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Solvent extraction of calcium ion from cation-exchange resin regeneration wastewater using D2EHPA and saponified D2EHPA

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ABSTRACT

Solvent extraction experiments of Ca^{2+} with D2EHPA and 15% saponified D2EHPA from cation-exchange resin regeneration wastewater have been performed. Compared with the extraction efficiency (E) of Ca^{2+} with D2EHPA, the use of 15% saponified D2EHPA significantly increases the extraction efficiency (E) of Ca^{2+}. In this work, a systematic study on the extraction of Ca^{2+} from cation-exchange resin regeneration wastewater using saponified D2EHPA has been carried out. To study the extraction efficiency and advantages of the method in the removal of Ca^{2+}, various parameters such as saponification ratio of D2EHPA, D2EHPA mass fraction, reaction temperature, phase mass ratio, initial pH of wastewater, transfer-speed, and transfer-time are studied and optimized. The results show that Ca^{2+} in wastewater can be effectively removed by saponified D2EHPA. An extraction efficiency of more than 99.9% is attained at the optimized parameters and the cation-exchange resin regeneration waste-water can be discharged directly by two levels of extraction, and it meets the Chinese National Emission Standards.

Keywords: D2EHPA; Saponified D2EHPA; Ca^{2+} from regeneration wastewater; Extraction

1. Introduction

Cation-exchange resin has a wide range of application in the preparation of soft water, pharmaceutical, metallurgical, and chemical separation areas. When the cation exchange equilibrium of the resin is reached, the regeneration process of it will emit large quantities of wastewater, which mainly consist of calcium and magnesium ions. So, the wastewater with high mineralization and conductivity can accelerate the electrochemical reaction, which can accelerate corrosion of the equipment and may result in land salinization, soil compaction, crop rot et al. [1]. Studies have shown that the wastewater also has a great impact on groundwater quality [2]. The removal and recovery of metal ions from cation-exchange resin regeneration wastewater attracts increasing interest because of the growing importance of the environment protection.

As an effective extractant, D2EHPA has been widely used for the extraction of Ni(II) [3], Co(II) [3,4], Cd(II) [5], Zn(II) [5,6], Fe(III) [6], and Cu(II) [7]. So, the D2EHPA is employed as an extractant to remove calcium ion from cation-exchange resin regeneration wastewater.

In the solvent extraction of metals with acidic extractants, the hydrogen ion is liberated during the process, which can adversely affect the metal

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extraction reaction. To overcome this problem, the use of the acidic extractants saponified with NaOH was tried [8–10]. Partial saponification was preferred to avoid gel formation and the solubility of the saponified extractant in the aqueous phase. So, the saponified D2EHPA is introduced to remove metals from cation-exchange resin regeneration wastewater.

Since the cation-exchange resin regeneration wastewater mainly consists of calcium and magnesium ions, solvent extraction experiments of Ca^{2+} with D2EHPA and 15% saponified D2EHPA from cation-exchange resin regeneration wastewater have been performed. The aim of this work is to study the effects of various factors on the extraction of Ca^{2+} using D2EHPA and saponified D2EHPA.

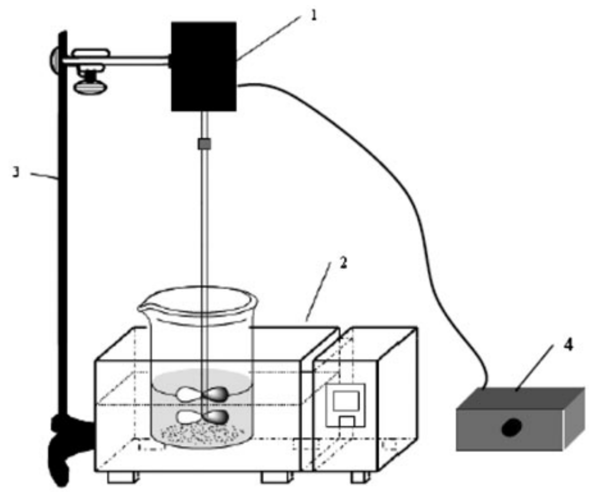

Fig. 1. The extraction experimental configuration (1) agitator; (2) thermostatically controlled water bath; (3) holder; and (4) agitator controller.

2. Material and methods

2.1. Materials and equipment

The diluent used in this work is kerosene produced by Luo yang Zhongda Chemical Company (China). D2EHPA are employed as an extractant produced by Luo yang Zhongda Chemical Company (China) (AR grade). $CaCl_2$ is purchased from Ke Long Chemical Company (China) (AR grade). NaOH is purchased from Ke Long Chemical Company (China) (AR grade). Deionized water is produced by Aquapro making-water machine (ABZ1-1001-P) in our laboratory. The solution's pH is measured with a pH meter from Shanghai Precision & Scientific Instrument Co., Ltd.

2.2. Extraction procedure and parameters that could affect the extraction process

Saponified D2EHPA is prepared by adding a stoichiometric amount of a concentrated NaOH solution to the extractant in kerosene and by stirring the mixture for 36 h to form a single phase. The saponification percentage is determined by using titration method with NaOH solution. In the solvent extraction experiments with the saponified D2EHPA, the degree of the saponification is kept at 15%.

The generator is composed of a 500 mL beaker containing aqueous solution with 600 mg/L Ca^{2+} concentration, organic solvent, and a central stirrer as shown in Fig. 1. The beaker is initially filled with 100 mL aqueous solution and 50 mL organic solvent, and agitated at 350 r/min with 25 min of reaction time.

In order to study calcium ion removal efficiency and advantages of the extraction process, various parameters that could affect the process must be optimized. The parameters to be optimized are the saponification ratio of D2EHPA, D2EHPA mass fraction, reaction temperature, phase mass ratio (A/O), initial pH of wastewater, transfer speed, and reaction time.

2.3. Analysis

The concentration of calcium ion is determined by atomic absorption spectrophotometry (GF3000), and that of Ca^{2+} in the organic phase is calculated using a mass balance equation.

3. Results and discussion

3.1. Effect of saponification ratio of D2EHPA

The extractant D2EHPA is a dimer as H_2A_2. With the increasing saponification ratio of D2EHPA, the dimer molecule H_2A_2 is broken up, and the extractant compound is likely to be NaA. Obviously, there are more free extractants participating in the extraction reaction by saponificated with NaOH. So, increasing the saponification ratio of D2EHPA will increase the extraction efficiency (E). However, when the saponification ratio of D2EHPA increases to reach a certain value, which is 15% from Fig. 2, the extraction efficiency (E) remains almost unchanged, this is because the extraction reaction reaches equilibrium.

3.2. Effect of extractant mass fraction (%)

The D2EHPA mass fraction (%) has a great impact on the extraction efficiency (E). With the D2EHPA mass fraction (%) increasing, as can be seen from

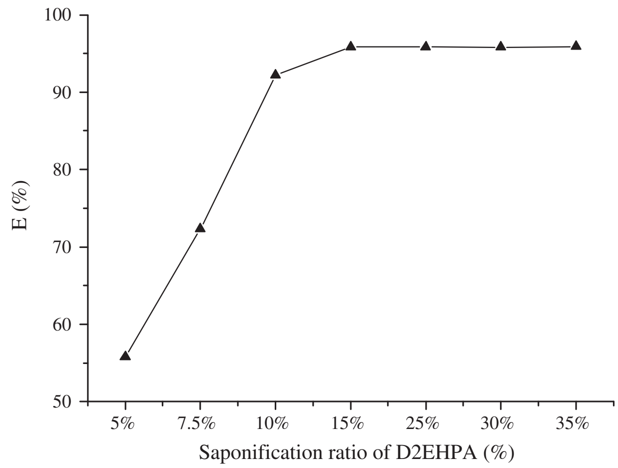

Fig. 2. The extraction efficiency (E) versus the saponification ratio of D2EHPA. Diluent: kerosene; concentration of NaOH: 6 mol/l; D2EHPA mass fraction (%): 30%; phase ratio (A/O): 2:1; transfer speed: 350 r/min; initial Ca^{2+} concentration: 600 mg/L; initial pH of regeneration wastewater: 6; reaction time: 25 min; and reaction temperature: 30℃.

Fig. 3, the extraction efficiency (E) also increases fastly. As Xie [11] reported that the increasing D2EHPA concentration in solvent phase will increase the amount of extractant and the numbers of free extractants participating in the extraction reaction.

What is more surprising is the effect of saponification D2EHPA on extraction efficiency (E), which shows the same trend as D2EHPA. Yet saponified D2EHPA does increase the extraction efficiency (E) considerably, the extraction efficiency (E) of more than 95.8% with an increase in the saponification of D2EHPA up to 15%, far higher than the extraction efficiency (E) with non-saponificated D2EHPA.This is because there are more free extractants taking participate in the extraction reaction with the increasing saponification D2EHPA.

3.3. Effect of phase ratio (A/O)

The phase ratio (A/O) has a significant effect on extraction efficiency (E) and entrainment. This effect is studied by changing the phase ratio (A/O) from 1:1 to 5:1. The results plotted in Fig. 4 clearly show that the phase ratio of 1:1 gives the highest extraction of Ca^{2+}. The reason for this phenomenon is that the fixed free extractants taking participate in the extraction reaction; increasing phase ratio in the extraction process will enhance the amount of Ca^{2+}. So, the extraction efficiency (E) decreases with the increasing phase ratio. Xie [11] also reported the same trend.

3.4. Effect of reaction time

The results of the experiments are plotted in Fig. 5. The figure indicates that the extraction efficiency (E) of Ca^{2+} is improved with the increasing reaction time. However, it is also observed that the extraction

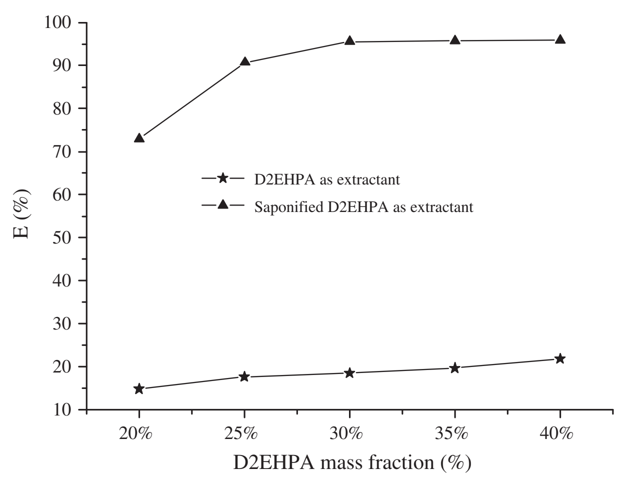

Fig. 3. The extraction efficiency (E) versus the D2EHPA mass fraction (%). Diluent: kerosene; concentration of NaOH: 6 mol/l; saponification ratio of D2EHPA:15%; phase ratio (A/O): 2:1; transfer speed: 350 r/min; initial Ca^{2+} concentration: 600 mg/L; initial pH of regeneration wastewater: 6; reaction time: 25 min; and reaction temperature: 30℃.

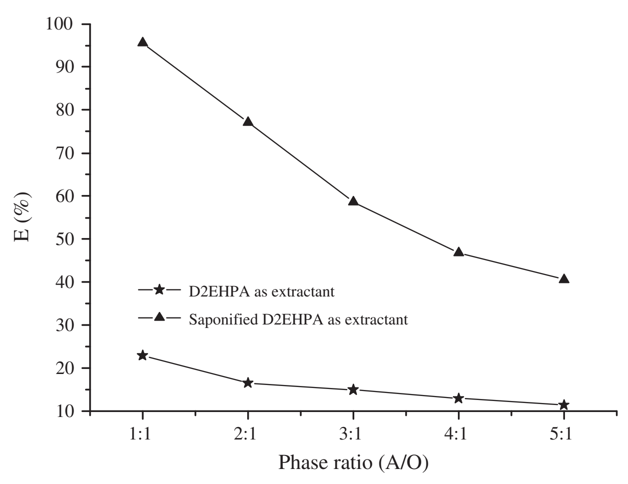

Fig. 4. The extraction efficiency (E) versus the phase ratio (A/O). Diluent: kerosene; concentration of NaOH: 6 mol/l; saponification ratio of D2EHPA:15%; D2EHPA mass fraction (%): 30%; transfer speed: 350 r/min; initial Ca^{2+} concentration: 600 mg/L; initial pH of regeneration wastewater: 6; reaction time: 25 min; and reaction temperature: 30℃.

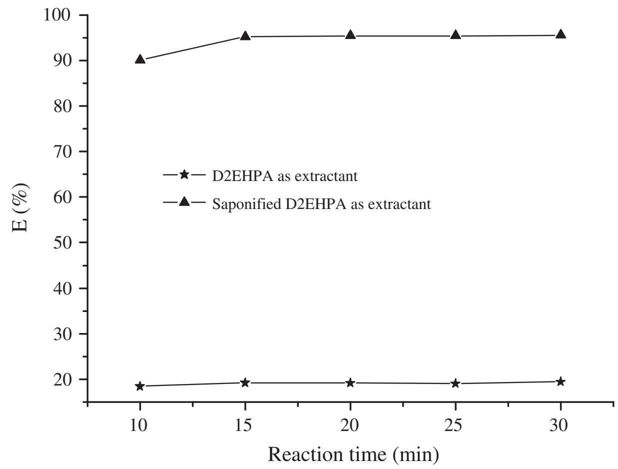

Fig. 5. The extraction efficiency (E) versus the reaction time. Diluent: kerosene; concentration of NaOH: 6 mol/l; D2EHPA mass fraction (%): 30%; saponification ratio of D2EHPA:15%; Phase ratio (A/O): 2:1; transfer speed: 350 r/min; initial Ca^{2+} concentration: 600 mg/L; initial pH of regeneration wastewater: 6; and reaction temperature: 30℃.

efficiency (E) does not increase greatly with the increasing reaction time when the reaction time points to 15 min. This means that the equilibrium time for the extraction needs at least 15 min.

3.5. Effect of initial pH of regeneration wastewater

D2EHPA (HA) contains dissociable H^+, so the mechanism of extracting Ca^{2+} with HA perhaps accords with the cation exchange. In general, the extraction reaction can be described as follows:

$$nq\mathrm{Ca}^{2+}_{(\mathrm{a})} + \frac{q(s+2n)}{m}(\mathrm{HA})_{m(o)} \rightarrow (\mathrm{Ca}_n\mathrm{A}_{2n}\cdot \mathrm{sHA})_{q(o)} + 2nq\mathrm{H}^{+}_{(\mathrm{a})}$$

$$K = \frac{[(\mathrm{Ca}_n\mathrm{A}_{2n}\cdot \mathrm{sHA})_q]_{(o)}[H^+]^{2nq}_{(a)}}{[\mathrm{Ca}^{2+}]^{nq}_{(a)}[(\mathrm{HA})_m]_{(o)}^{\frac{q(s+2n)}{m}}} \quad (1)$$

Here, m is the aggregation number of D2EHPA.

Then, the equilibrium constant K is given as

$$\left[(\mathrm{Ca}_n A_{2n}\cdot \mathrm{sHA})_q\right]_{(o)} = \frac{1}{qn}[\mathrm{Ca}^{2+}]_{(o)} \quad (2)$$

And the distribution ratio of Ca^{2+} can be expressed as

$$D = \frac{[\mathrm{Ca}^{2+}]_{(o)}}{[\mathrm{Ca}^{2+}]_{(a)}} \quad (3)$$

$$\log D = \log K + 2nqpH + \log nq + \frac{q(s+2n)}{m}\log[(\mathrm{HA})_m]_{(o)} + (nq-1)\log[\mathrm{Ca}^{2+}]_a \quad (4)$$

The plot of $\log D$-pH as shown in Fig. 6 is a straight line with the slope of approximately 0.048, suggesting that $2nq$ = 0.05, which indicates that the chelate complex of (CaA_2. 18HA) can be obtained when the D2EHPA is employed as extractant. Yet, the slope of approximately 0.069, suggesting that $2nq$ = 0.07, which indicates that the chelate complex of (CaA_2. 15HA) can be obtained with saponification D2EHPA as extractant. The reason for this phenomenon is that the dimer molecule H_2A_2 is broken up with saponification, and the extractant compound is likely to be part of A^- ions in saponification D2EHPA compound.

According to the mechanisms of the extraction of Ca^{2+} with HA with the cation exchange [12] and chelation, the extraction distribution ratios (D) of Ca^{2+} increase rapidly as the initial pH of regeneration wastewater rises in the extraction system.

3.6. Effect of reaction temperature

From the Fig. 7, the extraction efficiency (E) decreases when the reaction temperature rises up. This means that the extraction of Ca^{2+} with D2EHPA is an exothermic reaction. It is interesting to find that the extraction efficiency (E) with saponified D2EHPA

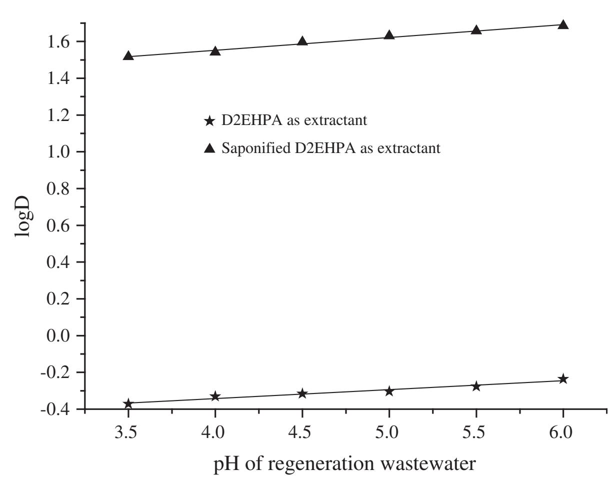

Fig. 6. The extraction efficiency (E) versus the pH of regeneration wastewater. Diluent: kerosene; concentration of NaOH: 6 mol/l; D2EHPA mass fraction (%): 30%; saponification ratio of D2EHPA:15%; phase ratio (A/O): 2:1; transfer speed: 350 r/min; initial Ca^{2+} concentration: 600 mg/L; reaction time: 25 min; and reaction temperature: 30℃.

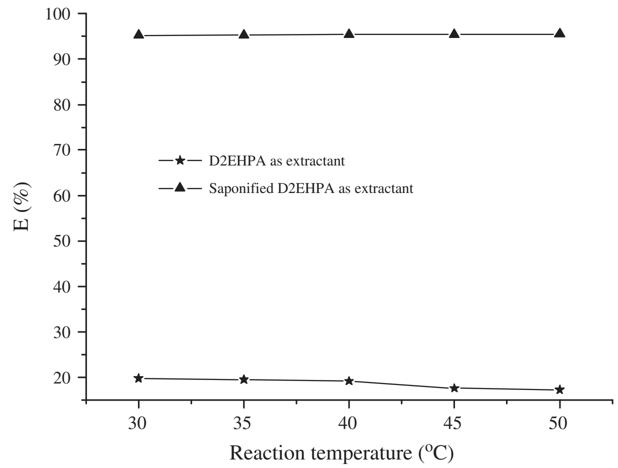

Fig. 7. The extraction efficiency (E) versus the reaction temperature. diluent: kerosene; concentration of NaOH: 6 mol/l; D2EHPA mass fraction (%): 30%; saponification ratio of D2EHPA:15%; phase ratio (A/O): 2:1; transfer speed: 350 r/min; initial Ca^{2+} concentration: 600 mg/L; initial pH of regeneration wastewater: 6; and reaction time: 25 min.

increases slowly from 95.26 to 95.49% as the temperature rises to 50 degree from 30 degree, obviously, which is an endothermic reaction.

3.7. Effect of transfer speed

The effect of transfer speed on the extraction efficiency (E) has been shown in Fig. 8. The extraction efficiency (E) increases slowly when the transfer speed

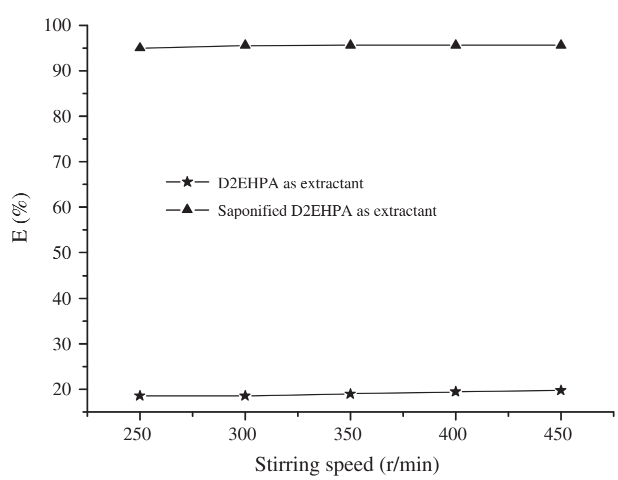

Fig. 8. The extraction efficiency (E) versus the transfer speed. Diluent: kerosene; concentration of NaOH: 6 mol/l; D2EHPA mass fraction (%): 30%; saponification ratio of D2EHPA:15%; phase ratio (A/O): 2:1; initial Ca^{2+} concentration: 600 mg/L; initial pH of regeneration wastewater: 6; reaction time: 25 min; and reaction temperature: 30℃.

increases. This is because by increasing the transfer speed, the area for mass transfer increases, so the extraction efficiency (E) increases too.

4. Examination

A kind of practical waste solution containing 550 mg/L calcium and 425 mg/L magnesium ions is used in this work. The regeneration wastewater is then extracted under the above mentioned optimal technology conditions. The results show that calcium and magnesium ions in the regeneration wastewater can be effectively removed by extraction process with saponification D2EHPA. An extraction efficiency of more than 99.9% is attained under optimum conditions and the regeneration wastewater calcium and magnesium concentration <1.5 mg/L by two levels of extraction. It can be discharged directly, as it meets the Chinese National Emission Standards.

5. Conclusions

Based on the results of this research on the removal of Ca^{2+} from wastewater with D2EHPA and 15% saponified D2EHPA, the following specific conclusions can be drawn:

(1) The saponified D2EHPA can be used as an effective extractant for the removal of Ca^{2+} from regeneration wastewater.
(2) The optimized parameters affecting the process are as follows: saponification ratio of D2EHPA is 15%¸ D2EHPA mass fraction is 30%, reaction temperature is 35℃, phase mass ratio is 2:1, initial pH of regeneration wastewater is 4.0, transfer speed is 350r/min, and reaction time is 20 min.
(3) An extraction efficiency of more than 99.9% of Ca^{2+} is attained at the optimized parameters and the aqueous waste solution can be discharged directly.

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