram of fluorate removal from the aqueous phase.
reaction temperature, the absorption ability of SIO is higher than that of TBP.\textsuperscript{33,34} Thus, no chemical reactions take place; however, physical absorption in the organic phase does occur, and the reaction process mainly occurs in the aqueous phase or at the interface of the organic phase and the aqueous phase.

The results shown in Figures 1a, 2a, and 4 suggest that fluorine ions combined with hydrogen ions to generate HF, which then entered the organic phase until the separation system reached equilibrium. Because no chemical reactions occurred in the organic phase, the HF mainly entered the organic phase in the form of bubbles under the high-temperature and high-acidity conditions. If fluorine ions entered the organic phase in the form of HF bubbles, the bubbles should be visible in the loaded organic phase under an inverted fluorescence microscope. When the HF bubbles are forced out of the loaded organic phase using a sufficiently high temperature, they migrate to the sodium hydroxide solution, resulting in no or few bubbles in the organic phase and a measurable amount of fluorine ions in the sodium hydroxide solution. To verify this hypothesis, two groups of experiments were designed for both TBP and SIO. Each group contained four experiments for comparison: a blank experiment (pure organic reagents), a control experiment (pure organic reagents with deionized water), an unheated experiment (pure organic reagents with feed solution), and a heated experiment (pure organic reagents with feed solution). Moreover, all the experiments in each group were conducted under the reaction conditions described in section 2.1.5, and then the loaded organic phase was separated from the aqueous phase in each of the four experiments. The loaded organic phases from the blank experiment, control experiment, and unheated experiment were directly analyzed under an inverted fluorescence microscope. The loaded organic phase of the heated experiment was heated and then analyzed.

Figure 5 shows that there was almost nothing to observe in the loaded organic phases from the blank experiment and the control experiment. However, unexpectedly, bubbles were found in the loaded organic phase from the unheated experiment, and they disappeared when this phase was heated. Similarly, Figure 6 shows that almost nothing was found in loaded organic phases from the blank experiment and the control experiment. However, bubbles were observed in the loaded organic phase from the unheated experiment, and they disappeared when this phase was heated. In addition, 80.4% of the fluorine ions in the loaded organic phase moved to the sodium hydroxide solution. This result suggests that the bubbles observed in the unheated experiments are HF bubbles. All of these experimental results are consistent with our hypothesis. As shown in Figure 1a, a higher temperature and lower pH result in a higher extraction rate of fluorine, which indicates that under lower pH and higher temperature conditions, HF bubbles can more easily form and enter the organic phase.\textsuperscript{35–37}

2.1.7. Reaction Kinetics of the Separation System. To determine the control type of the separation reaction, a series of experiments were carried out in a constant interfacial cell.

![Figure 4](image1.png)  
*Figure 4. (a) Comparison of the FTIR spectra of TBP before and after the reaction. (b) Comparison of the FTIR spectra of SIO before and after the reaction.*

![Figure 5](image2.png)  
*Figure 5. Inverted fluorescence microscopy images of the comparative experiments using TBP (the letters (a–d) correspond to the blank experiment, control experiment, unheated experiment, and heated experiment, respectively).*

![Figure 6](image3.png)  
*Figure 6. Inverted fluorescence microscopy images of the comparative experiments conducted with SIO (the letters (a–d) correspond to the blank experiment, control experiment, unheated experiment, and heated experiment, respectively).*
The volumes of the aqueous and organic phases were constant and equal to 400 mL. The stirring speeds of the aqueous and organic phases were equal, and the interfacial area between the two phases was varied. First, the stirring speed was varied from 0 to 400 rpm to investigate the effect of stirring speed on the fluorne separation rate. The other reaction conditions were set as follows: temperature of 90 °C, pH = 0.46, volume ratio (TBP/SIO v/v) of 7:3, interfacial area of 28.26 cm², and reaction time of 50 min. Then, the interfacial area was varied from 3.14 to 113.04 cm² to investigate the effect of the interfacial area on the fluorne separation rate. The other reaction conditions were set as follows: temperature of 90 °C, pH = 0.46, volume ratio (TBP/SIO v/v) of 7:3, stirring speed of 200 rpm, and reaction time of 50 min. As shown in Figure 7, the separation rate increases with increasing stirring speed. At stirring rates below 200 rpm, the separation rate increased linearly with increasing stirring speed. However, above 200 rpm, the separation speed changes very little, and this is called the dam region. The separation speed increases linearly with increasing interfacial area, and the line does not pass through the origin. Hence, the separation process occurs through hybrid control (diffusion control and interfacial reaction control).30

The results shown in Figures 4 and 7 indicate that the main chemical reactions in the separation process take place in the interfacial area between the two phases instead of in the organic phase. From a kinetic perspective, fluorne ions aggregate in the form of small HF bubbles near the interface of the aqueous phase and organic phase during heat treatment. The small bubbles begin to diffuse from the interface into the TBP layer and the SIO layer. Some HF bubbles aggregate at the interface of TBP and SIO and then begin to diffuse from the interface into the SIO layer; the TBP acts as the surfactant in this process, facilitating diffusion by decreasing the surface tension, and the SIO acts as the adsorbent.38,39 According to Taylor and Zhang et al.,27 the diameter of the HF bubbles at a particular stage can be estimated by eq 10 as

$$\sigma = \frac{r}{2} \rho g h$$

where $A$, $B$, and $C$ are Antoine constants; $T$ is the thermodynamic temperature; $P$ is the saturated vapor pressure in eq 9; $\sigma$ stands for the surface tension; $r$ is the capillary radius; $\rho$ is the density; $g$ is gravitational acceleration; and $h$ is the height of the liquid column in eq 10. The critical temperature can be calculated by combining and solving eqs 9 and 10. By controlling the critical temperature, some behaviors of the HF bubbles in the organic phase can be investigated. According to Taylor and Zhang et al.,27 the diameter of the HF bubbles at a particular stage can be estimated by eq 10 as follows

$$R_b \approx \left[ \frac{\sigma}{g(\rho_l - \rho_g)} \right]^{1/2}$$

where $R_b$ is the diameter of the HF bubble, $\sigma$ is the surface tension, $g$ is the gravitational acceleration, $\rho_l$ is the density of the liquid, and $\rho_g$ is the density of the gas. Based on the report by Shen et al.,27 the number of HF bubbles absorbed in the organic phase can be calculated by the Gibbs adsorption formula using eqs 11 and 12

$$\Gamma = \frac{a}{RT} \left( \frac{\partial \sigma}{\partial \alpha} \right)_T$$

$$\Gamma = -\frac{c}{RT} \frac{\partial \sigma}{\partial c}$$

where $\Gamma$ is the adsorption capacity of the solute, $a$ is the activity of the solute, $\sigma$ is the surface tension, $c$ is the concentration of the solution, $R = 8.31 \times 10^7$ erg mol⁻¹ K⁻¹, and $T$ is the thermodynamic temperature. In general, if the concentration of the solution is not sufficiently large, $\Gamma$ should be calculated by eq 13 instead of eq 12. Experiments were conducted to determine the relative parameters, which could
be used to calculate the theoretical values of $R_b$ according to eq 11. The final results are shown in Table 1. To verify the accuracy of the kinetic theory, the theoretical values and the actual values from the kinetic experiments were compared. The actual values of $R_b$ were obtained as shown in Figure 8. The theoretical values and the actual values were quite similar. Thus, the separation mechanism based on the passage of bubbles through a membrane was confirmed based on the kinetic data.

### 2.2. Scrubbing and Stripping

#### 2.2.1. Determination of the Best Stripping Agent

After scrubbing the loaded organic phase with deionized water, samples of the loaded organic phase were mixed with different stripping agents at the same molar concentration (2.5 mol/L). The reactions were performed with the temperature maintained at 25 °C with a water bath, a stirring speed of 200 rpm, a loaded organic to stripping aqueous phase ratio (O/A) of 1:4, and a reaction time of 1 h. As shown in Table 2, sodium hydroxide solution provided the best fluorine stripping rate (% $S$ of 63.2%).

| Stripping Agent | Fluorine in Raffinate (mg) | Fluorine in Organic (mg) | Stripping Rate (%) |
|-----------------|--------------------------|--------------------------|-------------------|
| NaOH solution   | 6.72                     | 3.92                     | 63.2              |
| H$_2$SO$_4$ solution | 0.03             | 10.61                    | 0.28              |
| KCl solution    | 0.05                     | 10.59                    | 0.47              |

Table 2. Fluorine Stripping Results with Different Stripping Agents under the Same Reaction Conditions

![Figure 8](image)

Figure 8. (a) Actual value of $R_b$ at 75 °C. (b) Actual value of $R_b$ at 90 °C.

![Figure 9](image)

Figure 9. (a) Effects of temperature on % $S$. (b) Effects of [NaOH] and reaction time on % $S$.

provided the best fluorine stripping rate (% $S$ of 63.2%). Its stripping rate was far better than those of H$_2$SO$_4$ solution (% $S$ of 0.28%) and KCl solution (% $S$ of 0.47%). Hence, sodium hydroxide solution was chosen as the best stripping agent.

#### 2.2.2. Effects of Temperature

Temperatures ranging from 15 to 100 °C were tested to investigate the effects of temperature on % $S$. The other reaction parameters were maintained as follows: the concentration of the sodium hydroxide solution [NaOH] was set as 2.5 mol/L, the stirring speed was 200 rpm, the phase ratio (O/A) was 1:4, and the reaction time was 1 h. Figure 9a shows that % $S$ increased at temperatures greater than a critical point (30 min). 30 min, % $S$ was 77.3%, and it reached its maximum value (79.1%) at 120 min. Hence, 30 min was chosen as the reaction time.

### 2.2.3. Effects of the Concentration of the Sodium Hydroxide Solution and the Reaction Time

To determine the optimal concentration for the sodium hydroxide solution, experiments using [NaOH] concentrations between 1 and 12 mol/L were conducted. The other reaction conditions were maintained as follows: the temperature was maintained at room temperature, the stirring speed was 200 rpm, the phase ratio (O/A) was 1:4, and the reaction time was 1 h. As shown in Figure 9b, % $S$ first increased and then decreased as [NaOH] was increased. % $S$ reached its maximum value (79.6%) at 2 mol/L. Hence, 2 mol/L was chosen as the best sodium hydroxide concentration for the stripping solution.

With [NaOH] set at 2 mol/L, the temperature set at room temperature, the stirring speed set at 200 rpm, and the phase ratio (O/A) set at 1:4, experiments using different reaction times ranging from 10 to 120 min were carried out to determine the best reaction time. As shown in Figure 9b, the % $S$ rapidly increased and then gradually increased at times greater than a critical point (30 min). At 30 min, % $S$ was 77.3%, and it reached its maximum value (79.1%) at 120 min. Hence, 30 min was chosen as the reaction time.

#### 2.2.4. Effects of the Volume Ratio of the Loaded Organic Phase to the Stripping Aqueous Phase

Volume ratios of the loaded organic phase to the stripping aqueous phase (O/A) ranging from 1:10 to 2:1 were tested to investigate the effects of the loaded organic phase to stripping aqueous phase ratio on the % $S$. The other conditions were maintained as follows: the temperature was set at room temperature, stirring speed was set at 200 rpm, [NaOH] was set at 2 mol/L, and reaction time was set at 30 min. Figure 10 shows that % $S$ decreased with increasing phase ratio (O/A) and reached a maximum value of 90.1% at 1:10. These results suggest that a lower phase ratio (O/A) will generate a higher % $S$.

![Figure 10](image)

Figure 10. Effect of the phase ratio (O/A) on the % $S$. 

### Table 1. Relevant Parameter Values and Theoretical Values of $R_b$ in the SIO Phase

| $T$ (°C) | $\sigma$ (mN/m) | $\rho_a$ (kg/m$^3$) | $\rho_b$ (kg/m$^3$) | $\eta$ (mPa·s) | $R_b$ (µm) |
|---------|----------------|--------------------|--------------------|----------------|------------|
| 75      | 21.1           | 0.97               | 0.70               | 232            | 2.79       |
| 90      | 20.8           | 0.96               | 0.67               | 193            | 2.67       |

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3. CONCLUSIONS

In this study, an efficient separation method based on a bubble membrane for removing fluorine ions from WPA using a solvent was introduced. TBP was mixed with SIO as the organic phase, and sodium hydroxide solution was chosen as the stripping agent. The best extraction rate (98.4%) was achieved at a temperature of 90 °C, a pH of −0.46, a volume ratio (TBP/SIO v/v) of 7:3, a phase ratio (O/A) of 1:10, a stirring speed of 200 rpm, and a reaction time of 50 min. The best stripping rate (90.1%) was achieved at room temperature, a [NaOH] of 2 mol/L, a phase ratio (O/A) of 1:10, a stirring speed of 200 rpm, and a reaction time of 30 min. The McCabe–Thiele diagram showed that two theoretical stages were needed to completely remove the fluorine. The reaction mechanism and kinetics were also investigated. The separation system functioned under hybrid control (diffusion control and interfacial reaction control). The separation system had a very high selectivity for fluorine ions and almost no impact on the phosphoric acid. The results of this study meet the requirements for the industrial production of WPA. In summary, this separation method based on a bubble membrane not only has substantial commercial advantages, such as high efficiency, high selectivity, low pollutant generation, operational simplicity, and direct extraction capability, but also has a high practical value and broad applicability.

4. EXPERIMENTAL SECTION

4.1. Materials. TBP (C_{12}H_{27}PO_{4}, 99.5%), SIO (C_{3}H_{7}SiO-C_{3}H_{9}SiO-, 99%), sulfuric acid (H_{2}SO_{4}, 95.5%), and phosphoric acid (H_{3}PO_{4}, 95.5%) were purchased from Damao Chemical Reagent Factory in Tianjin, China) and were of analytical grade. Deionized water was used in all experiments. The phosphate ore used in our experiments was obtained from Weng’an, Guizhou Province, China. To determine the trace components in the phosphate ore, the following steps were performed: first, a certain quantity of aqueous solution, and 0.03207 is a mass coefficient. The stripping yield of fluorine (% S) in the loaded organic phase was calculated with the following equation:

\[
C_{100} = \frac{[m_{1} - m_{2}] - (m_{3} - m_{4})}{m} \times 0.03207 \times 100
\]

where \(m_{1}\) is the mass of precipitated quinoline phosphomolybdate and the crucible, \(m_{2}\) is the mass of the crucible, \(m_{3}\) is the mass of the precipitate and the crucible in the blank control experiment, \(m_{4}\) is the mass of the crucible in the blank control experiment, \(m\) is the mass of sample that was obtained from a certain quantity of aqueous solution, and 0.03207 is a mass coefficient. The stripping yield of fluorine (% S) in the loaded organic phase was calculated with the following equation:

\[
\% S = \frac{[F^{-}]_{SL} - [F^{-}]_{AF} \times 100}{[F^{-}]_{SL} - [F^{-}]_{AF} \times 100}
\]

where \([F^{-}]_{SL}\) is the weight of fluorine ions in the strip liquor and \([F^{-}]_{AF}\) and \([F^{-}]_{AF}\) are the same as those in eq 14.

Table 3. Contents of Different Components in the Phosphate Ore (wt %)

| P | Ca | Mg | Fe | Al | S | F | others |
|---|----|----|----|----|---|---|--------|
| 14.26 | 33.65 | 2.41 | 0.95 | 1.14 | 0.59 | 3.68 | 43.32 |

4.2. Apparatus and Analyses. The trace amounts of various components in the phosphate ore were determined by ICP-MS (Agilent 7900, Japan). The content of fluorine in WPA was determined by a potentiometric titrator with a fluorine ion-selective electrode and a saturated calomel electrode (Shanghai Youyi Yoyilab PF-1-02/232-01). The content of phosphoric acid in WPA was determined by the quinoline phosphomolybdate gravimetric method. The functional groups of the organic reagents were analyzed by FTIR spectroscopy (IRAffinity-1, Japan). The loaded organic phase was investigated under an inverted fluorescence microscope (Nikon Ti-s, Japan).

4.3. Procedures. 4.3.1. Fluorine Ion Standard Solution Preparation. The solution of fluorine (0.1 mg/mL) was prepared using NaF (GB/T1264) that had been dried to a constant weight at 120 °C. Then, 1, 2, 3, 5, and 10 mL of the fluorine ion solution were transferred to five separate 50 mL volumetric flasks. Next, the concentration of fluorine in each flask was measured with the ion-specific electrode method. The standard curve of fluorine was prepared from the above experimental data. The equation of the standard curve obtained was \(y = 25.1829x - 171.3418\) with an \(R^2\) of 0.9997. With that standard curve in hand, the content of fluorine in WPA could be accurately calculated in the subsequent experiments.

4.3.2. Feed Solution Preparation. Phosphoric ore powder (10.5 g, < 0.12 mm) was placed in a 100 mL beaker. Deionized water (40 mL) and 8 mL of phosphoric acid were added to the breaker, which was then placed in a 75 °C water bath. The mixture was stirred at 200 rpm for 2 h, and then 6 mL of sulfuric acid was added. After 30 min, the reaction mixture was vacuum-filtered to collect the filtrate. The filtrate was diluted with deionized water to 1000 mL in a volumetric flask. The obtained solution is the feed solution, which had a pH of 1.21 and a fluorine concentration of 320 mg/L, and the leaching rate of fluorine was 82.8%.

4.3.3. Separation Process and Analytical Methods. The feed solution and organic phase were combined in a beaker. The beaker was kept in a constant-temperature water bath and was stirred for a certain time. The mixture was transferred to a separatory funnel and allowed to stand until the mixture fully separated into layers. The aqueous phase was drained from the funnel, and the loaded organic phase was scrubbed and stripped to obtain the strip liquor. The aqueous phase and the strip liquor were gathered for testing. The above steps represent the entire separation process, and the values of all the reaction parameters were set according to the subsequent practical experiments.

The equation for the extraction ratio of fluorine ions (% E) was as follows:

\[
% E = \frac{[F^{-}]_{AF} - [F^{-}]_{AF}}{[F^{-}]_{AF}} \times 100
\]

where \([F^{-}]_{AF}\) and \([F^{-}]_{AF}\) represent the masses of fluorine ions in the aqueous phase before and after the reaction, respectively. The content of phosphoric acid in the aqueous phase was calculated from the following equation:

\[
\frac{[m_{1} - m_{2}] - (m_{3} - m_{4})}{m} \times 0.03207 \times 100
\]

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