Experimental Study on Ion Exchange Membrane Coupled Electrolytic Electrodialysis Purification and Concentration of Wet Phosphoric Acid

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Abstract: Wet-process phosphoric acid is a mainstream production technology with low cost and low energy consumption, but impurities including Fe^{3+}, Ca^{2+} and Mg^{2+} in crude acid limit its high-end applications. Traditional purification processes are long with high reagent consumption, and cannot realize purification and concentration simultaneously. Using a two-chamber electrolytic electrodialysis device, this study investigated the effects of static diffusion, current density and temperature on metal ion removal, phosphoric acid concentration and leakage rate with simulated wet-process phosphoric acid. Results show that static diffusion without electric field presents very low removal efficiency, and electric field driving is essential for effective separation. Within 10~30 $mA \cdot cm^{-2}$, the ion removal rate and concentration efficiency rise obviously with current density, and the concentration rate peaks at 15.8% under 30 $mA \cdot cm^{-2}$. Higher temperature promotes ion migration but aggravates phosphoric acid leakage and reduces concentration efficiency. This technology can efficiently purify and concentrate dilute wet-process phosphoric acid (≤30%) in a green and low-carbon way, providing a new approach for phosphoric acid purification.

***Keywords*:** wet phosphoric acid; electrolytic electrodialysis; ion exchange membrane; metal ion removal; Phosphoric acid concentration

1. Introduction

Phosphoric acid is the core raw material of phosphorus chemical industry and is widely used in agriculture, food, medicine, electronics and other fields. In the context of "dual carbon", "dual control of energy consumption" and tightening of environmental protection policies, the environmental protection advantages of wet phosphoric acid have been highlighted, and have been supported by national policies, and the "Guiding Opinions on Promoting the High-quality Development of the Petrochemical and Chemical Industry in the 14th Five-Year Plan" clearly proposes to improve the utilization rate of phosphate rock1[1] and promote the development of phosphorus chemical industry in the direction of green, low-carbon, high-end and integration[2].

Electrodialysis technology is regarded as a prospective technology for wet phosphoric acid purification, and many researchers at home and abroad have explored it. He Bingbing[3] et al. carried out pilot tests using plate-frame diffusion dialysis membrane modules, which confirmed that most of the cationic impurities could be removed. Zheng Xiujun[4] introduced ultrafiltration and nanofiltration in the solvent extraction process to effectively remove metal ions and some organic matter; Luo Jilin[5] et al. combined electrodialysis and reverse osmosis processes to successfully prepare electronic-grade high-purity phosphoric acid. Liu Dehui[6] theoretical analysis showed that electrolytic electrodialysis could remove anions and cations, but the removal rate of iron ions was low, and the low current density and low phosphoric acid concentration were more conducive to purification and concentration. Abroad, Touaibia[7] et al. used a specific anion exchange membrane test to achieve a 26-hour metal ion removal rate of 95% at 4 mol/L phosphoric acid concentration, but there was proton leakage. Elleuch[8] et al. treated 12 mol/L wet phosphoric acid with electrodeionization, and the removal rate of most metal ions was 30%, and the iron ions were only 16%. Studies by Machorro[9], Ottosen[10], Loest[11], and others further confirm the effectiveness of electrodialysis.

Ion exchange membrane electrolytic electrodialysis is in line with the green concept, but there are still technical bottlenecks. Based on this, this paper takes simulated wet phosphoric acid as the research object, carries out static diffusion test, current density gradient test and temperature gradient test to systematically analyze the effects of electric field diffusion, current density and temperature on the removal rate of metal ions, phosphoric acid concentration rate and phosphoric acid leakage rate, clarifies the optimal operation interval, reveals the parameter influence mechanism, and provides basic data and theoretical basis for the industrial application of ion exchange membrane coupled electrolytic electrodialysis technology to purify wet phosphoric acid.

2. Experimental part

2.1 Materials and Reagents

Simulated wet-process phosphoric acid solution was prepared with analytical-grade reagents, including 85 wt% phosphoric acid, anhydrous magnesium sulfate, ferric chloride, calcium chloride dihydrate, and ultrapure water. All reagents were used as received. A CEM8040 homogeneous cation exchange membrane was adopted, which was based on styrene-divinylbenzene grafted with sulfonic acid groups, featuring good ion selectivity, mechanical strength, and chemical stability suitable for cation separation in acidic media. Ir-Ta coated titanium mesh anode and pure titanium mesh cathode were used for their high corrosion resistance and catalytic activity, enabling stable operation in acidic environments.

2.2 Apparatus and Equipment

A two-compartment electrolytic electrodialysis cell was employed, consisting of an anode compartment, cathode compartment, ion exchange membrane, electrodes, DC power supply, and thermostatic water bath. The effective membrane area was 110.25 cm^2, electrode area 87 cm^2, and effective volume of both compartments 200 mL. Key instruments included ICP-OES for determining Fe^{3+}, Ca^{2+}, Mg^{2+} concentrations, conductivity meter, pH meter, electronic balance, stabilized DC power supply, and thermostatic water bath.

2.3 Preparation of Simulated Feed Solution

Simulated solutions were prepared according to practical impurity composition, with phosphoric acid concentration ranging from 5% to 30% and Fe^{3+}, Ca^{2+}, Mg^{2+} all at 500 mg/kg. All solutions were prepared with ultrapure water to avoid interference.

2.4 Experimental Methods

Batch operation was adopted: simulated phosphoric acid was added to the anode compartment and ultrapure water to the cathode compartment. Three sets of experiments were conducted:

(1) Static diffusion: No electric field applied; diffusion lasted 8 h with hourly sampling.

(2) Current density: At 25 ℃, current densities of 10, 20, 30, 40, 50 $mA \cdot cm^{-2}$ were tested for 8 h.

(3) Temperature: At 30 $mA \cdot cm^{-2}$, temperatures of 10, 20, 30, 40, 50 ℃ were tested for 8 h.

2.5 Analysis and Data Processing

Metal ion concentrations were measured by ICP-OES, and phosphoric acid concentration by ion chromatography. Ion removal rate, phosphoric acid concentration rate, and leakage rate were calculated accordingly.

3. Results and Discussion

3.1 Effect of static diffusion on metal ion removal

In the absence of an electric field, ions only cross the membrane via concentration gradient diffusion. Static diffusion tests over 8 hours showed extremely low metal ion removal efficiency, with removal rates of Fe^{3+}, Ca^{2+}, and Mg^{2+} being only 1.1%, 5.2%, and 5.7%, respectively.

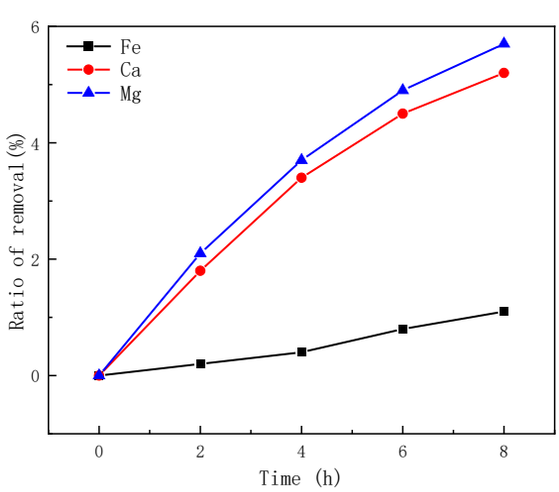

Figure 1. Relationship of metal ion removal rate in wet phosphoric acid without current with time

There are two main reasons: first, without electric field driving, ion migration relies merely on thermal motion and concentration difference with very weak driving force; second, Fe^{3+} tends to form stable complexes with phosphate radicals, resulting in large hydration radius and high diffusion resistance. The results prove that static diffusion cannot effectively purify wet-process phosphoric acid, and electric field driving is a necessary prerequisite for efficient metal ion removal, providing fundamental experimental support for the application of electrolytic electrodialysis.

3.2 Effect of current density on purification and concentration effect

Current density is the key operating parameter in electrolytic electrodialysis, which directly determines the driving force of ion migration and significantly affects metal ion removal, phosphoric acid concentration and system energy consumption. At 25 °C, within the range of 10–30 mA·cm^{-2}, the increase of current density enhances the electric field driving force and obviously improves the removal rates of metal ions: Mg^{2+} from 38.3% to 88.1%, Ca^{2+} from 34.5% to 87.2%, and Fe^{3+} from 7.8% to 52.4%. The removal order is $Mg^{2+} > Ca^{2+} > Fe^{3+}$, which is related to ionic hydration radius, charge number and complexation. Fe^{3+} is the most difficult to migrate due to stable complexes.

The concentration rate of phosphoric acid first increases and then decreases, reaching a peak of 15.8% at 30 mA·cm^{-2}. Beyond this value, concentration polarization and phosphate leakage intensify, resulting in lower concentration efficiency, higher energy consumption and severer membrane damage. Comprehensively, 30 mA·cm^{-2} is the optimal current density. The specific data are shown in Figure 2.

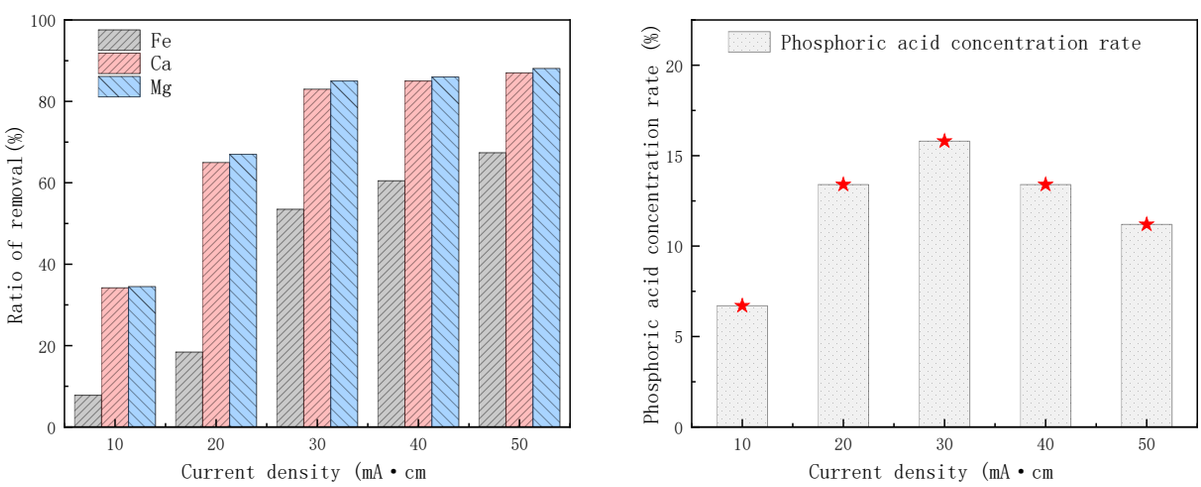

Figure 2. Changes in ion removal rate and phosphoric acid concentration rate with current density

3.3 Effect of temperature on purification and concentration effect

Temperature has a dual effect on the separation performance of electrolytic electrodialysis by changing the viscosity of the solution, the rate of ion diffusion, the structure of the membrane and the resistance of ion migration. Under the condition of current density of 30 mA·cm^{-2}, Fig. 4 shows that the temperature increase has a promoting effect on ion removal: with the increase of temperature from 10 °C to 60 °C, the viscosity of the solution decreases, the ion migration rate accelerates, the concentration polarization is alleviated, and the removal rates of Mg^{2+}, Ca^{2+}, and Fe^{3+} continue to increase.

However, warming has a significant negative impact on phosphate concentration. The increase of temperature will change the migration law of water in the membrane and reduce the directional concentration efficiency, as shown in Fig. 5, the phosphoric acid concentration rate decreases from 16.3% to 12.7%. More importantly, temperature directly affects the structural stability of the ion exchange membrane, 60 °C is the upper limit of the safe operating temperature of the CEM8040 membrane, in the actual operation process, the temperature should be controlled in the range of 50~60 °C, which can not only ensure a high impurity removal rate, but also avoid membrane thermal damage and maintain a good phosphoric acid concentration effect. The specific data are shown in Figure 3.

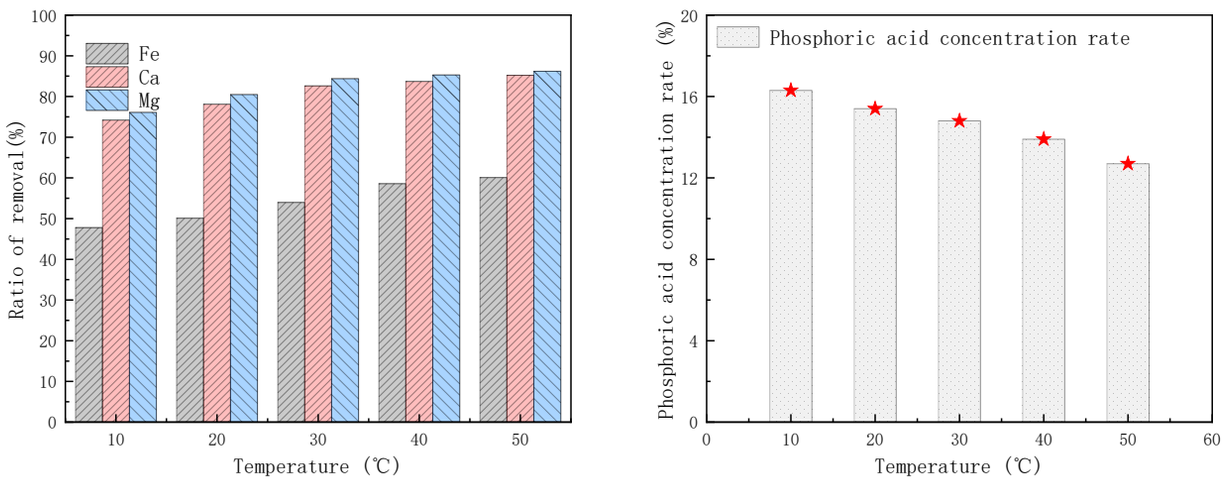

Figure 3. Changes in ion removal rate and phosphoric acid concentration rate with current density

4. Conclusions

In this paper, the effects of static diffusion behavior, current density and temperature on metal ion removal and phosphoric acid concentration are systematically studied by simulating wet phosphoric acid solution and using ion exchange membrane coupled electrolytic electrodialysis technology, and the following main conclusions are drawn:

(1) Static diffusion without electric field cannot remove metal ions efficiently, and electric field driving is necessary for high-performance separation.

(2) Within 10–30 mA·cm^{-2}, higher current density improves purification and concentration; 30 mA·cm^{-2} is optimal with a peak concentration rate of 15.8%.

(3) Rising temperature promotes ion removal but aggravates phosphoric acid leakage. The safe temperature is 60 ℃, and 50–60 ℃ is recommended.

(4) The removal selectivity follows $Mg^{2+} > Ca^{2+} > Fe^{3+}$, determined by ionic radius, charge and complexation.

(5) Electrolytic electrodialysis realizes simultaneous purification and concentration of phosphoric acid, featuring short process, green and low-carbon merits, with good industrial prospects.

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