Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22396

114 (2018) 163–168
May

Citric acid removal from aqueous solutions using a polymer inclusion membrane based on a mixture of CTA and CA

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Received 27 December 2016; Accepted 20 April 2018

ABSTRACT

This research work focuses on the transport of citric acid from aqueous solutions using a polymer inclusion membrane (PIM). The PIM contains calix[4]resorcinarene as the carrier, mixture of cellulose triacetate and cellulose acetate (CA) as the base polymers, and 2-nitrophenyl octyl ether as a plasticizer. The transport percentage of citric acid was found to be dependent on various factors such as the concentration of the carrier and the plasticizer in the membrane phase, pH of the aqueous feed phase, and stirring speed. The corresponding stirring speed, pH of feed phase, the initial concentration of citric acid in feed phase, carrier content, and plasticizer were: 600 rpm, 2, 10–2 M, 0.15 g/g of support, and 0.03 mL, respectively. The 86% of citric acid was transported from feed phase to stripping phase in 5 d. This study shows that PIM composition has a great influence on citric acid recovery. It may be concluded that PIM with calix[4]resorcinarene (RC8) as the carrier can be successfully used for the extraction of citric acid from aqueous solutions.

Keywords: Citric acid transport; Polymer inclusion membrane; Calix[4]resorcinarene; Cellulose derivatives; Membrane process; Facilitated transport

1. Introduction

Citric acid (E330) is a natural substance that appears as an intermediate in the basic physiological citric acid or Krebs cycle in every eukaryote cell. Citric acid is soluble in water and some organic liquids and is very hydrophilic. Currently, this acid is produced mainly by fungi *Aspergillus niger* in the fermentation process. It has been produced for many years in high volumes; current global production is estimated to approach 1,000,000 tons/year [1,2]. It has a wide dispersive use, being added to processed food and beverages as preservative and acidity regulator, used in pharmaceutical preparations and in household cleaners, as well as in special technical applications. Citric acid is reported to function in cosmetics as a chelating agent, pH adjuster, or fragrance ingredient. Due to its physicochemical characteristics, citric acid is highly mobile in the environment and will partition to the aquatic compartment.

Wastewater discharge is a primary source of citric acid release into the environment. The development of new technology for removal of the small organic molecule from aqueous solutions remains an important scientific endeavor [3]. An alternative separation technology is transport across liquid membranes, which offers a potentially attractive alternative to solvent extraction process and combines the process of extraction and stripping in a single-unit operation. Today, a remarkable increase of the applications of the liquid membrane in the separation process is observed. These membranes include bulk liquid membrane [4–7], emulsion liquid membranes [8], liquid surfactant membranes, and supported liquid membranes [9,10]. A novel type of liquid membrane system called polymer inclusion membranes (PIMs) has been developed [11–18]. PIMs are usually composed of a base polymer commonly cellulose

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triacetate (CTA) or polyvinylchloride which constitutes the support of the membrane. The plasticizer commonly 2-nitrophenyl octyl ether (2-NPOE) provides elasticity/flexibility, the plasticizer decreases the glass transition temperature of the membrane and improves the solubility of the extracted species in the membrane liquid phase [19]. Likewise, the carrier (extractant) is essentially a complexing agent, responsible for binding to target species and transporting them through the PIM. CTA membrane incorporating a carrier has been used for the transport of inorganic species such as heavy metals [11–13,20–24], as well as small organic molecule such as lactic acid [15], phenol [25–27], carbohydrate [28,29], amino acids [30,31], thiourea [32], and antibiotics [33]. The transport of citric acid from acidic aqueous solutions through a PIM with 1-alkylimidazol as a carrier has been studied by Gajewski and Bogacki [34]. The carrier with longer length alkyl chain was found to have a good affinity to citric acid transport. Maximal flux was obtained when the alkyl group contained nine carbon atoms (R = $-C_9H_{19}$). These membranes show high transport efficiency of citric acid. The main of this work is to study the extraction of citric acid from aqueous solution using PIM based on a mixture of cellulose acetate (CA) and CTA with calix[4]resorcinarene as a carrier.

2. Materials and methods

2.1. Chemicals

The structure and abbreviation of the carriers (RC4, 8) and plasticizer used in the present study are shown in Fig. 1. The carriers, (C-octyl) calix[4]resorcinarene and (C-butyl) calix[4]resorcinarene, respectively, abbreviated as RC8 and RC4 were synthesized in our laboratory [35].

Citric acid, resorcinol, aldehydes, ethanol, hydrochloric acid, potassium hydroxide, salts, dichloromethane, CTA, CA, and 2-NPOE were analytical grade reagents purchased from Sigma-Aldrich (Fluka). Aqueous solutions were prepared by dissolving the respective analytical grade reagent in deionized water with a resistivity not less than 18.2 MΩ cm obtained with a Milli-Q Plus system. The pH adjustment was done by addition of dilute hydrochloric acid (0.01 M) or sodium hydroxide (0.25 M) to prepare the desired pH solution.

2.2. Membrane preparation

PIMs were prepared according to the procedure reported by Sugiura et al. [36]; the amount of each constituent was a function of the series of experiments to be performed. Thus, for the mixture of CTA and CA membrane, 10 mL of a polymers solution (0.1 g of polymers in dichloromethane), calix[4]resorcinarene (RC4, 8; 0–0.06 g/g mixture of polymers), and plasticizer (0–2.5 g of plasticizer/g mixture of polymers) were placed into a Petri dish of 9.0 cm diameter. This solution was allowed to evaporate overnight at room temperature (25°C ± 1°C). The film was then carefully peeled out of the bottom of the Petri dish and stored in deionized water for 24 h.

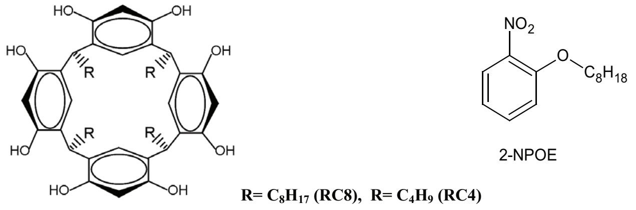


Fig. 1. Chemical structure of calix[4]resorcinarenes (RC4, 8) and plasticizer (2-NPOE). R = C_8H_{17} (RC8) and R = C_4H_9 (RC_4).

2.3. Transport experiments

A typical laboratory scale device was used for citric acid transport experiments through the PIM. The PIM cell consists of two compartments made of Teflon with a maximum capacity of 400 mL separated by the PIM [17]. The PIM area exposed to the aqueous phase was of 12.56 cm². In order to minimize the boundary layer thickness, both source and stripping compartments were provided with a mechanical stirrer adjusted to 600 rpm. One of them contained 10^{-2} M of citric acid as the feed phase, and the other, the stripping phase, contained deionized water (pH = 6.8). The transport can take place by diffusion. All transport experiments were carried out in duplicate at 25°C ± 1°C. The reported error bars in all figures represent the standard deviation of the data. The performance of the system was studied in terms of its citric acid removal (%), defined by Eq. (1) and its initial flux (J_0), calculated by Eq. (2):

$$\text{Citric acid removal (\%)} = [\text{Citric acid}]_{s,t}/[\text{Citric acid}]_{f,0} \times 100 \quad (1)$$

where $[\text{Citric acid}]_{s,t}$ refers to the citric acid concentration in the stripping phase at time t, and $[\text{Citric acid}]_{f,0}$ refers to the initial concentration of citric acid in the feed phase.

$$J_0 = (V/S)\,(\Delta[\text{citric acid}]_f/\Delta t) \quad (2)$$

where V is the volume of feed phase and S the exposed surface area of the PIM.

2.4. Citric acid analyses

The influence of the studied parameters on the transport of citric acid was analyzed during 5 d. Samples of 4 mL were manually extracted with a pipette from both half-cells each day, and the citric acid quantification in the transport experiments was carried out by measuring the conductivity of the receiving phase taking into account the presence of ions with citric acid. The measured value of the conductivity was converted to the concentration of citric acid.

3. Results and discussions

3.1. Effect of carrier nature and base polymers

The effect of the nature of carrier and base polymer on the efficiency transport of citric acid through the PIM was studied (Table 1). It was observed that when the PIM was prepared with the mixture of 75% CTA/25% CA, the transport of citric acid was higher and reached 86%, but in the case of PIM with CA polymer alone, the transport efficiency of the target decreased, probably due to the hydrophilic character of CA. Likewise, we observed that the flux of citric acid

Table 1
Effect of support nature for PIM preparation on the transport of citric acid

Base polymers (%)	Initial flux J_0 (mol/m^2 s) × 10^7 ± STDs	
	RC4	RC8
CTA (100%)	4.17 (0.34)	7.58 (0.63)
CTA (75%) + CA (25%)	5.98 (0.47)	10.32 (0.85)
CTA (50%) + CA (50%)	1.87 (0.08)	5.21 (0.42)
CA (100%)	2.21 (0.16)	4.56 (0.35)

transport depended on the length of alkyl chain of groups on the calix[4]resorcinarene, which resulted in the decrease diffusion rate of the carrier in membrane phase.

3.2. Effect of contact time

Fig. 2 shows the time dependence of citric acid transport across the PIM system. It was found that under the optimum conditions, the transport of citric acid from the aqueous source phase to receiving phase is still noticeable after 5 d. The transport of the target molecule through the membrane takes place in a gradual manner until the fifth day when almost 90% of the solute is transferred to the receiving phase.

3.3. Effect of stirring speed

To optimize the stirring rate to transport the maximal quantity of citric acid through the PIM, extraction experiments were carried out at different stirring rates from 200 to 800 rpm, the obtained values are presented in Fig. 3.

As shown in Fig. 3, between 200 and 600 rpm, the quantity transported of target does not exceed 60%, while above 600 rpm, the extraction efficiency decreases. Indeed, however, stirring at speed higher than 600 rpm resulted in cavitations and bubbles in the solution. Therefore, 600 rpm was chosen as the optimum stirring rate and used for all further experiments.

3.4. Effect of initial concentration of citric acid in feed phase

The effect of initial citric acid concentration at a range from 0 to 0.025 M in feed phase on the transport flux is presented in Fig. 4. Transport percentage increases with increasing citric acid concentrations from 0 to 0.01 M and tends to stabilize for higher concentrations at 0.015 M after 4 d of transport time; the occurrence of a milky layer was observed on the membrane surface. This observation was likely one of the reasons of the flux limit. However, another reason could be related to the kinetics of the citric acid uptake: a different stoichiometry could occur at high concentrations, which may lead to hamper solute and/or carrier solubility within the PIM core.

3.5. Effect of carrier content

Fig. 5 shows the influence of the content of carrier RC8 in the organic phase of the membrane on the transport efficiency of citric acid. As it seen from Fig. 5, the flux of target increases with increasing content of RC8 in the membrane phase up to a 0.15 g/g support value, while a further increase in the carrier concentration results in a slight decrease in extraction efficiency is observed a similar behavior for the carrier concentration in the PIM has already been reported in the literature [25,27]. This could be due to the release of the citric acid into the receiving phase, as a result of its binding to the carrier and/or the important viscosity of membrane phase caused by increasing carrier quantity.

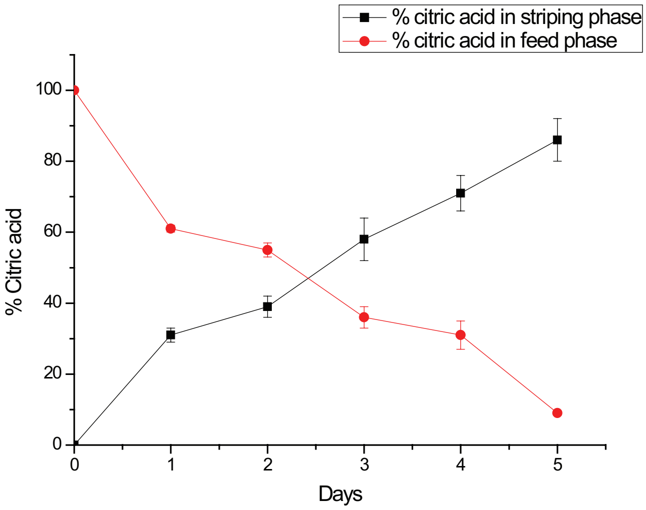


Fig. 2. Effect of contact time on removal of citric acid. Transport conditions: Feed phase: citric acid 10^{-2} M and pH 2. Stripping phase: deionized water, pH 6.8. Membrane: 12.60 cm^2 of surface area, calix[4]resorcinarene: RC8 (0.15 g/g mixture of polymers) and 1.5 g 2-NPOE/g mixture of polymers.

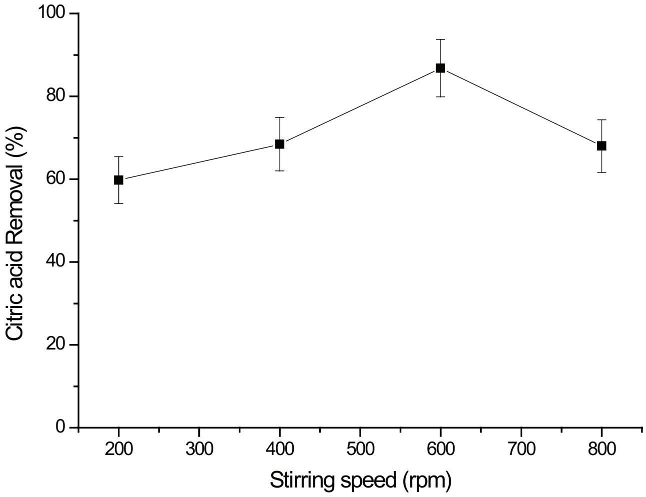


Fig. 3. Effect of stirring speed on removal of citric acid. Transport conditions: Feed phase: citric acid 10^{-2} M and pH 2. Stripping phase: deionized water, pH 6.8. Membrane: 12.60 cm^2 of surface area, calix[4]resorcinarene: RC8 (0.15 g/g mixture of polymers) and 1.5 g 2-NPOE/g mixture of polymers. Values obtained after 5 d of transport.

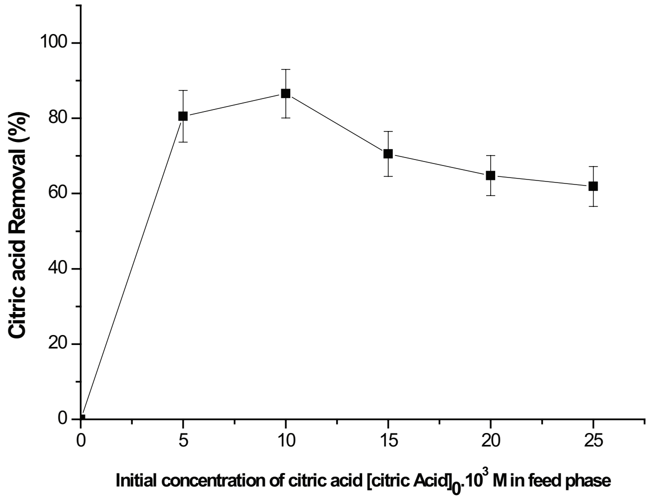


Fig. 4. Effect of initial concentration of citric acid. Transport conditions: Feed phase: citric acid (0–0.025 M) and pH 2. Stripping phase: deionized water, pH 6.8. Membrane: 12.60 cm^2 of surface area, calix[4]resorcinarene: RC8 (0.15 g/g mixture of polymers) and 1.5 g 2-NPOE/g mixture of polymers. Values obtained after 5 d of transport.

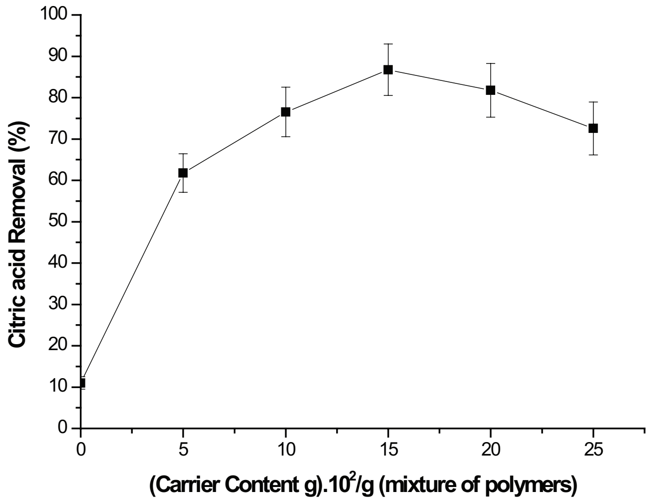


Fig. 5. Effect of carrier contents on the transport of citric acid. Transport conditions: Feed phase: citric acid 10^{-2} M and pH 2. Stripping phase: deionized water, pH 6.8. Membrane: 12.60 cm^2 of surface area, calix[4]resorcinarene (0–0.25 g/g mixture of polymers) and 1.5 g 2-NPOE/g mixture of polymer. Values obtained after 5 d of experimentation.

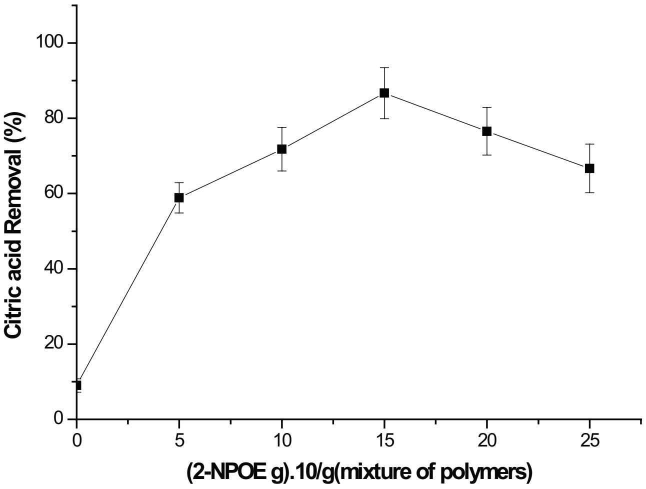


Fig. 6. Effect of plasticizer (2-NPOE) content on the transport of citric acid. Transport conditions: Feed phase: citric acid 10^{-2} M and pH 2. Stripping phase: deionized water, pH 6.8. Membrane: 12.60 cm^2 of surface area, calix[4]resorcinarene: RC8 (0.15 g/g mixture of polymers) and 0–2.5 g 2-NPOE/g mixture of polymers. Values obtained after 5 d of transport.

3.6. Effect of plasticizer content

Plasticizer plays a vital role in the transport of target as well as for membrane softness and flexibility in the PIMs. The influence of the plasticizer 2-NPOE content in the PIM on the elimination of citric acid was investigated by preparing PIMs with a fixed the quantity of calix[4]resorcinarene RC8 (0.15 g/g mixture of polymers) and varying plasticizer amounts (0–2.5 g/g mixture of polymers; Fig. 6). PIM prepared with the different amount of plasticizer was transparent with uniform thickness. Moreover, PIM preparation with carrier RC8 but no plasticizer led to a low transport rate of citric acid; a further increase in the amount of 2-NPOE gave higher transfer efficiency up to 1.5 g of 2-NPOE, which might be due to the favorable plasticization effect. However, beyond this value, a decrease in transport of citric acid was observed, attributed to the intermolecular interaction between target and plasticizer molecule resulting in a lower mass transfer.

3.7. Effect of pH of feed phase

In this section, the effect of feed phase pH on the transport of citric acid was studied. The pH of stripping phase was neutral (pH = 6.8). It can be observed in Fig. 7. When the feed solution pH is 2, the removal efficiency of citric acid from feed phase reaches the maximum, and the elimination percentage decreases when pH departs from 2. The decrease in transport with increasing pH in feed phase from 2 to 12 is due to the decreasing tendency of complex formation between carrier and target. Of interest, the acidity of the strip phase was measured at end of transport process; it was observed that when we increase feed phase acidity, the acidity of the strip phase also decreases. This decrease may be due to a higher transport of protons toward the receiving phase, then reducing the transport efficiency of the target. The variation of the flux with pH tends to confirm that the transport process is based on the pH gradient between the aqueous phases.

3.8. Stability of PIMs

In this study, one PIM was tested and reused, whereas the feed and strip phases were replaced after one cycle with fresh ones in five experiments, and each experiment lasted for 4 d. As observed in Fig. 8. The initial flux of PIM shows a gradual decrease with increasing of cycle's reuse, which may be caused by the loss of carrier from membrane [37]. The initial flux is 7.37 × 10^{-7} mol/m^2 s in the first cycle and reaches 6.83 ×10^{-7} mol/m^2 s.

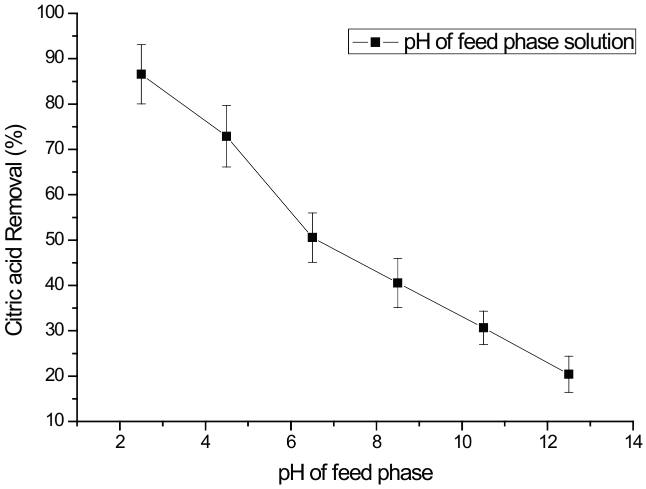


Fig. 7. Effect of pH solution of feed phase on the removal efficiency of citric acid. Transport conditions: Feed phase: citric acid 10^{-2} M and pH 2–12. Stripping phase: deionized water, pH 6.8. Membrane: 12.60 cm^2 of surface area, calix[4]resorcinarene (0.15 g/g mixture of polymers), and 1.5 g 2-NPOE/g mixture of polymers. Values obtained after 5 d of experimentation.

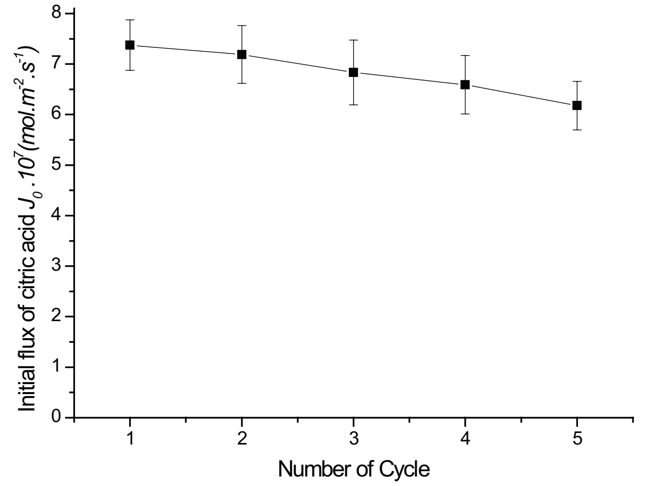


Fig. 8. Fluxes of citric acid in consecutive transport experiments performed on the PIM with RC8 and 2-NPOE. Transport conditions: Source phase (synthetic aqueous solution of citric acid: 10^{-2} M and pH 2) and stripping phase (deionized water, pH 6.8) were stirred at 600 rpm, membrane area of 12.56 cm^2 with 0.15 g of carrier (RC8), and 1.5 g of 2-NPOE and T = 25°C.

In the cycle three, the PIM used in this study was found to be quite stable for at least 8 d. However, when the same membrane was used for the fifth time, the system reveals some 12% decrease in the membrane efficiency for transport of citric acid.

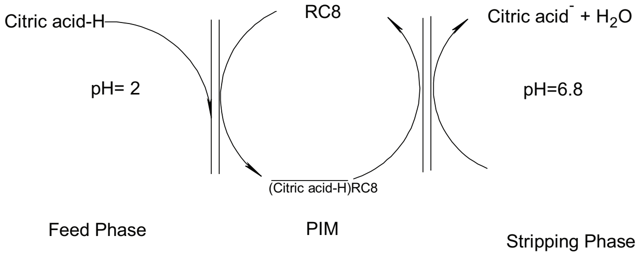
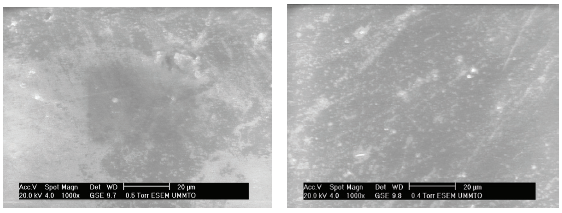


Fig. 9. Representation of the transport mechanism of citric acid by carrier across PIMs system.



PIM : CTA+NPOE+RC8

PIM: (CTA75%+CA 25%) +NPOE+RC8

Fig. 10. SEM of prepared PIMs. PIM: CTA + 2-NPOE + RC8 and PIM: (CTA 75% + CA 25%) + 2-NPOE + RC8.

3.9. Suggested mechanism

Transport of citric acid by using the calix[4]resorcinarene RC8 as carrier obeys a facilitated co-transport as it is shown in Fig. 9. The citric acid forms a single charge complex at the interface feed phase/membrane and after forming a hydrophobic pair complex; the complex diffuses through the membrane phase to the membrane/strip phase interface. Then, the free carrier diffuses back across the PIM phase (core), and the cycle starts again. The net result is the mass transfer of citric acid from source phase to the receiving phase through a PIM system.

3.10. Scanning electron microscopy

In order to investigate membranes structure, scanning electron microscopy (SEM) pictures of the surface Fig. 10 were done. The PIMs present a nonporous structure; the PIM with CTA alone has a smooth surface. Similarly, membrane with mixture of CTA 75% and CA 25% are characterized by a homogeneous and smooth surface. It was found out that membranes prepared in this study presenting a similar structure like other membrane of this type [17,27,38].

4. Conclusion

In this study, the PIM was prepared and successfully applied for the removal of citric acid from aqueous solution. The mixture of CTA and CA was found to be the optimum base polymer for quantitative transport of citric acid. Moreover, the nature of carrier especially alkyl chain length, stirring rate, and pH of feed phase are also important factors affecting the increased rate of citric acid transport. Hence, from the results obtained, it can be seen that the investigated calix[4]resorcinarene are effective extractant for citric acid and that their extraction abilities depend on the alkyl chain length of the substituent in the macrocycle. Choosing the appropriate length of alkyl chain, very selective system can be designed. The excellent efficiency of the citric acid transport by the proposed PIM system reveals its potential application for the selective removal, concentration, and purification of citric acid from different media.

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