An ultrasonic assisted microchannel extraction (UAME) method was developed for the extraction of Fe(III) from wet-process phosphoric acid with di(2-ethylhexyl)phosphoric acid (D2EHPA). The influences of ultrasonic power, extractant concentration, water phase velocity and the ratio of the organic and aqueous phases (O/A) on the extraction rate of Fe(III) were systematically studied. The results showed that the extraction efficiency of Fe(III) reached 91.08%, which was significantly higher than that for ultrasound extraction and microchannel extraction respectively. Response surface methodology was adopted to obtain the optimal conditions and to evaluate the significance of variables affecting the extraction efficiency. The extraction efficiency of Fe(III) reached 92.24% under the following optimum conditions: extractant concentration, 2.1 mol/L; aqueous phase velocity, 0.055 mL/min; ratio of organic phase and aqueous phase, 2.98.

1. Introduction

Phosphoric acid is a basic raw material widely used in many areas such as agricultural feed, fertilizers, detergents, and food additives. Commercial phosphoric acid is commonly manufactured by thermal and wet processes. Wet process phosphoric acid (WPA) is produced by decomposition of phosphate rock with mineral acid which is thus far acknowledged as a more economical, environmental-friendly method of production [1]. However, WPA is accompanied by a number of undesirable impurities including solids and organic matter so that purification is required during downstream production [2-3]. Ferric iron is one of the most troublesome impurities [4]. Removal of iron from WPA is becoming increasingly important for improving the quality of WPA. Up to now, several ways have been developed to remove Fe from WPA, such as precipitation [5], adsorption [6], membrane separation [7], solvent extraction [8], ion-exchange [9] and so on. Nowadays, solvent extraction has been proved to be the most effective way to remove ferric iron from WPA. Unfortunately, there are some drawbacks in the conventional solvent extraction process (CE), such as long extraction time and high organic solvent consumption, which limit the application of solvent extraction in phosphoric acid industry.

As a mass transfer enhancement technology, ultrasound is widely applied in chemical engineering, the food industry, and other fields. The mass transfer process from solute to extractant can be significantly enhanced by increasing the interfacial area between the two phases caused by ultrasonic cavitation [10-12]. As a typical example, Xingbin Lv [13] found that ultrasound-assisted extraction was an effective technique for increasing the extraction ratio.
In recent years, microreactors have increasingly attracted attention in the extraction field because of their high mass transfer efficiency. Microfluidic solvent extraction has been investigated for liquid-liquid extraction of uranium, rare earth elements, cesium, platinum, palladium, lanthanum, silver, and plutonium [14-16]. Leblebici et al. [17] reported that the entire mixing and phase separation process could be completed in 10 – 20 s when a microchannel was used in the solvent extraction of rare earth. Therefore, use of a microchannel is a good way to obtain higher extraction rates in a short time.

So far, studies have shown that ultrasound extraction can increase the extraction rate, as well as microchannel extraction. However, no attempt has been made to combine ultrasound with the use of a microchannel to improve the extraction rate. In order to combine the advantages of ultrasound and a microchannel in solvent extraction, an ultrasonic assisted microchannel extraction method was developed to remove Fe(III) from WPA in this work. The effect of extraction conditions on the extraction efficiency were investigated in detail, and the extraction conditions were optimized using the response surface methodology (RSM).

2. Experimental

2.1 Chemicals and materials

The extractant di(2-ethylhexyl) phosphoric acid (abbreviated as D2EHPA or simply HA) was obtained from Luoyang Zhongda Chemical Co. (Henan, China). Kerosene was provided by Zhongcui Chemical Co. (Sichuan, China). D2EHPA (purity $\geq 95\%$) was used without any further purification, and kerosene was distilled to collect the 200-260 °C fraction (colorless and aliphatic in nature). This was used as the diluent to obtain the desired D2EHPA concentration. The required initial concentration of Fe(III) (0.04 mol/L) was produced by dissolving ferric sulfate in phosphoric acid (P$_2$O$_5$ =20%). Ferric sulfate, phosphoric acid, 1,10-phenanthroline and hydroxylammonium chloride were of analytical reagent and supplied by Kelong Chemical Co. (Sichuan, China).

2.2 Ultrasonic assisted microchannel extraction

Ultrasonic assisted microchannel extraction was carried out using an ultrasonic probe processor (Scientz-IIID, Ningbo scientz biotechnology Co., Ningbo, China), which had a maximum input power of 950 W and an operating frequency of 20 kHz. The extraction apparatus is shown in Figure 1. The ultrasonic probe processor was introduced through a layer of perspex sheet under the microchannel chip. The microchannel, made by ourselves, is shown in Figure 2. It consists of two perspex sheets and a grooved stainless steel plate (microchannel chip). The thickness of the plexiglass was 16 mm, which ensures that the original shape was maintained under pressure. Fourteen holes were opened 8 mm from the two edges for bolt reinforcement. The angle between the two inlet channels is 60 °, the length is 15 mm, the width is 0.75 mm, and the depth is 1 mm. Two-phase fluid passes through the mixing section. The mixing area was a rectangular channel with a length of 2100 mm, a width of 1 mm and a depth of 1 mm, and the total volume of the channel was 2.17 mL.

First, two 20 mL syringes filled with a certain concentration of organic phase and aqueous phase, respectively, were fixed on two microsyringe pumps (LSP01-1A, Longer Pump Co., Baoding, China). Then, the organic and water phases were pumped into the microchannel extractor via two inlets. The organic phase and aqueous phase were intensively mixed in the microchannel under ultrasonic power, and separated in a
separating funnel after passing through the microchannel. The Fe(III) content of the aqueous phase was determined using o-phenanthroline ultraviolet spectrometry.

![Figure 1. Schematic representation of the apparatus for the ultrasound-assisted microchannel extraction.](image1)

**2.3 Experimental design**

First, the effects of extractant concentration, aqueous phase velocity and the ratio of organic phase and aqueous phase (O/A) on the extraction under ultrasonic assisted microchannel treatment were investigated, respectively. The range of variables and the optimal parameters are listed as follows in Table 1.

| Variables                        | Range researched | Optimal parameters |
|----------------------------------|------------------|-------------------|
| Extractant concentration (mol/L) | 1.5-2.5          | 2.5               |
| Aqueous phase velocity (mL/min)  | 0.05-0.15        | 0.05              |
| Effect of O/A                    | 1-3              | 3                 |

Extractant concentration (A), aqueous phase velocity (B) and the ratio of the organic and aqueous phases (C) were investigated to access their interaction effects at three equidistant levels [18]. The variables and
their levels, as well as both coded values and natural values were investigated in this study and displayed in Table 2. Given the consequences of the preliminary single factor, the ranges of three independent variables of the extraction process were controlled. The Box-Behnken design (BBD) included 17 experimental runs and 5 replicates of the central points. The experiments were performed so as to decrease the effect of unexpected variability in the observed response from extraneous factors. Table 3 exhibits the design matrix for the experiments and the regression model proposed for response is given by the following equation:

\[ Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i<j}^{3} \beta_{ij} X_i X_j \]  

(1)

where \( Y \) is the predicted response, \( \beta_0 \), which is (0, 0, 0), is the value of the fixed response at the central point of the experiment. \( \beta_i, \beta_{ii} \) and \( \beta_{ij} \) are the linear, quadratic and interactive coefficients, respectively. \( X_i \) and \( X_j \) are independent variables. Analysis of variance (ANOVA) was carried out to identify the adequacy of the developed model and the statistical significance of the regression coefficients.

Table 2. Variables and their levels employed in the BBD design.

| Variables                        | Symbol | Coded levels | Natural levels |
|----------------------------------|--------|--------------|----------------|
| Extractant concentration(mol/L)  | A      | -1 0 1       | 1.5 2 2.5      |
| Aqueous phase velocity(mL/min)   | B      | 0 -1 1       | 0.05 0.10 0.15 |
| O/A                             | C      | 1 -1 1       | 1 2 3          |

Table 3. The BBD arrangement for the extraction of Fe (III) and the observed responses for extraction yield.

| Run | Extractant concentration (mol/L) | Aqueous phase velocity (mL/min) | O/A | E (%)  |
|-----|---------------------------------|---------------------------------|-----|--------|
| 1   | 2.5                             | 0.15                            | 2   | 59.56  |
| 2   | 2                               | 0.10                            | 2   | 82.70  |
| 3   | 2                               | 0.15                            | 1   | 68.71  |
| 4   | 2.5                             | 0.02                            | 2   | 83.42  |
| 5   | 2                               | 0.10                            | 2   | 82.70  |
| 6   | 1.5                             | 0.15                            | 2   | 59.06  |
| 7   | 1.5                             | 0.05                            | 2   | 62.79  |
| 8   | 0.1                             | 0.10                            | 2   | 82.70  |
| 9   | 0.15                            | 0.15                            | 3   | 85.29  |
| 10  | 0.1                             | 0.10                            | 2   | 82.70  |
| 11  | 0.1                             | 0.10                            | 1   | 71.83  |
| 12  | 0.1                             | 0.10                            | 2   | 82.70  |
| 13  | 0.05                            | 0.05                            | 3   | 91.08  |
| 14  | 0.05                            | 0.05                            | 1   | 71.42  |
| 15  | 0.1                             | 0.10                            | 3   | 74.36  |
| 16  | 0.1                             | 0.10                            | 1   | 55.37  |
| 17  | 0.1                             | 0.10                            | 3   | 62.45  |
2.4 Determination of Fe(III) in solution

The concentration of Fe(III) in the aqueous phase was determined by the 1,10-phenanthroline method after reduction to Fe(II) with hydroxylammonium chloride. The standard curve method was used for the quantification of iron (the standard equation \( C = 0.19627 \cdot A + 0.00813, R^2=0.99943 \), where \( C \) is the concentration of the iron ion, \( A \) is the solution absorbance, and \( R \) is the correlation coefficient). In all the experiments, each data point represents a mean value of three independent measurements. The extraction yield was calculated based on the following equation:

\[
E(\%) = \frac{C_0V_0 - C_eV_e}{C_0V_0} \times 100\%
\]  

(2)

where \( E \) is the extraction efficiency, \( C_0 \) is the initial concentration of Fe(III) in the aqueous phase, \( C_e \) is the concentration of Fe(III) remaining in the aqueous phase, and \( V_0 \) and \( V_e \) are the volumes of the initial aqueous phase and raffinate phase, respectively.

3. Results and Discussion

3.1 Effect of ultrasonic power on the extraction efficiency of Fe(III)

The effect of varying ultrasonic power on the extraction of Fe(III) from WPA has been studied. Other fixed conditions were as follows: concentration of D2EHPA, 2 mol/L; aqueous phase velocity, 0.05 mL/min; concentration of Fe(III), 0.04 mol/L; O/A, 3:1. From the results illustrated in Figure 3, the extraction yields increase sharply with the ultrasonic power from 10 to 85 W. After that, the extraction yields remain unchanged. Subsequent experiments were therefore conducted in a range of 78 to 85 W.

3.2 Effect of extractant concentration on the extraction process

The effect of varying the concentration of D2EHPA for the extraction of Fe(III) from WPA has been studied. Other fixed conditions were as follows: ultrasonic power, 78-85 W; aqueous phase velocity, 0.1
mL/min; O/A, 1:1; concentration of Fe(III), 0.04 mol/L. From the results illustrated in Figure 4, the extraction yields increase significantly with the extractant concentration from 0.5 to 2 mol/L. After that, the rate of increase decreases and only a little increase was observed from 2 to 2.5 mol/L. This was probably because the higher extractant concentration caused a greater concentration difference, which accelerated the mass transfer and facilitates the iron ion diffusion into the organic phase. Therefore, 2 mol/L was used as the optimal extractant concentration in the following extraction experiments.

In addition, the results showed that the extraction efficiency of the ultrasonic assisted microchannel extraction was greater than the ultrasound-assisted method. On the other hand, the difference between the extraction yields of the two extraction techniques increased with the increasing concentration of D2EHPA in this work. This phenomenon indicated that the greater the concentration of D2EHPA used, the better was the effect of the ultrasonic assisted microchannel extraction technology.

![Figure 4. Effect of extractant concentration on the extraction efficiency of Fe(III).](image)

**3.3 Effect of aqueous phase velocity on the extraction process**

The relationship between flow rate with residence time and extraction efficiency are respectively shown in Figure 5 and Figure 6. The ultrasonic assisted microchannel extraction experiments were carried out using 2 mol/L D2EHPA at a power of 78 – 85 W and a temperature of 20°C. Comparing the two extraction techniques at different aqueous phase velocity, it was found that the extraction yield decreased sharply from 47.05% to 18.7% with aqueous phase velocity from 0.05 mL/min to 0.4 mL/min, while the extraction yield decreased slowly with increasing aqueous phase velocity. When the aqueous phase velocity was 1.0 mL/min, the extraction yield reached 50.55%. This was better than the extraction yield at the best aqueous phase velocity without ultrasound. Above all, the ultrasonic assisted microchannel method markedly intensified the extraction.
3.4 Effect of O/A on the extraction process.

The effect of O/A on the residence time and extraction yield of Fe(III) from WPA with 2 mol/L D2EHPA at an aqueous phase velocity of 0.05 mL/min has been investigated and shown in Figure 7 and Figure 8. From the figure, it was found that the extraction yield with the help of ultrasonic power increased faster than without ultrasonic power. This showed that the cavitation effect of ultrasound can significantly enhance the mass transfer between the two phases, eliminate the blocking layer of the intersecting interface and obviously improve the extraction effect.
3.5 Optimization of extraction conditions

Obtaining the optimal conditions for ultrasonic assisted microchannel extraction of Fe(III) from WPA will be beneficial in the development of the UAME process in industry. Based on the single factor investigation, the optimal levels of the significant factors (extraction concentration, aqueous phase velocity, O/A) and their interaction effects on the extraction yields were explored by a Box-Behnken design (BBD) of the response surface method (RSM). The experimental conditions and the corresponding experimental data are displayed in Table 4. The predicted model is described by

\[ Y = 0.83 + 0.062 A - 0.045 B + 0.057 C - 0.050 AB - 0.011 AC - 0.0077 BC - 0.15 A^2 - 0.017 B^2 - 0.019 C^2 \] (3)

where \( Y \) is the predicted extraction yield; \( A \), \( B \) and \( C \) are extractant concentration, aqueous phase velocity, and O/A, respectively. Positive coefficients indicate a favorable effect on extraction yield, while negative
coefficients indicate an unfavorable effect on extraction yield. Thus, from Eq. (3), it is demonstrated that there was a positive influence caused by both the extractant concentration and O/A on extraction yield. However, the effect of water phase velocity was unfavorable, which corresponded with the results of the previous single factor experiment.

| source                     | Sum of squares | df | Mean square | F Value | p-value | Prob>F |
|---------------------------|----------------|----|-------------|---------|---------|--------|
| Model                     | 0.18           | 9  | 0.020       | 10.07   | 0.0030  |        |
| A-concentrate             | 0.031          | 1  | 0.031       | 15.23   | 0.0059  |        |
| B-aqueous phase velocity  | 0.016          | 1  | 0.016       | 8.10    | 0.0248  |        |
| C-O/A                     | 0.026          | 1  | 0.026       | 13.07   | 0.0086  |        |
| AB                        | 0.010          | 1  | 0.010       | 5.04    | 0.0597  |        |
| AC                        | 0.0005176      | 1  | 0.0005176   | 0.26    | 0.6275  |        |
| BC                        | 0.0002372      | 1  | 0.0002372   | 0.12    | 0.7414  |        |
| A²                        | 0.092          | 1  | 0.092       | 45.91   | 0.0003  |        |
| B²                        | 0.001195       | 1  | 0.001195    | 0.59    | 0.4659  |        |
| C²                        | 0.001504       | 1  | 0.001504    | 0.75    | 0.4158  |        |
| Residual                  | 0.014          | 7  | 0.002011    |         |         |        |
| Lack of Fit               | 0.014          | 3  | 0.004692    |         |         |        |
| Pure Error                | 0.000          | 4  | 0.000       |         |         |        |
| Cor Total                 | 0.20           | 16 |             |         |         |        |

The model F-value of 10.07 implies the model is significant. There is only a 0.30% chance that a “Model F-value” this large could occur due to disturbance. Values of “Prob>F” less than 0.0500 indicate that the model terms are significant. In this case, A, B, C, A² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Figure 9. Response surface plot showing the effect of extractant concentration and aqueous phase velocity on the extraction yield of Fe(III) from WPA.
Figure 10. Response surface plot showing the effect of extractant concentration and O/A on the extraction yield of Fe(III) from WPA.

Figure 11. Response surface plot showing the effect of aqueous phase velocity and O/A on the extraction yield of Fe(III) from WPA.

From the analysis using Eq. (3), the optimal extraction conditions using the model were as follows: extraction concentration, 2.1 mol/L; aqueous phase velocity, 0.055 mol/L; O/A, 2.98. Under the optimal extraction conditions, the model predicts a maximum extraction yield of 91.15%. To verify the results of the BBD experiments as well as to confirm the reliability of this model, experiments were made with the above optimized extraction conditions. A mean value of 92.24% was obtained, slightly higher than the predicted
value. The consistency of the experiment result and the predicted value proved the utility of this model, also further explained that optimizing the RSM parameters was very successful.

| Optimum conditions | Extraction yield (%) |
|-------------------|----------------------|
| Extractant concentration | Aqueous phase velocity | O/A | Predicted value | Experimental value |
| 2.1 | 0.055 | 2.98 | 91.15 | 92.24 |

a Mean ± SD (n = 3)

4. Conclusion

In this study, an ultrasonic assisted microchannel extraction process for the extraction of Fe(III) ions from wet-process phosphoric acid was developed. The effects of various factors, including the extractant concentration, aqueous phase velocity and the ratio of the organic and aqueous phases were systematically investigated. The extraction rate increased markedly comparing with the traditional extraction method. Based on the results of single factor experiments, a Box-Behnken design for response surface methodology was applied to determine the optimal experimental conditions. The ultrasonic assisted microchannel extraction efficiency of Fe(III) reached 92.24% under the following optimum conditions: extractant concentration, 2.1 mol/L; aqueous phase velocity, 0.055 mL/min; O/A, 2.98. On the basis of the ANOVA statistical analysis, the extractant concentration for the ultrasonic assisted microchannel extraction was the most significant parameter, following by O/A and aqueous phase velocity. As the ultrasonic assisted microchannel extraction increases mass transfer for any two phase systems, the ultrasonic assisted microchannel method could be easily extended to other extraction systems for higher efficiency.

References

1) X. Li, J. Li, Y. Jin, M. Chen, D. Y. Feng, Y. H. Guo, J. Serb. Chem. Soc., 82, 579–592 (2017).
2) J. Luo, J. Li, K. Zhou, Y. Jin, Korean J. Chem. Eng., 28, 1105-1109 (2011).
3) L. Monser, M. B. Amor, M. Ksibi, Chem. Eng. Proc., 38, 267-271 (1999).
4) A. A. M. Daifullah, N. S. Awwad, S. A. El-Reefy, Chem. Eng. Process, 43, 193-201 (2004).
5) A. Orabi, E.El-Sheikh, M.Hassanin, M.E. Kady, M. Abdel, Khalek, A. Mowafy, Miner. Eng., 122, 113-121 (2018).
6) X. H. Li, S. D. Deng, H. Fu, J. Appl. Electrochem., 41, 507-517 (2011).
7) L. C. Zhang, Q. L. Chen, C, Kang, X, Ma, Z. L. Yang, J. Rare. Earth., 34, 717-723 (2016).
8) S. X. Wu, L. S. Wang, P. Zhang, et al., Hydrometallurgy, 175, 109-116 (2018).
9) M. B. C. Elleuch, M. B. Amor, G. Pourcelly, Sep. Purif. Technol., 51, 285-290 (2006).
10) M. Kauer, V. Belova-Magri, C. Cairos, G. Linka, R. Mettin, Ultrasound. Sonochem., 48, 39-50 (2018).
11) B. Pestic, T. Zhou, J. Miner. Met. Mater. Soc., 41, 42-45 (1989).
12) F. Flisak, A. Perna, Ultrasonics, 15, 27-29 (1997).
13) X. B. Lv, D. Liu, J. Y. Ji, J. J. Chen, T. Yang, Solvent. Extr. Res. Dev., Jpn., 24, 11-22 (2017).
14) A. A. Fereydani, Z. Azizi, J. Therm. Anal. Calorim., 133, 945-950 (2018).
15) M. Tokeshi, T. Minagawa, T. Kitamori, Anal. Chem., 72, 1711-1714 (2000).
16) O. Tamagawa, A. Muto, Chem. Eng. J., 167, 700-704 (2011).
17) M. Maeki, Y. Hatanaka, K. Yamashita, M. Miyazaki, K. Ohto, *Solvent. Extr. Res. Dev., Jpn.*, **21**, 77-82 (2014).

18) S. Amiri, A. Shakeri, M. R. Sohrabi, S. Khalajzadeh, E. Ghasemi, *Food. Chem.*, **271**, 762-766 (2019).