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Short communication

# A membrane process to recover extractant D2EHPA in aqueous phase

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ABSTRACT

A membrane adsorption–extraction process to recover di-(2-ethylhexyl) phosphate (D2EHPA) from the raffinate is developed, i.e. a hollow fiber membrane extraction module, in which raffinate flows in the tube side and *n*-heptane used as the “extractant” flows in the shell side. The emulsion with D2EHPA, *n*-heptane and Triton X-114 was used as the simulated raffinate, and it was proved that both the affinity of membrane for oil droplets and the extraction of D2EHPA by *n*-heptane contribute to the method. Via recycling the feed, the final recovery efficiency of D2EHPA could be as high as 90%. The effects of two main operating conditions, tube side velocity and shell side velocity, were investigated. The tube side velocity was found to be an essential operation factor, while the shell side velocity had a slight influence.

## 1. Introduction

Extraction is an important process that is widely applied in petroleum industry, pharmaceutics, hydrometallurgy and nuclear industry [1], and there is a certain loss of extractant which costs a lot and needs to be complemented. Generally, the expense caused by solvent loss (extractant and diluent) is accounted for 10% of the product cost. For example, when extracting copper from its 1 g/L solution with Lix64N, the entrainment of solvent by the aqueous phase reaches 100 mg/L, and the cost for this reason is 50 dollars per ton of copper [2]. The loss of extractant is mainly caused by entrainment, dissolution, degradation, interphase coagulation and other factors such as evaporation, leaking, etc. A report by Beijing General Research Institute of Mining & Metallurgy [2] shows that the extractant loss in copper hydrometallurgy is distributed as follows: 24.4% by raffinate phase entrainment, 13% by stripping phase entrainment, 8% by dissolution, 27% by interphase pollutant and 27.6% by other factors.

Some operations concern the extractant recovery, and most of them are physical processes, such as adsorption, gravity settler, air-induced flotation, fibrous beds, lamellar coalescer and so on. Active carbon [3], resin [4] and clay [5] are often used as sorbent to remove organic substance from aqueous phase. The problem is the regeneration of sorbent and the limited throughput. Gravity settler [6,7] needs some time for the feed to experience phase separation spontaneously, which results a low efficiency and a large equipment volume. Air-induced flotation [8] needs energy to pump and eject the air. Fibrous bed [9] has a reasonable efficiency. Phase separation in lamellar coalescer [10] is based on the forces of mechanical and/or electrical origin acting during the adhesive processes at the inclined filling plates. Both the fibrous bed and lamellar coalescer need subsequent separators such as gravity settler, adsorption column or air-induced flotation. The secondary liquid–liquid phase separation loop in a pilot plant was examined by Spasic et al. [10]. The loop consisted of a lamellar coalescer, four flotation cells in series, a settler unit and an adsorption column unit. Finally, the overall efficiency of the loop for recovering the entrained light phase was 92%.

Hein [11] developed a set of technology to recover extractant from raffinate by contacting it with diluent. The extractant was expected to be removed to the diluent phase. But surfactant makes the phase separation difficult and entrainment cannot be eliminated.

Some new kinds of phase separation are related with membrane technology, e.g., membrane filtration [12–14]. Also, membrane is used as a coalescer [15–18], where emulsion permeate through the membrane and the droplets become larger, mainly because of the porous structure of membrane and its affinity for droplets. Selectivity of membrane for substances is widely investigated in recent years. Membrane material has been studied as sorbent to remove deleterious reagents from water [19]. Also, the existence of adsorption in membrane filtration process was discussed in previous work

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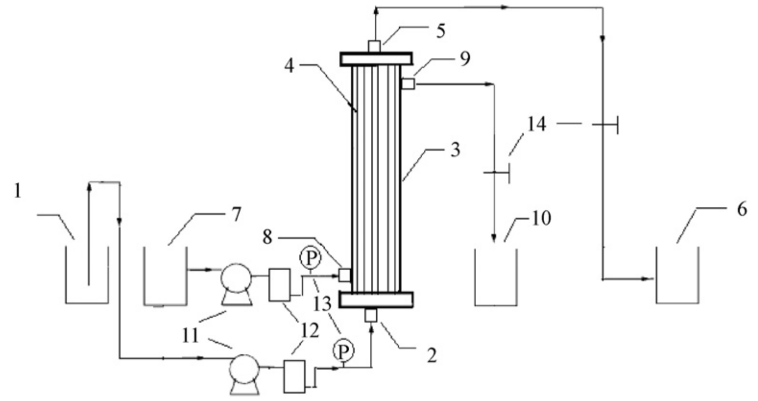

**Fig. 1.** Schematic view of experimental unit. (1) Feed tank, (2) inlet of tube, (3) hollow membrane module, (4) hollow membrane fibers, (5) outlet of tube, (6) treated feed tank, (7) diluent tank, (8) inlet of shell, (9) outlet of shell, (10) enriched diluent tank, (11) axial piston pump, (12) flux buffer, (13) pressure gauge, (14) valve.

[20,21]. Membrane extraction is another important application of membrane technology, in which mass transfer occurs at the membrane surface that separates the aqueous and organic phase. Unlike traditional extraction processes, there is no phase dispersion and coalescence, which results entrainment [22].

The aim of this paper is to develop a membrane adsorption–extraction process, where the raffinate phase is contacted with another "extractant", diluent, via hydrophobic membrane. The extraction behavior of extractant residual in the raffinate with diluent, adsorption capacity of membrane and the effects of flow rates in both tube and shell side have been studied.

## 2. Experiment

Di-(2-ethylhexyl) phosphate (D2EHPA) was chosen as the extractant to be recovered and *n*-heptane as the diluent. An oil/water emulsion which contained D2EHPA, *n*-heptane and nonionic surfactant Triton X-114 was prepared to simulate the raffinate. The initial concentration of D2EHPA ($C_{\text{ini}}$) is 87.0 mg/L and the mass ratio of these reagents in emulsion was maintained as 1:1.640:0.062 (D2EHPA:*n*-heptane:Triton X-114). The volume ratio of D2EHPA and *n*-heptane was about 3:7, which was mainly referred to the composition of solvent in the industrial process [2]. The critical micelle concentration (CMC) of Triton X-114 at room temperature is about 109 mg/L [23] and its concentration in our feed was less than this value, which indicated that the solution was the emulsion.

The emulsion was prepared as follows: an appropriate amount of the D2EHPA, *n*-heptane and Triton X-114 was added to distilled water, emulsification occurred due to the shear forces in the magnetic mixer and was stabled in energy added by the ultrasound system (200 W, 50 kHz).

### 2.1. Chemicals

D2EHPA and *n*-heptane were supplied by Sinopharm Chemical Reagent Co. (China) and Triton X-114 was supplied by Aldrich. All reagents are chemically pure reagents and used without further purification.

### 2.2. Experiment

#### 2.2.1. Equilibrium experiment

The solutions of D2EHPA in *n*-heptane with various concentrations were prepared and 10 mL of each solution was mixed with 10 mL water in a beaker flask. The flask was then sealed and swayed with hand for 30 min. After phase separation which needed about 12 h, the aqueous phase was taken out and the concentration of D2EHPA ($C_{\text{aq}}$) was measured. The partition coefficient ($D$) of D2EHPA between *n*-heptane and water was calculated as

$$D = \frac{C_{\text{org}}}{C_{\text{aq}}} \tag{1}$$

where the concentration of D2EHPA in organic phase ($C_{\text{org}}$) was calculated with the material balance.

#### 2.2.2. Membrane adsorption experiment

The emulsion flowed in tube side and shell side was filled up with air. The transmembrane pressure difference ($\Delta P$) was maintained to prevent feed permeation. Samples were collected from the outlet of tube at certain time intervals and the D2EHPA concentration ($C_{\text{aq}}$) was analyzed.

Fig. 1 shows the schematic view of the experimental unit. The emulsion and the diluent were transferred from tanks by axial piston pumps to the inlet of membrane module. The transmembrane pressure difference was indicated by the pressure gauge connected to the tube and shell side and was varied by adjusting the valves.

The hollow fiber membrane module is made of polyvinylidene fluoride, which is highly hydrophobic [24], with an effective length of 313 mm, an inner diameter of 42 mm, a total membrane area of 0.2 $\text{m}^2$ and 254 hollow membrane fibers. The inner diameter of fiber is 0.8 mm, with 0.3 mm in wall thickness and 0.1 $\mu$m in effective pore size.

The removal efficiency of D2EHPA ($R$) was calculated as follows:

$$R = 1 - \frac{C_{\text{aq}}}{C_{\text{ini}}} \tag{2}$$

where $C_{\text{ini}}$ is the initial concentration of D2EHPA in the emulsion.

#### 2.2.3. Steady process of membrane adsorption–extraction

As shown in Fig. 1, the emulsion flowed in the tube side and *n*-heptane in the shell side. Samples were collected from the outlet of tube at certain time intervals and the D2EHPA concentration was analyzed.

#### 2.2.4. Unsteady process of membrane adsorption–extraction

In this experiment, both emulsion (0.4 L) and *n*-heptane (0.5 L) were recycled from the module outlet to the respective tank. Other operations stayed the same as above.

### 2.3. Analytical method

The total phosphorous in the emulsion phase was measured using Ammonium Molybdate Spectrophotometric Method (GB 11893-89, China) and an ultraviolet spectrometer (HP8453, Agilent,

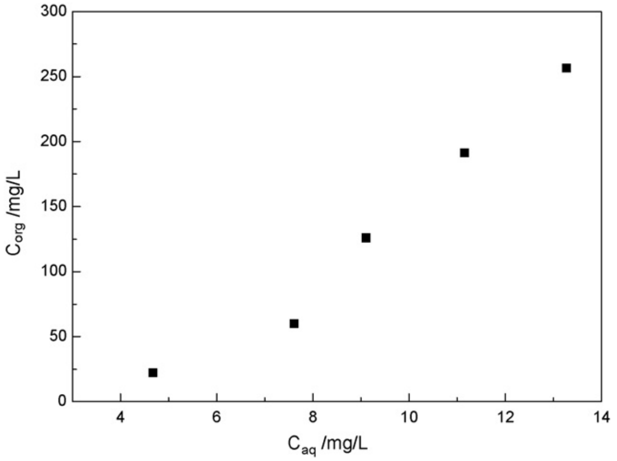

**Fig. 2.** The partitioning of D2EHPA between *n*-heptane and water.

USA) was used. The concentrations of D2EHPA can be calculated on the basis of material balance of phosphorous.

## 3. Results and discussion

### 3.1. Distribution property of D2EHPA between heptane and water

The partition coefficient of D2EHPA between *n*-heptane and water is an important factor of thermodynamics. As shown in Fig. 2, it can be seen that the partition coefficient is higher with a larger D2EHPA concentration in the aqueous phase. As the solubility of D2EHPA in water is 12 mg/L at room temperature, while the D2EHPA concentration in the aqueous phase at equilibrium can reach to <12 mg/L. It implies the possibility of removing D2EHPA from the raffinate.

By regression the data in Fig. 2, the correlation equation for the equilibrium of water/D2EHPA/heptane system can be obtained with the correlative coefficiency ($r = 0.9924$) as

$$C_{org} = 1.9685C_{aq}^2 - 5.4405C_{aq} \tag{3}$$

### 3.2. Adsorption capacity of membrane surface

Fig. 3 shows the removal efficiency of D2EHPA with time. $R$ decreases from a higher value to constant. The membrane used is highly hydrophobic, and also D2EHPA and *n*-heptane are more hydrophobic (log $P$ are 1.51 and 4.66, respectively [25]), therefore, oil droplets in the emulsion can be adsorbed on the surface. At the beginning, the membrane surface is fresh and has a larger adsorption capacity; but the main adsorption function is imposed by the wetted oil on the membrane and the adsorption capacity slows down with time. While unlike other adsorption processes, the $R$ value does not approach to 0 with time, which indicates that the adsorption capacity is not exhausted because of the coalescence effect by formed oil film. The similar phenomena had been pointed out in previous work [26].

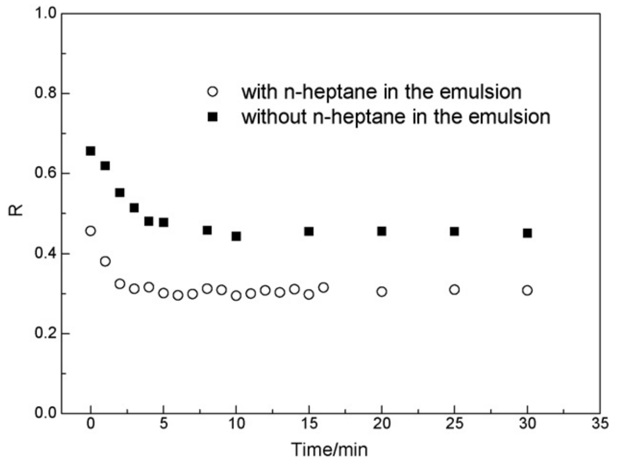

**Fig. 3.** The adsorption of D2EHPA on membrane. $C_{ini} = 87$ mg/L, $v_1 = 0.0015$ m/s, $\Delta P = -2$ kPa.

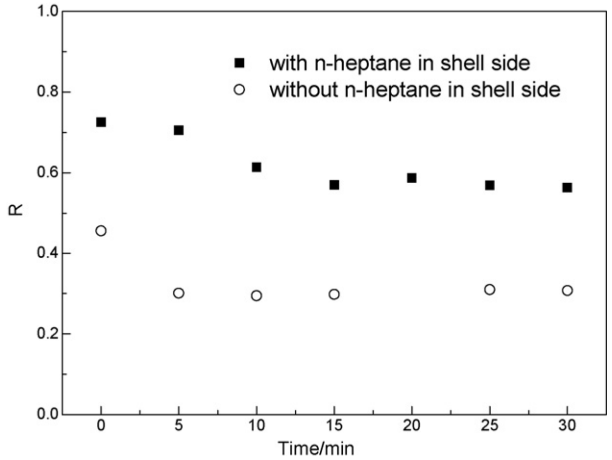

**Fig. 4.** Influence of *n*-heptane in the shell side on the removal efficiency. $C_{ini} = 87$ mg/L, $v_1 = 0.0015$ m/s, $v_2 = 0.0004$ m/s.

The experiment for an emulsion without *n*-heptane was conducted also, and the initial concentration of D2EHPA remains the same. As shown in Fig. 3, a higher $R$ was obtained due to without competitive adsorption of *n*-heptane.

### 3.3. Membrane adsorption–extraction of D2EHPA

In the experiment, the emulsion flowed in the tube side and *n*-heptane in the shell side. Fig. 4 shows the D2EHPA removal efficiency from the outlet with time, and it is also compared with the result of membrane adsorption. It can be seen that the $R$ is higher when there is *n*-heptane in the shell side under similar conditions. The difference of $R$ proves the solvent extraction of D2EHPA with *n*-heptane in the shell side exists and the adsorption by membrane is equivalent to the extraction by *n*-heptane.

### 3.4. Unsteady process of membrane adsorption–extraction

The length of membrane module strongly confines the final removal efficiency of D2EHPA. In order to simulate the best removal efficiency of D2EHPA for this process, the emulsion was recycled from the module export to the feed container.

Fig. 5 shows the removal efficiency of D2EHPA from the outlet with time. $R$ descends first, then goes through an increase, and finally stabilizes at a steady point about 90% (in about 80 min). This trend can be explained by the larger adsorption rate of membrane surface at the beginning and the decrease of the D2EHPA concentration at the inlet with time due to recycle. As it is mentioned above, at the beginning the membrane surface is fresh, and has a larger adsorption capacity. As time goes by, the main adsorption function is imposed by the wetted oil on the membrane and the adsorption capacity slows down, therefore, $R$ descends. While since the emulsion recycles, the D2EHPA concentration at the inlet decreases with

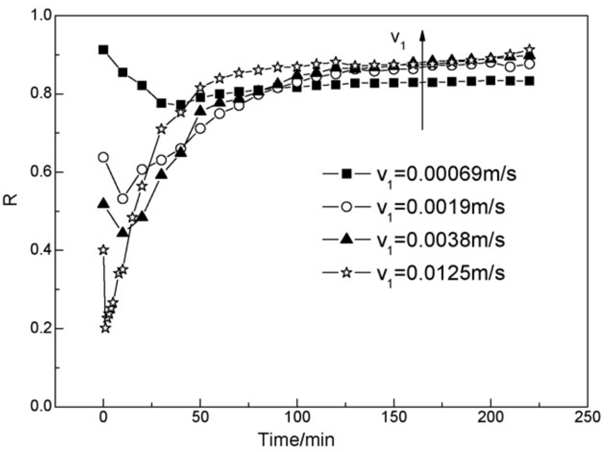

**Fig. 5.** Influence of tube side velocity on the removal efficiency. $C_{\mathrm{ini}} = 87$ mg/L, $v_2 = 0.0004$ m/s, $\Delta P = 0.4$ kPa.

time and $R$ is the sum of each feed, $R$ at the outlet increases with time after the startup period. Finally, when the concentration of D2EHPA in the emulsion is low enough, equilibrium is achieved between the emulsion and *n*-heptane in the shell side, and $R$ stabilizes.

Thermodynamic equilibrium limits the removal of D2EHPA. In the experiment, 0.4 L of emulsion in the tube side and 0.5 L *n*-heptane in the shell side are both recycled. Therefore, the final $R$ should depend on the equilibrium for one contact stage. On the basis of the equilibrium correlative Eq. (3) and the material balance, the largest $R$ in this experiment should be 91.68% if neglecting the amount absorbed on the membrane, while the experimental result is 91.15%. Obviously, a higher $R$ can be obtained by using multiple contact stages.

In order to gain a better understanding of the process, the effect of flow rates for both phases on the removal performance of D2EHPA were investigated. As shown in Figs. 5 and 6, a higher velocity in tube side results in a more rapid increase of $R$ and a higher steady value within 4 h, while the flow rate in the shell side does not affect $R$ apparently.

As it is pointed out, the process can be considered as the combinative function of membrane adsorption and extraction. As the membrane absorption of extractant occurred on the inner wall of fibers, and depends on the flow rate in the tube side, but not the flow rate in the shell side. For the membrane extraction process, although there is accumulation of extractant on the inner wall of fibers from the membrane adsorption, the superimpose models of mass transfer resistance for membrane extraction can be used as the reference. For a hydrophobic membrane with the organic phase on the shell side, the mass transfer driving force based on the aqueous phase concentration, and no chemical reaction, the resistance-in-series equation for membrane extraction process is [27]

$$\frac{1}{K_{\mathrm{w}}d_{\mathrm{i}}} = \frac{1}{k_{\mathrm{w}}d_{\mathrm{i}}} + \frac{1}{Dk_{\mathrm{m}}d_{\mathrm{lm}}} + \frac{1}{Dk_{\mathrm{o}}d_{\mathrm{o}}} \tag{4}$$

Where $K_{\mathrm{w}}$ is the overall mass transfer coefficient, $k_{\mathrm{w}}$, $k_{\mathrm{m}}$ and $k_{\mathrm{o}}$ are the mass transfer coefficients at aqueous boundary layer, membrane, and organic boundary layer, respectively. $d_{\mathrm{o}}$, $d_{\mathrm{lm}}$, and $d_{\mathrm{i}}$ are diameters of the fiber outside, log mean and inside, respectively. In the membrane extraction process, $k_{\mathrm{m}}$ can be assumed to be from two parts, the wet membrane from the membrane adsorption and the fiber, therefore it only depends on the flow rate of the tube side. In this experiment, as $D > 1$ (20–250), the mass transfer behavior parameter, $K_{\mathrm{w}}$, does not depend on the second and the third items in Eq. (4) apparently. Therefore, the $R$ is not sensitive to the flow rate in shell side although $k_{\mathrm{o}}$ increases with it, and the flow rate in tube side is a sensitive factor which affects the mass transfer process.

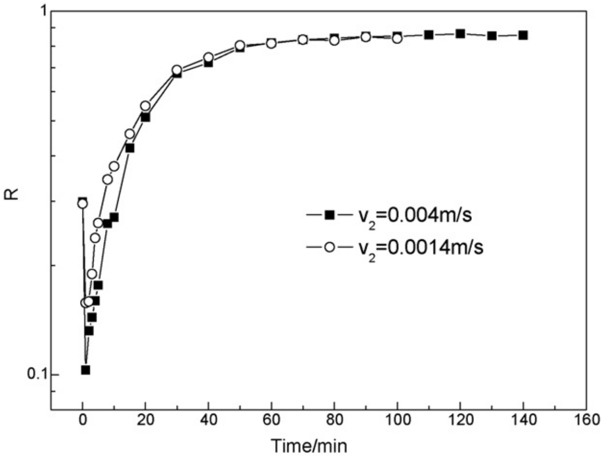

**Fig. 6.** Influence of shell side velocity the removal efficiency. $C_{\mathrm{ini}} = 87$ mg/L, $v_1 = 0.0125$ m/s, $\Delta P = 0.4$ kPa.

## 4. Conclusions

Both the affinity of membrane for oil and the extraction effect of diluent contribute to the method. The membrane adsorption–extraction process has been shown to be an effective, relatively simple way to recover extractant from raffinate phase and break oil-in-water emulsion. A good removal efficiency of D2EHPA was achieved via recycling the feed and that the tube side velocity has a strong effect on the process while the shell side velocity is an unimportant factor.

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