Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23575

144 (2019) 185–200
March

Polymer inclusion membranes with dinonylnaphthalene sulfonic acid as ion carrier for Co(II) transport from model solutions

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Received 12 April 2018; Accepted 7 December 2018

ABSTRACT

In this study, recovery of Co(II) from aqueous solution by polymer inclusion membrane (PIM) composed of dinonylnaphthalene sulfonic acid (DNNSA) as the ion carrier, plasticized with four different plasticizers, and cellulose triacetate as the polymeric base was investigated. The membrane composition and aqueous phase parameters were considered, respectively. Carrier concentration as an important parameter in the recovery efficiency was investigated and the membrane composed of 15%wt. of DNNSA was found as most efficient membrane forextraction of Co(II) ions. The study also included the effects of nature and concentration of plasticizers. Extraction across membranes plasticized with dioctyl adipate (DOA), dioctyl phthalate, triethyl phosphate, and tributyl phosphate were evaluated and the membrane plasticized with DOA (62%wt.) showed the maximum flux and extraction. Also, the aqueous phase parameters including the rate of mixing, initial ion concentration, pH of source phase, kind of receiving phase, receiving phase acid concentration were evaluated after studying membrane composition parameters. Then, extraction of cobalt across PIM was considered in a long life experiment to extract all content of heavy metal. The reproducibility of cobalt extraction was investigated by 10 replicate measurements. Finally, presence of nanoparticles in the PIM structure was considered as a new technique to modify the membrane extraction capacity. The results showed that SiO_2 and TiO_2 enhance the ion extraction 5.4% and 3.3%, respectively.

Keywords: Polymer inclusion membrane; Cobalt(II) separation; Dinonylnaphthalene sulfonic acid; Aqueous solutions; Nanoparticles

1. Introduction

Toxic heavy metals such as cadmium, chromium, cobalt, lead and mercury are amajor concern in the field of water pollution [1,2]. Cobalt which is a strategic metal and obtained from the different ores, is employed by the various manufactures of catalyst synthesis, alloys, steels, etc. [3]. Cobalt is a natural element that exists in the certain ores of the Earth's crust. While it is essential element for life in the smidgen, and it is the major constituent in thevitamin B_{12}; but in the higher concentration, it is very harmful and destructive. Many industries and activities like galvanization, rechargeable batteries, metal plating, paints and pigment industries, mining operations, and nuclear power plants produce various liquid and solid wastes rich in Co(II) [4,5]. The critical doze of Co(II) contributes to the several human diseases including asthma, lung irritations, diarrhea, pneumonia, weight loss, vomiting, etc. In addition, extra amount of cobalt in the humanbody leads to the gene mutation and cancer disease [6].

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1.1. Polymer inclusion membranes

In many cases, the environmental cobalt pollution is available in the aqueous form, and it is required to extract the cobalt ions from the wastewater. There are some industrial techniques including membrane filtration, electrodialysis and photocatalysis to eliminate the heavy metal pollutants. Recently, many efforts have been devoted to develop adsorption [7,8] and ion-exchange technologies [9], to remove the Co(II) ions from the aqueous solutions, which they have focused on introducing a more selective technology [10,11]. Thus, it is required to find a selective and efficient strategy to remove the heavy metals with lower energy consumption, less chemical usage [12], lower investment cost [9], and easy to handle [13]. In this way, membrane processes have been developed as apromising technique to eliminate the heavy metals from the aqueous solutions [14]. Recently, liquid membranes have attracted much attention for heavy metal ions separation, which they are categorized in three different classes including: emulsion liquid membranes (ELM), bulk liquid membranes (BLM), and supported liquid membranes (SLM) [15]. But the liquid membranes have some drawbacks such as emulsion stability for ELMs, small surface area and low mass transfer rate for BLMs, also wasting membrane phase to aqueous phase for SLMs [16]. Hence, polymer inclusion membranes (PIMs) have been developed due to their adequate stability compared with the liquid membranes, negligible loss of the carrier, high selectivity, and appropriate efficiency [17–19]. Thus, these qualities have introduced the PIMs as an interesting technique than other existing onesonthe laboratory scale treatment.

All PIMs have three main components that constitute the structure of the membrane. These components include polymer, plasticizer, and the carrier [20]. The polymer provides mechanical strength and a framework that accommodates other components to make a stable structure [21]. The membrane thickness directly relies on the amount of polymer. Thick membranes display more stability and mechanical strength; on contrary, less ion extraction ability is observed in the ion separation process by a thick membrane in accordance with the first Fick's law [22]. Despite the recent progresses on the employed polymers in the different industries, cellulose triacetate (CTA) and polyvinyl chloride (PVC) are the two polymers which are extensively utilized for PIM studies [14,23,24]. Moreover, Gardner et al. [17] investigated the feasibility of some cellulose derivatives (including cellulose acetate propionate and cellulose acetate butyrate). They studied the ion extraction and observed that the PIM composed from the CTA has more efficiency than other considered polymers [23–25].

PIMs include another main component as 'carrier'. The carrier plays a crucial role in the PIM, because it is the only component that facilitates the extraction of solute by forming a complex or an ion-pair [20,26]. Actually, PIMs without the carrier does not have extraction effect and it is a barrier for the ion extraction [27]. Almeida et al. [28] studied the PIMs (containing commercial dinonylnaphthalene sulfonic acid (DNNSA) as the carrier) potential to employ as a semi-permeable barrier in a passive sampler for the accumulation of ammonia. The PIMs which provided the highest extraction rates and the best stability was contained 70%wt. CTA and 30%wt. commercial DNNSA for the CTA-based membranes; also 80%wt. PVC, 10%wt. commercial DNNSA and 10%wt. 1-tetradecanol as a modifier for PIMs with PVC base.

The plasticizer also has a vital role in the PIMs operation. The PIM without the plasticizer has a rigid structure in which the ions diffuse merely. In addition, adding the polar plasticizer to base polymer structure facilitates the neutralization of the polar groups. Then, the forces between the polymer molecules are reduced and the ions diffusion improved by creating the transport channels [29,30]. The permeability of halides and oxo anions through the PIM as a function of plasticizer type has been investigated by Gardner et al. [31]. They found that the plasticizers operate differently for each anions extraction. It is worth mentioning that the carrier and the plasticizer have a dependent performance and tight interactions inside the PIM structure. As the carrier concentration increases in the PIM structure, the interactions between the carrier and the plasticizer increase, consequently. At this step, the plasticizer molecules move towards the carrier molecules, inside the polymer chains, and constitute the liquid micro-channels. Meanwhile, further increment of the carrier leads to the stickiness of micro-channels together and constitute the continuous pathways between the source phase/membrane and receiving phase/membrane interfaces. Also, the ions transport is occurred when the transport pathways are created in the PIM structure [32]. The facilitating effect of plasticizers in the PIMs is shown schematically in Fig. 1.

The hydrometallurgical separation of Co(II) from Mn(II) was studied by Baba et al.[33]. They investigated the development of a PIM for separation of Co(II) and Mn(II) metal ions, efficiently. The proposed PIM was contained 40%wt. D_2EHAG as a carrier, 30%wt. CTA as a base polymer and 30%wt. dioctyl phthalate as a plasticizer. The potential of this membrane for Co(II) separation and pre-concentration was considered by the complete transfer of Co(II) from a feed phaseto a sulfuric acid receiving phase, it is worth mentioning that the Mn(II) extraction in a similar situation was less than 5% during the same period [33].

1.2. Nanoparticles

Recently, adding nanoparticles to the polymeric membranes as modifier have been investigated by some researchers. Abedini et al. [34] studied the effect of adding TiO_2 on the structure of the cellulose acetate membrane. A similar study was accomplished by Homayoonfal et al. [35]. It was demonstrated that adding nanoparticles change the polymeric membrane structure. According to Homayoonfal et al. [35] and Amin et al. [36] studies, the membrane pore size was increased by nanoparticles addition to a specific nanoparticle concentration, so the cation extraction through the membrane was facilitated. Since no studies have been reported regarding SiO_2, TiO_2, and Fe_2O_3 embedded PIMs, for removal of heavy metals from the aqueous solutions, despite their diverse applications in the water treatment [37,38]. The behavior of PIMs after adding nanoparticles has been depicted in Fig. 2.

1.3. Objective

The application of modified PIM for the extraction of Co(II) from the aqueous solutions is an interesting issue for

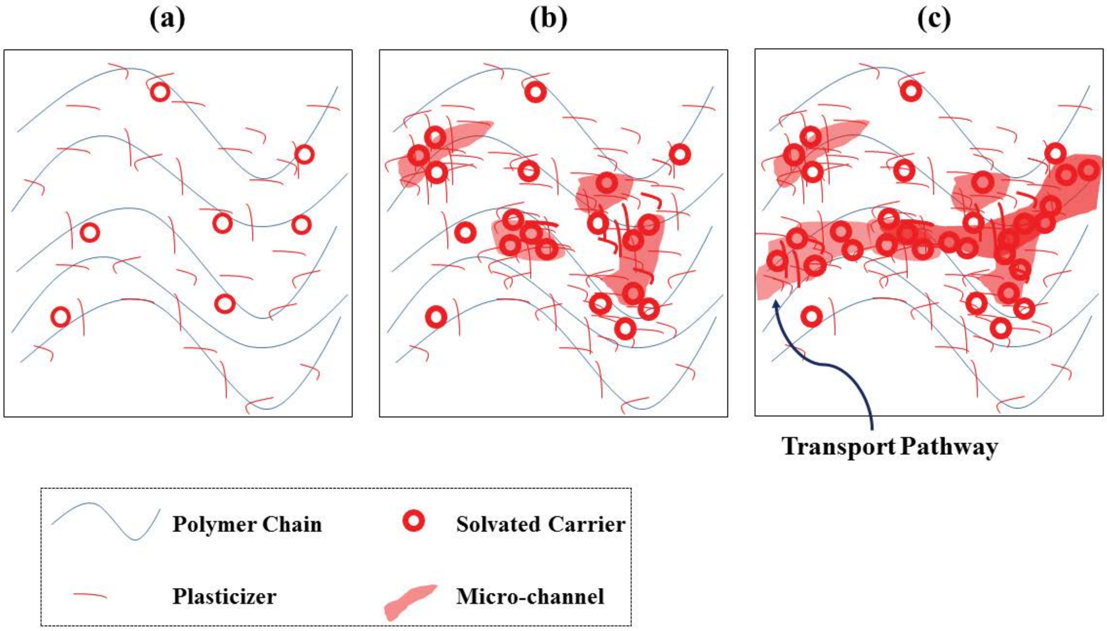


Fig. 1. The facilitating effect of plasticizers in PIMs [32], (a) low concentration of plasticizer, (b) the liquid micro-channels constitution, and (c) the continuous pathways constitution.

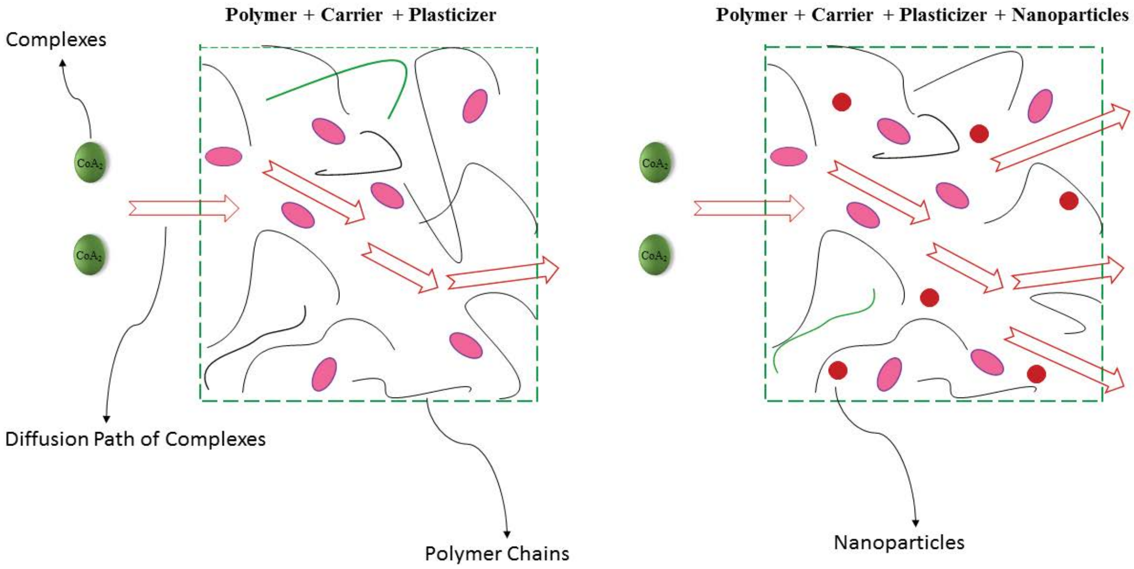


Fig. 2. The behavior of PIMs after adding nanoparticles.

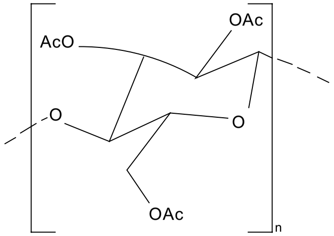
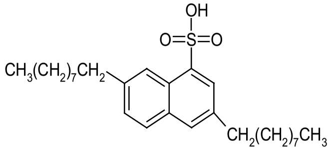
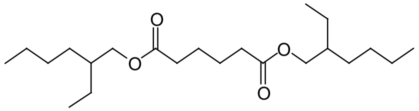
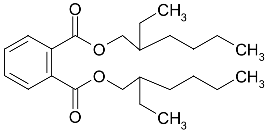
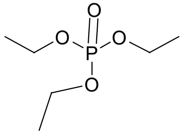
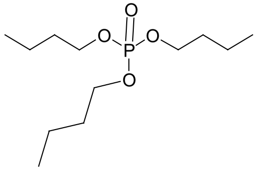
the water purification studies. Thus in this work, a durable, efficient, and selective membrane has been considered to this goal. The basic aim of this study is the investigation of efficiency of the cobalt recovery using the PIM with different compositions and aqueous solutions. In this way, the effect of compositions and aqueous solution parameters on the recovery process have been investigated. Then, by adding nanoparticles to the PIMs, their performances for extraction of Co(II) ions from the aqueous solutions have been investigated. In current study, different CTA/DOA/DNNSA PIMs have been prepared using SiO_2, TiO_2, and Fe_2O_3 nanoparticles to obtain new PIMs with higher extraction capacity.

2. Experimental

2.1. Chemicals

The dichloromethane, HCl, bis(2-ethylhexyl) adipate, bis(2-ethylhexyl) phthalate and the employed buffer materials for the source phase were prepared from Merck (Germany), CTA was obtained from Fluka (Germany). All three nanoparticles including Fe_3O_4, TiO_2, and SiO_2(with the sizes of 5–25 nm, <100 nm, and 10–20 nm, respectively) were provided from Sigma–Aldrich (Germany). Also, all solutions were supplied with freshly doubly distilled water. The main physical properties of the used materials have been reported in Table 1 [39].

Table 1
Some physical properties of applied materials for casting polymer inclusion membranes

Material	Properties							
	Name	Chemical formula	Molecular weight (g/mol)	Density (g/mL)	Melting point (°C)	Boiling point (°C)	Appearance	2D view
CTA	Cellulose triacetate	C40H54O27	Variable	–	300	–	Pellets; Shrink resistant, wrinkle resistant, generally washable at high temperatures	
DNNSA	Dinonylnaphthalene sulfonic acid	C28H44O3S	460.717	0.852	259.5	600.4	Black oily liquid; Insoluble in water	
DOA	Diocty ladipate	C22H42O4	370.57	0.922	-67.8	214	Colorless oily liquid	
DOP	Dioctyl phthalate	C24H38O4	390.564	0.98	–25	220	Colorless oily liquid	
TEP	Triethyl phosphate	C6H15O4P	182.15	1.068	–56.5	215	Colorless liquid with characteristic odor	
TBP	Tributyl phosphate	C12H27O4P	266.318	0.982	–80	288.88	Colorless, odorless, and viscous liquid	

2.2. PIM preparation

The organic solution of polymer was prepared by dissolving an appropriate amount of polymer in 20 mL of dichloromethane [40]. Another dichloromethane solution containing an appropriate amount of DNNSA in 15 mL of solvent was stirred and prepared for 15 min. Then, a plasticizer was added to the DNNSA solution. After mixing for 10 min, the solution was ultrasonicated for 2 min to obtain a homogeneous solution. This solution was added to the polymer solution and mixed for 60 min. The solvent of the mixed solution was allowed to evaporate through the overnight in a membrane mold comprising a 9.0 cm glass ring which attached to a glass plate with CTA-dichloromethane glue [41]. The synthesized membrane was separated from the glass plate by cutting the around of its circumference and immersing in the cold water. The membrane was peeled off carefully, and soaked in the aqueous solution (0.1 mol L^{-1}) for 12 h, then stored in the distilled water.

For preparing PIM containing nanoparticles, certain amount of nanoparticles was added to the carrier solution and ultrasonicated for 60 min. Then, the resulted homogenous solution was combined withthe polymer solution and stirred for 120 min by a magnetic stirrer. Then, the PIM containing nanoparticles was obtained by allowing the solvent evaporation. Indeed, the dichloromethane is a highly volatile solvent which evaporated rapidly (boiling point: 39.77°C at 760 mmHg), and dispersed nanoparticles without agglomeration. Hence, the nanoparticles were homogeneously dispersed after the solvent evaporation.

2.3. Membrane extraction experiment

The Co(II) extraction process has been demonstrated schematically in Fig. 3. The ions react at the source phase/membrane surface. The complexes of Co(II) and DNNSA diffuse through the membrane and finally, the ions are released at the receiving phase/membrane surface.

The membrane extraction experiment was carried out in a two-sided stainless steel ion extraction vessel that is showed in Fig. 4. The right side of the compartment was screwed to the other side tightly and the obtained force led to seal the equipment, properly. The membrane film was clamped tightly, between two sides byusing two rubber O-rings and their faceswere covered meticulously, to avoid any leakage. The source and receiving aqueous phases were separated by the membrane (diameter 31 mm). The volume of the aqueous solution in each side of the ion extraction vessel was 80 mL.

A mechanical stirrer with a glass impeller was employed to stir each aqueous phase which the stirring rate was equal for each side. The source phase was the citric acid/hydrogen phosphate buffer. In this way, 1 mL samples were periodically taken at the regular time intervals via sampling port by a syringe, from the source and receiving phases, and were analyzed to determine the cobaltcontent by inductively coupled plasma optical emission spectrometry. All experiments were accomplished at the room temperature.

2.4. Ion extraction through the membrane

The kinetics of extraction process through PIMs has been described as a first-order reaction according to Eq. (1) [42–44]:

$$\mathrm{Ln}\left(\frac{C_S}{C_i}\right) = -k \times t \tag{1}$$

where C_i and C_S are the Co(II) concentration at the initial and given time t (mg L^{-1}) in the source phase, respectively. Also, k is the rate constant (min^{-1}) and t is the extraction time (min). The value of the rate constant and the values of r^2 are calculated by plotting the $\mathrm{Ln}(C_S/C_i)$ vs. the time.

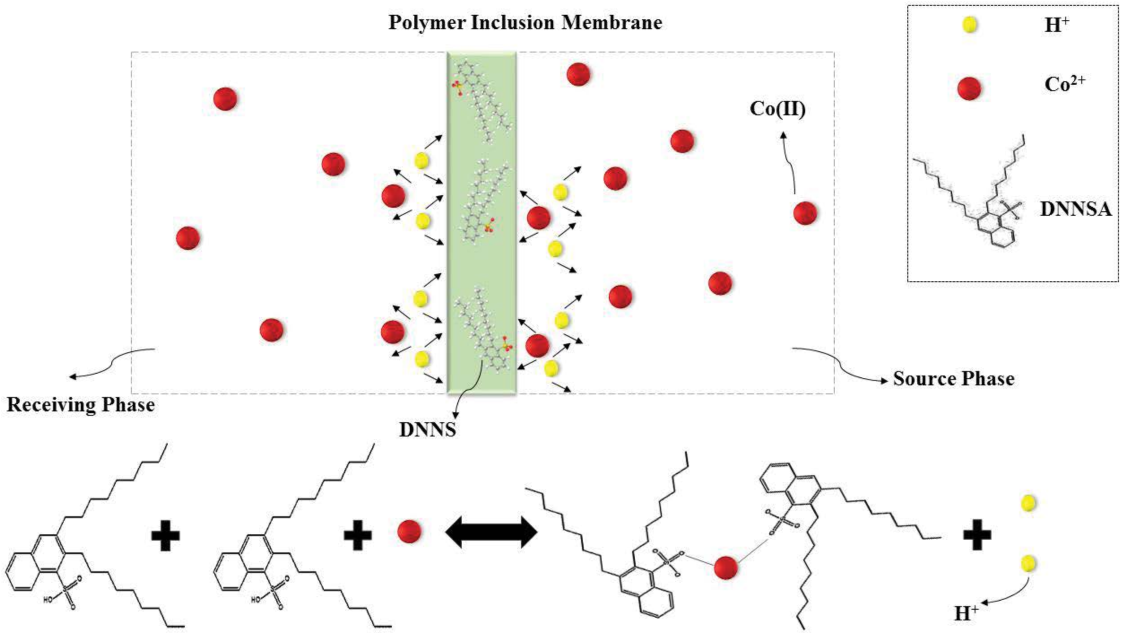


Fig. 3. The schematic of Co(II) extraction through the membrane.

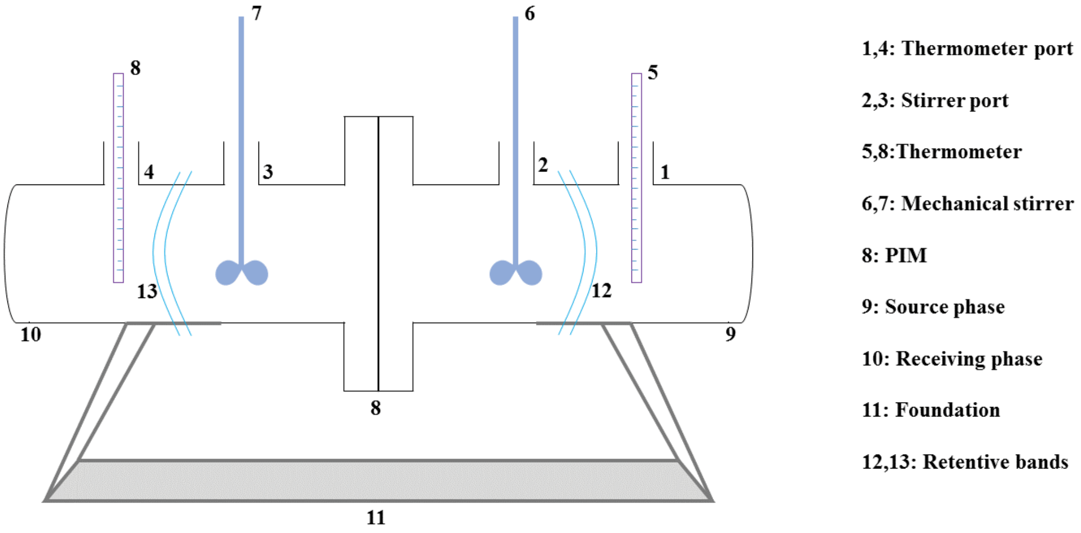


Fig. 4. The two-sided stainless steel ion extraction vessel used in experiments.

In the following (3.9 section), it has been proved that the ion extraction through the PIM is described as a first-order reaction. The permeability coefficient (*P*) is calculated using the following relation:

$$P = \left(\frac{V}{A}\right)k \tag{2}$$

here *V* is the volume of the source phase (m^3) and *A* implies the effective area of the membrane, which equals with 0.00075 m^2 [45]. Then, by employing the measured permeability coefficient, the initial membrane flux (J_i) can be determined by:

$$J_i = P \times C_i \tag{3}$$

To express the efficiency of Co(II) extraction from the source phase, the extraction (E) is considered, which can be calculated by the following equation [46]:

$$E = \frac{C_i - C_S}{C_i} \times 100 \tag{4}$$

2.5. Effect of the membrane composition

The values of CTA as apolymer were constant in all experiments. The effects of carrier amount in the membrane phase, plasticizer type and concentration were studied in three different experiments. The permeability coefficient, initial flux or the extraction value were calculated to investigate the type, amount of the plasticizer and the carrier concentration effects on the ion extraction efficiency.

2.5.1. Carrier concentration

PIMs with different concentrations of DNNSA as the carrier were synthesized. The concentrations of carriers, ranging from 5% to 35%wt., were tested to evaluate their effects on the cobalt extraction through the membrane. The membranes were contacted with an aqueous source phase at pH = 5, containing 40 mg L^{-1} Co(II) for 9 h. The receiving phase was contained 1 mol L^{-1} HCl. Also, both source and receiving phases were stirred at 200 rpm.

2.5.2. Type of plasticizer

In this study, dioctyl phthalate (DOP), dioctyl adipate (DOA), triethyl phosphate (TEP), and tributyl phosphate (TBP) were tested as plasticizers. The source phase was contained 40mg L^{-1} Co(II) at pH = 5, and the receiving phase was 1 mol L^{-1} HCl. The membranes were composed 15% the DNNSA, 62% the plasticizer, and 23% the CTA.

2.5.3. Concentration of plasticizer

To investigate the effect of the plasticizer concentration on the cobalt extraction, some experiments with PIMs containing 0.1211 g CTA, 0.0789 g DNNSA and variable amounts of DOA were conducted. The source phase was contained 40 mg L^{-1} Co(II) at pH = 5,also the receiving phase contained 1 mol L^{-1}. Both the source and receiving phases were stirred at 200 rpm.

2.6. Effect of aqueous phases

2.6.1. Rate of mixing

The source and receiving phases were stirred by three-bladed glass propellers, at eight different mixing rates: 50, 100, 150, 200, 250, 300, 350, and 400 rpm. The membrane was contained 23%wt. the CTA, 15% the DNNSA and 62% the DOA. The source phase was also contained 40 mg L^{-1} Co(II) and the receiving phase was 1 mol L^{-1}HCl.

2.6.2. pH of source phase

The Co(II) extraction is assumed to occur via the following chemical reaction at the membrane/aqueous source phase interface between the metal ions (Co^{2+}) and the DNNSA (HA):

$$\left(\mathrm{Co}^{2+}\right)_{\mathrm{aq}} + 2\left(\mathrm{HA}\right)_{m} \rightleftarrows \left(\mathrm{CoA}_2\right)_{m} + \left(2\mathrm{H}^{+}\right)_{\mathrm{aq}} \qquad (5)$$

In this equation *m* represents the concentration in the membrane and the aqsubscript displays the concentration in the aqueous source phase [47].

The pH gradient between the source and receiving phases is one of the most important driving forces for Co(II) ion permeation through the PIM. The DNNSA is an acidic extraction reagent. It is expected that the pH of the source phase affects the efficiency of the cobalt ion extraction [48]. The source phase was contained 40 mg L^{-1} of Co(II) at seven different pHs, and the receiving phase was also contained 1 mol L^{-1} HCl. Both phases were stirred at 200 rpm for 9 h. The membrane was composed of 23% the CTA, 15% the DNNSA, and 62% the DOA.

2.6.3. Initial ion concentration

The effect of Co(II) concentration in the source phase on the extraction was studied using solutions with differentinitial cobalt concentrations including:10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, and 160 mg L^{-1} at pH = 5 and the stirring rate of 200 rpm. The membrane wascontained 23% the CTA, 15% the DNNSA, and 62% the DOA.

2.6.4. Kind of receiving phase

Three aqueous solutions containing HCl, H_2SO_4, and HNO_3 with 1 mol L^{-1}acidity and ethylenediaminetetraacetic acid (EDTA) at pH = 5.5 as complexing agent were considered as receiving phases. The extractions were calculated after 7 h to compare the effect of each receiving phase on the ion extraction. In addition, the source phase containing 60mg L^{-1} Co(II) at pH = 5 was stirred at 200 rpm. The membrane was contained 23%wt. the CTA, 15% the DNNSA, and 62% the DOA.

2.6.5. Receiving phase acid concentration

A re-extraction reaction occurs on the opposite side of the membrane. In the re-extraction step, the carrier which is stripped, converted to the ionic form [49]. The re-extraction reaction associates with H^+ consumption [14]. Therefore, the H_2SO_4 concentration at the receiving phase affects the ion extraction. This process was considered as an important factor. The concentration of H_2SO_4 varied inthe range of 0.25 up to 2.5 M. The source phase was contained 60 mg L^{-1} Co(II) at pH = 5, and both phases were stirred at 200 rpm. The membrane was synthesized with 23% the CTA, 62% the DOA, and 15% the DNNSA as the carrier.

2.6.6. Kinetics of membrane extraction

The extraction through the PIM was studied by varying the DNNSA and DOA concentrations at the membrane phase also Co(II) concentration at the source phase, as shown in Table 2. The source phases were phosphate/citrate buffer at pH = 5 in all experiments, and receiving phases were 1 mol L^{-1} HCl.

3. Results and discussion

3.1. Carrier concentration

The extraction plot of the metal ions extraction process through the variable carrier concentrations is depicted in Fig. 5. As can be found, an increment of cobalt extraction was observed by increasing the DNNSA concentration in the membrane up to 15%wt. and beyond 15%wt., up to 35%wt., the Co(II) ion extraction was decreased, which the maximum extraction was obtained in 9 h for the membrane containing 15%wt. carrier.

The enhancement ofthe DNNSA concentration in the membrane increases two parameters simultaneously: the

Table 2
Membrane compositions and initial ion concentration for Co(II) extraction through CTA polymer inclusion membrane with DNNSA as ion carrier (pH of source phases were at pH = 5 and receiving phases were HCl 1 mol L^{-1})

	Membrane composition			Source phase
	Plasticizer (%wt)	DNNSA (%wt)	CTA (%wt)	Initial ion concentration (mg L^{-1})
1	62% DOA	15	23	40
2	62% DOA	15	23	60
3	62% TBP	15	23	40
4	50% DOA	15	35	40
5	40% DOA	15	45	40
6	66% DOA	10	24	40

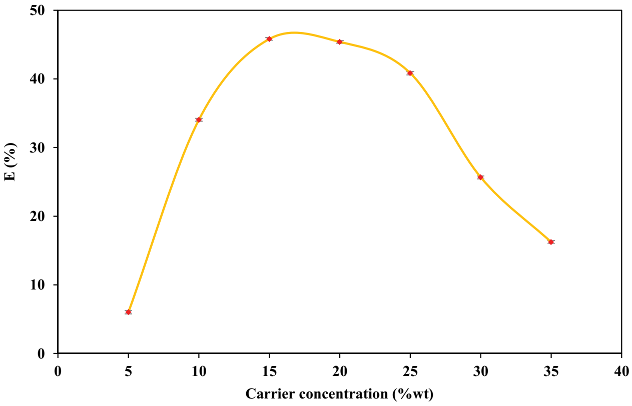


Fig. 5. Effect of DNNS concentration in the casting solution on the extraction of Co(II) (80 mL aqueous phases, citrate buffer at pH = 5 and 40 mg L^{-1} Co(II) solution as source phase; 1 mol L^{-1} HCl as receiving phase; 0.1211 g CTA as polymer and 0.3263 g DOA as plasticizer in the PIM structure).

carrier-ion complex concentration and the membrane viscosity. Increasing the carrier-ion complex concentration enhances the ion concentration gradient through the membrane. Consequently, the extraction increases due to the more driving force [50]. On the other hand, at the higher concentration, than 15%wt. of the carrier, the membrane becomes more viscous, thus the higher viscosity restricts the ion extraction [50,51]. Also, as can be observed, an extra amount of the carrier inside the polymer network over 15%wt. causes a maximum value in the extraction through the carrier concentration [14]. It indicates that anabundant mass of the created complexes at the interface of the membrane tends to diffuse through the pathways formed in the membrane. The lack of accessibility to transportpathways as well as, the increase of viscosity by the enhancement of the carrier concentration, led to a reduction in the extraction efficiency. Hence, the rate limiting step is the complexes diffusion through the membrane [51,52].

3.2. Type of plasticizer

The existence of plasticizer affects the membrane flexibility and softness. The plasticizer provides a flexible phase in which, the metal ion complex species can diffuse. The plasticizer polar groups that are imported between the polymer polar groups, neutralize them. Thus, the intermolecular forces reduce, also the distance between the polymer molecules increases; consequently, the ion extraction can be facilitated [14].

The permeability and initial flux have been considered to investigate the effect of different plasticizers. Results have been reported in Table 3. As can be observed, the DOA has the highest permeability and the initial flux, also the DOP has the lowest quantity. The permeability and the initial flux value decrease in order: DOP < TEP < TBP < DOA. It is worth mentioning that the main reason for this behavior is usually attributed to the plasticizer's physicochemical nature (including polarity and viscosity). Some physicochemical properties of four different plasticizers such as, the dielectric constant and viscosity are tabulated in Table 3 [53].

It can be seen from Table 3 that the viscosity of the DOP is much greater than the TEP and the TBP, so the initial flux slumps, significantly. As observed in Table 3, the TEP and the TBP have similar physicochemical properties, and consequently, the permeability and the initial flux are almost the same. On the other hand, the DOP has clearly a lower initial flux and permeability than DOA, because of higher viscosity of the DOP than the DOA and the same dielectric constant.

Table 3
Physicochemical parameters of plasticizers and effect of plasticizer type on Co(II) extraction through the PIM

Plasticizer	Dielectric constant (ε_r)	Viscosity (cP)	$P_i \times 10^7$ (m s^{-1})	$J_i \times 10^7$ (mol m^{-2} s^{-1})
DOA	5	14	2.12	1.44
DOP	5.1	54.8	0.42	0.29
TEP	13	1.6	0.95	0.65
TBP	8.3	3.3	1.06	0.72

3.3. Concentration of plasticizer

In this study, the enhancement of the amount of the DOA presented higher permeability up to 62%wt., and beyond of 62%wt. of the DOA resulted a reduction in the extraction (can be seen in Fig. 6). The permeability of the Co(II) was enhanced by increasing the concentration of the DOA up to 62%wt. As a result, the extraction of Co(II) was increased up to 62%wt. of the DOA; however, at the concentration of DOA higher than 62%wt., a reduction in the extraction of Co(II) was seen, which could be attributed to the lower mass transfer, due to the enhancement in the thickness and viscosity of the membrane [50,54].

Evidently, more thickness (Table 4) and viscosity detracted the ion diffusion rate based on the Fick's law and the Stokes–Einstein relation, respectively. Thus, the ion extraction is inversely proportional to the membrane thickness and viscosity [50,54].

3.4. Rate of mixing

Obviously, the increment of the rate of solution stirring reduces the stagnant liquid layer thickness which is near the membrane surface to the minimum size. Thus, the mass transfer increases, but the overall mass transfer coefficient is generally dominated by the diffusion through the membrane rather than, the stagnant liquid layer [54]. According to Fig. 7,

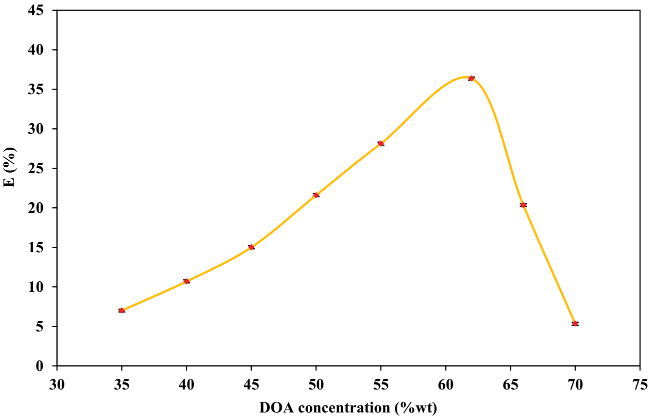


Fig. 6. Effect of DOA concentration in the casting solution on the extraction of Co(II) (80 mL aqueous phases, citrate buffer at pH = 5 and 40 mg L^{-1} Co(II) solution as source phase; 1 mol L^{-1} HCl as receiving phase; 0.1211 g CTA as polymer and 0.0789 g DNNSA as carrier in the PIM structure).

Table 4
Concentration of plasticizer Vs. Thickness of membrane (PIM contained 0.1211 g CTA, 0.0789 g DNNSA, and different quantities of DOA)

Concentration of plasticizer (%wt)	Thickness of membrane (μm)
40	59.9
50	65.3
62	71.1
72	76.6

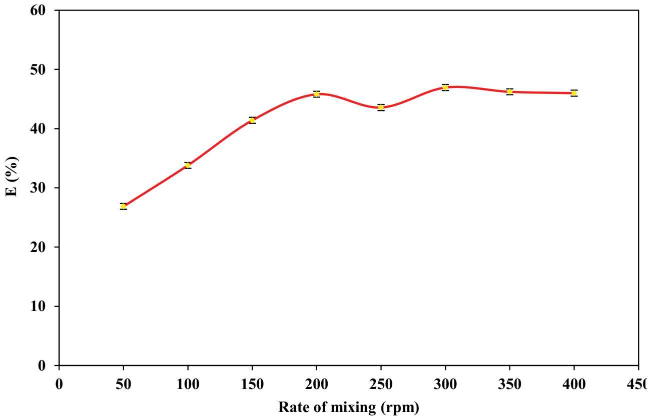


Fig. 7. Effect of mixing rate on the extraction of Co(II) (80 mL aqueous phases, citrate buffer at pH = 5 and 40 mg L^{-1} Co(II) solution as source phase; 1 mol L^{-1} HCl as receiving phase; 0.1211 g CTA as polymer, 0.0789 g DNNSA as carrier, and 0.3263 g DOA as plasticizer in the PIM structure).

mixing rate has been identified as a major contributory agent to the enhancement of Co(II) extraction up to 200 rpm, after that, the extraction of Co(II) is almost stable.

This observation proves that the total mass transfer is dominated by the diffusion of Co(II)/DNNSA complexes through the membrane, and consequently, the thickness of the stagnant liquid layers at the two membrane/solution interfaces cannot affect the overall extraction rate more than 200 rpm.

3.5. pH of source phase

The relation between the extraction of Co(II) and the pH of the source phase is shown in Fig. 8. The results showed that the extraction is maximized at pH = 5. Cobalt(II) extraction decreases at pH < 5, because of the reduction of the driving force between the source and the receiving phases.

Beyond the pH = 5, the ion extraction decreases also which it can be attributed to the hydroxide formation and the reduction of Co(II) solubility [19]. The formed $Co(OH)_2$ in the source phase is neutral to the carrier, and does not react with it. Consequently, it remains in the source phase permanently, and does not participate in the extraction process.

3.6. Initial ion concentration

The influence of the initial ion concentration on the extraction of Co(II) by DNNSA as a carrier was investigated in the range between 10–160 mg L^{-1}of initial ion concentration. The effect of the cobalt ion concentration in the source phase on the extraction is illustrated in Fig. 9. As can be observed, the extraction values enhanced by increasing the Co(II) ions concentration up to 60 mg L^{-1}. The difference between the cobalt ion concentration of the source and receiving phase is one of the most important driving forces that reinforces the extraction of the ions through the membrane. As the Co(II) concentration in the source phase raises, the driving force also increases. On the other hand, the enhancement of the carrier active sites reacted with the cobalt ions at the membrane/source phase interface with the increment of cobalt concentration in the source phase is another reason for elevating the extraction of Co(II). Beyond the 60 mg L^{-1} of Co(II) concentration, a reduction in the cobalt extraction was observed. This observation does not follow other reports [52], and it is comparable with Raut et al. [55] and Arslan et al. [14] studies. It should be noticed that the range of the investigated ion concentration must cover the entire range that affects the extraction. The Co(II) ions extraction beyond the 60mg L^{-1}was controlled by the diffusion of the cobalt ions species through the membrane. The decrease of extraction of Co(II) can be contributed to the diffusion rate reduction.

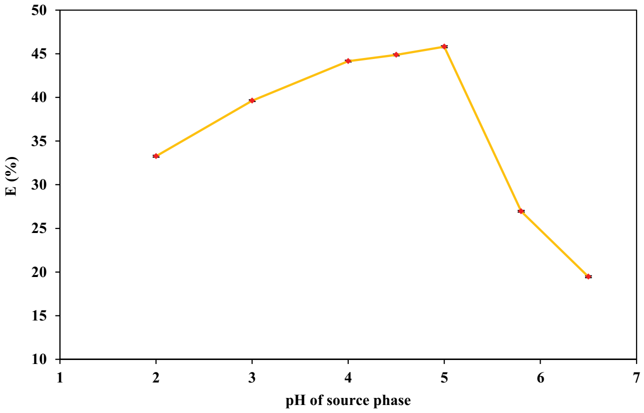


Fig. 8. Effect of pH of source phase on the extraction of Co(II) (80 mL aqueous phases, citrate buffer at different pH and 40 mg L^{-1} Co(II) solution as source phase; 1 mol L^{-1} HCl as receiving phase; 0.1211 g CTA as polymer, 0.0789 g DNNSA as carrier, and 0.3263 g DOA as plasticizer in the PIM structure).

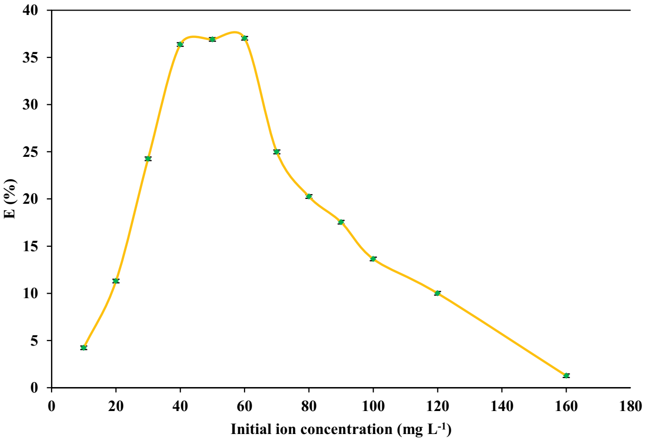


Fig. 9. Effect of initial ion (Co^{2+}) concentration on the extraction of Co(II) (80 mL aqueous phases, citrate buffer at pH = 5 as source phase and 1 mol L^{-1} HCl as receiving phase; 0.1211 g CTA as polymer, 0.0789 g DNNSA as carrier, and 0.3263 g DOA as plasticizer in the PIM structure).

3.7. Kind of receiving phase

It can be found from Eq. (5) that Co(II)/carrier complex formation needs low acidity. Moreover, in order to strip the metal ions from the membrane phase, the receiving phase should contain either higher concentration of the acid (as compared with the source) or a solution containing a ligand with a high complex ability towards the metal ion extraction. As shown in Fig. 10, different kinds of acids in the receiving compartment have similar effect on the Co(II) stripping, also the complexing agent EDTA due to low acidityis not an effective stripper. To explain this behavior, it should be considered that the basic important parameter to strip the cobalt ions is receiving phase acidity, and the kind of the acid is notdeterminative.

3.8. Receiving phase acid concentration

As the metal-extraction reaction occurs at the source phase/membrane interface, a simultaneous re-extraction step on the receiving phase/membrane side for extraction of Co(II) is also required. If the cobalt complexis not completely extracted from the membrane phase, the saturated membrane with the complex results in the extraction process to a lower efficiency. As a result, the rate of permeation decreases, drastically. Therefore, the acid concentration of the receiving phase also affects the Co(II) extraction efficiency [14]. According to Eq. (5), increasing the H^+ concentration gradient across the membrane increases the driving force of the Co(II) extraction process [47]. One of the possible ways to increase the H^+ concentration gradient is the increment ofthe acid concentration at the receiving phase. It is clear that the higher acid concentration in the receiving phase elevates the driving force. But the higher acid concentration may cause the degradation of the PIM and the extraction compartment. In fact, the reduction of H^+ ion concentration in the source phase leads to the formation of more Co(II)/carrier complexes at the membrane interface, and also the enhancement of H^+ ion concentration in the receiving phase helps to strip more Co(II) ions. As shown in Fig. 11, the increase of the H_2SO_4 concentration in the receiving phase (until 1.25 mol L^{-1}), contributed to the higher ion extraction and afterthat, no significant change was observed.

3.9. Kinetics of membrane extraction of Co(II)

The kinetics dependence of ln(c/ci) versus time for Co (II) extraction across the PIM is depicted in Fig. 12. As seen, the calculated r^2 values for six different conditions (Table 2) represent that the kinetics of the ion extraction across the PIMs is truly described as a first-order reaction in the metal-ion concentration [56]. The kinetics parameters for each experiment have been summarized in Table 5.

3.10. Long term extraction experiment

In this work, a 54 h test was accomplished with the aim of removing all Co(II) content from the source phase. The membrane was contained 15%wt. the DNNSA, 62%wt. the DOA, and 23%wt. the CTA. The source phase had 60 mg L^{-1} the cobalt ion at pH = 5 and the receiving phase was contained 1.25 mol L^{-1} of H_2SO_4. The samples were taken at the regular time intervals from the source and receiving phases to detect the Co(II) concentration. The results are shown in Fig. 13. It can be seen that the Co(II) ion concentration in the source phase after 54 h became about 1.4 mg L^{-1}. In other words, the extraction after 54 h was 97.8% which demonstrates that the heavy metal content of the source phase was almost removed with the rate constant (k) of 1.13 × 10^{-3} min^{-1}.

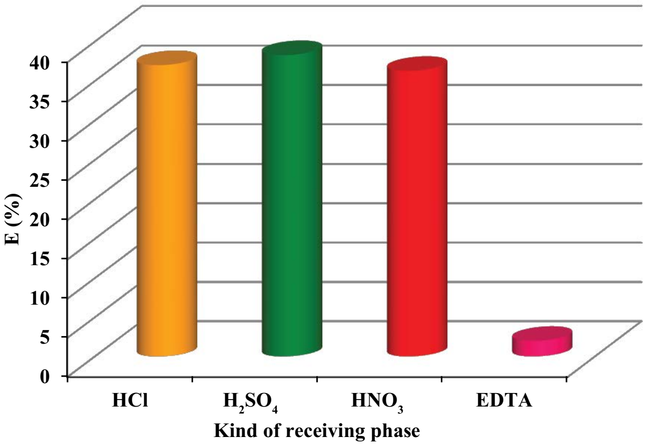


Fig. 10. Effect of kind of receiving phase on the extraction of Co(II) (80 mL aqueous phases, citrate buffer at pH = 5 and 60 mg L^{-1} Co(II) solution as source phase; 1 mol L^{-1} HCl as receiving phase; 0.1211 g CTA as polymer, 0.0789 g DNNSA as carrier, and 0.3263 g DOA as plasticizer in the PIM structure).

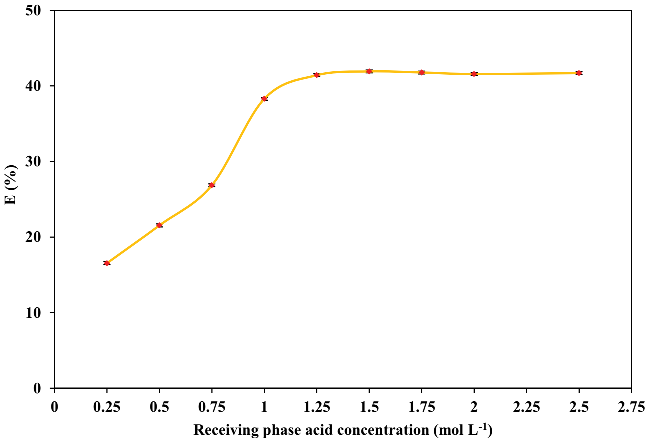


Fig. 11. Effect of receiving phase acid concentration on the extraction of Co(II) (80 mL aqueous phases, citrate buffer at pH = 5 and 60 mg L^{-1} Co(II) solution as source phase; variant concentration of H_2SO_4 as receiving phase; 0.1211 g CTA as polymer, 0.0789 g DNNSA as carrier, and 0.3263 g DOA as plasticizer in the PIM structure).

3.11. Reproducibility of the Co(II) extraction

One of the most important advantages of the PIMs is their durability. The reproducibility of Co(II) extraction was investigated with the PIM composed of 15%wt. the DNNSA and 62%wt. the DOA. In these extraction experiments, the membrane was involved in 10 replicate measurements, each one lasting for 14 h as repeated every 24 h. At each cycle, the feed and the stripping phases were renewed. The extraction varied slightly, and no sign of structural weakness was observed for the PIM. As an example, the results of the stability of the employed PIM in the experiments has been

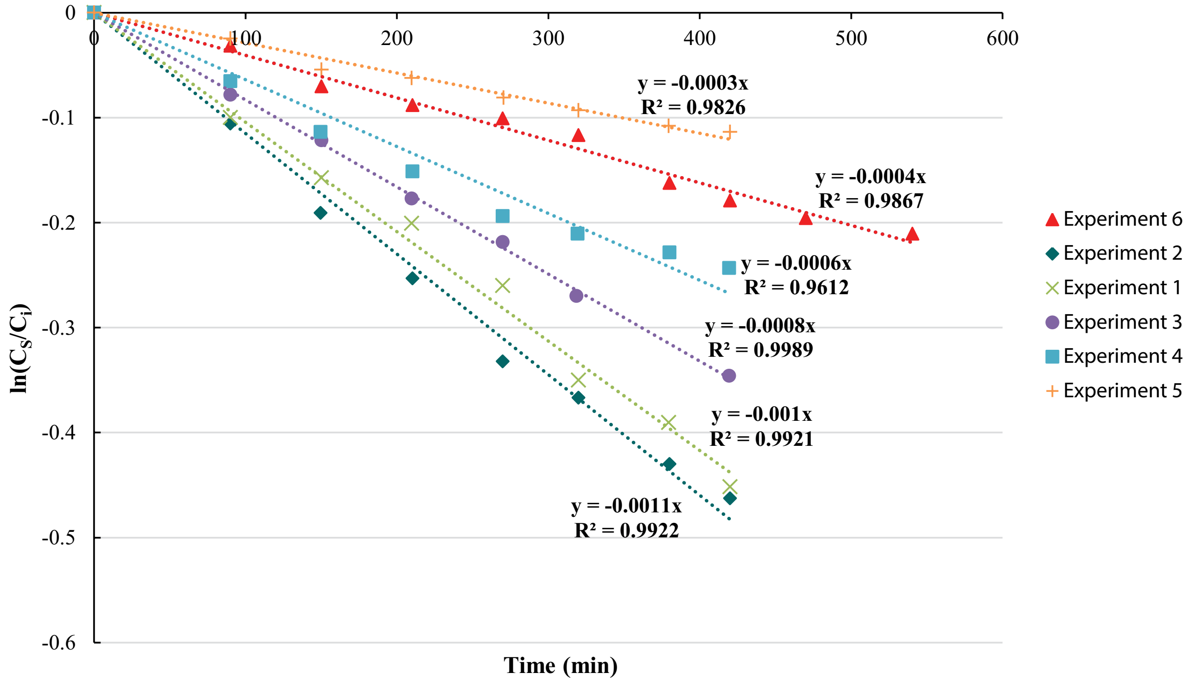


Fig. 12. The kinetics dependence of ln(c/ci) versus time for Co(II) extraction through PIMs with different compositions and various aqueous phase conditions referred in Table 2.

Table 5
Kinetic parameters for Co(II) extraction through CTA polymer inclusion membranes with different compositions and various aqueous phase conditions

	Rate Constants, $k \times 10^5(s^{-1})$	Permeability Coefficient, $P_i \times 10^7$ (m s^{-1})	Initial Flux, $J_i \times 10^7$ (mol m^{-2} s^{-1})
1	1.67	17.78	12.07
2	1.83	19.56	19.91
3	1.33	14.22	9.66
4	1.00	10.67	7.24
5	0.50	5.33	3.62
6	0.67	7.11	4.83

reported in Table 6.These results prove the high stability of PIMs [14,57]. On the other hand, when the initial ion concentration, pH of the source phase, receiving phase acid (H_2SO_4) concentration were 60 mg L^{-1}, 5 and 1.25 mol L^{-1}, respectively, the standard deviation was 1% (standard error = 0.19) for 10 experiments (Table 6). This low standard deviation approved that the outcomes are clustered closely around the mean value and highly reliable [58,59].

3.12. Effect of nanoparticles on Co(II) extraction

In this work, the PIMs containing nanoparticles were also studied. To this goal, nanoparticles were added to the membrane with 15%wt. the DNNSA, 62%wt. the DOA, and 23%wt. the CTA. The source phase was an aqueous solution at pH = 5 and contained 60 mg L^{-1}Co (II). The receiving phase was H_2SO_4 1.25 mol L^{-1} and both phases were stirred at 200 rpm. Each test was performed for a period of 24 h. The obtained results are illustrated in Fig. 14.

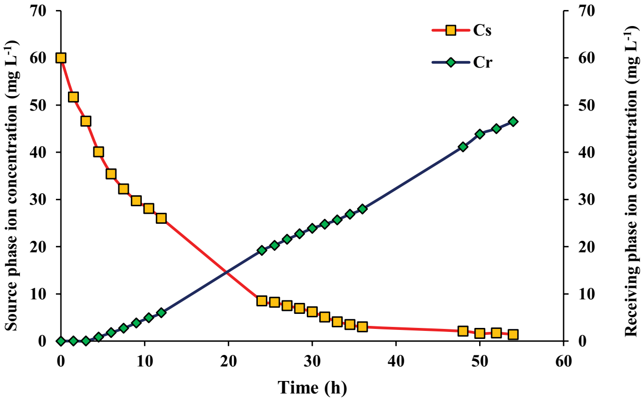


Fig. 13. Long term experiment to remove the Co(II) content of source phase (80 mL aqueous phases, citrate buffer at pH = 5 and 60 mg L^{-1} Co(II) solution as source phase; H_2SO_4 1.25 mol L^{-1} as receiving phase; 0.1211 g CTA as polymer, 0.0789 g DNNSA as carrier, and 0.3263 g DOA as plasticizer in the PIM structure)

As previously mentioned, complex diffusion through the PIM is the rate limiting step in theion transport process; hence, the increase of diffusion inside the PIM leads to the enhancement of the cobalt extraction efficiency. Nanoparticles were applied due to their specific characteristics to enhance the diffusion inside the PIM structure. Interestingly, it was observed that the cobalt extraction was modified by adding 20%wt. SiO_2 and TiO_2 as nanoparticles, separately, but no enhancement was observed by adding Fe_3O_4. These outcomes

Table 6
Co(II) extraction at replicate measurements, each one lasting for 14 h, repeated 24 h working cycles for PIM containing 15%wt. of DNNSA, 62%wt. DOA, and 23%wt. CTA

Cycle number	%E
1	61.9
2	61.6
3	62.3
4	61.4
5	62.1
6	61.9
7	60.8
8	62.1
9	60.4
10	61.3

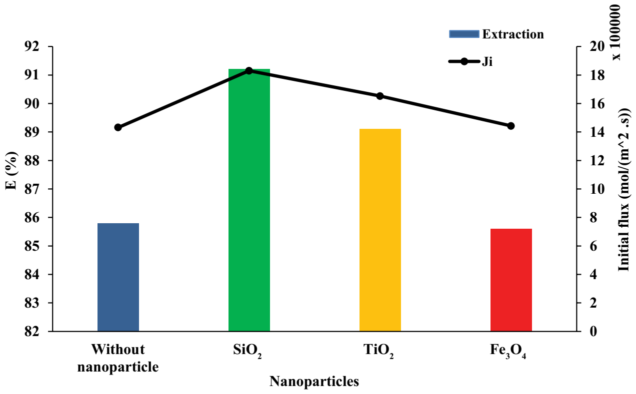


Fig. 14: Effect of 20%wt. (of total membrane weight) nanoparticles on Co(II) extraction (80 mL aqueous phases, citrate buffer at pH = 5 and 60 mg L^{-1} Co(II) solution as source phase; H_2SO_4 1.25 mol L^{-1} as receiving phase; after 24 h of experiment; 0.1211 g CTA as polymer, 0.0789 g DNNSA as carrier, and 0.3263 g DOA as plasticizer in the PIM structure).

have some important results which formerly was reported in some works [60–63], adding nanoparticles changes the PIM structure, and it facilitates the ion permeation through the membrane.

To best of our knowledge, there is not any similar study about the PIM containing nanoparticles. The cobalt extraction depends on the ion diffusion through the membrane. As we know, diffusion coefficient (D) increases by adding the nanoparticles to the membrane structure. The presence of nanoparticles in the PIM structure affects the ion extraction by disrupting the interaction between the polymer chain segment [32], and facilitating the complex transport through the PIM structure [35,64]. It can be seen from Fig. 14 that the SiO_2 and TiO_2 increased the ion extraction 5.4% and 3.3%, respectively, but Fe_3O_4 didn't affect the ion extraction. As previously mentioned, one of the most important parameter to facilitate the ion extraction is the difference between the acidity of the source and receiving phases. The Fe_3O_4 nanoparticles have high proton conductivity, thus the nanoparticles extract the H^+ ions from the receiving phase to the source phase. Hence, the acidity of the receiving phase is declined and the source phase is increased. Based on Eq. 5, this phenomenon adversely affects the ion extraction and compensates the modified effect of Fe_3O_4 addition to the PIM structure [65].

A summary of all experimental values of various tests for cobalt recovery and water treatment have been presented in Supplementary Information.

4. Conclusions

In this work, effective extraction of Co(II) through the PIM containing the DNNSA as ion carrier was studied. The extraction of the cobalt ion depends on different parameters comprising membrane structure and aqueous phase parameters. In this way, the carrier concentration, type of plasticizer, concentration of plasticizer as the membrane structure parameters also, the rate of aqueous phases mixing, initial ion concentration, pH of source phase, kind of receiving phase, receiving phase acid concentration as aqueous phases parameters were investigated, respectively. The results showed that the extraction of Co(II) ions enhanced by increasing the mixing rate up to 200 rpm, and after that became constant. The effect of pH and the initial Co(II) ion concentration on the extraction were considered between 2–6.5 mg L^{-1} and 10–160 mg L^{-1}. Also, the most efficient pH and the initial ion concentration were found as 5 and 60 mg L^{-1}, respectively. In addition, H_2SO_4 1.25 mol L^{-1} was determined to be the best receiving phase to strip the cobalt ion from the membrane phase. Based on the obtained results, Co(II)/DNNSA complexes diffusion through the membrane was the rate limiting step between the three steps of Co(II) transport, including: complexation, complex diffusion, and decomplexation.The kineticwas also studied and found it follows the first-order. A long term experiment with the aim of extraction of all cobalt ion content from the source phase was performed for 54 h and finally, the extraction was detected to be 97.8%. Indeed, this PIM is applicable for lab scale studies, and based on its capacities, it must be developed for larger scales. The reproducibility of the Co(II) extraction was investigated with 10 replicate measurements and found that the extraction varied slightly. In the final step, the effect of the nanoparticles on Co(II) extraction was considered and SiO_2 was determined as the most effective modifier. In addition, the optimal membrane compositions were detected including 15%wt. the DNNSA, 62%wt. the DOA as plasticizer, 23%wt. the CTA and modified by SiO_2 with 20%wt. of the PIM total weight.

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Supplementary Information

Summary of experimental data of different tests of Co(II) recovery to water treatment.

No.	Carrier concentration	Plasticizer	Polymer	Initial ion concentration (mg L^{-1})	pH of source phase	Receiving phase	Time (h)	Aqueous phase mixing rate (rpm)	*E* (%)	Nano-particle
1	DNNSA 0.0235 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	200	6.02	–
2	DNNSA 0.0497 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	200	34.04	–
3	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	200	45.80	–
4	DNNSA 0.1119 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	200	45.39	–
5	DNNSA 0.1491 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	200	40.85	–
6	DNNSA 0.1917 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	200	25.67	–
7	DNNSA 0.2409 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	200	16.23	–
8	DNNSA 0.0789 g	DOP 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	7	200	8.98	–
9	DNNSA 0.0789 g	TEP 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	7	200	12.59	–
10	DNNSA 0.0789 g	TBP 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	7	200	29.51	–
11	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	7	200	36.36	–
12	DNNSA 0.0789 g	DOA 0.1077 g	CTA 0.1211 g	40	5	1 M HCl	7	200	7.01	–
13	DNNSA 0.0789 g	DOA 0.1333 g	CTA 0.1211 g	40	5	1 M HCl	7	200	10.69	–
14	DNNSA 0.0789 g	DOA 0.1636 g	CTA 0.1211 g	40	5	1 M HCl	7	200	15.02	–
15	DNNSA 0.0789 g	DOA 0.2000 g	CTA 0.1211 g	40	5	1 M HCl	7	200	21.60	–
16	DNNSA 0.0789 g	DOA 0.2444 g	CTA 0.1211 g	40	5	1 M HCl	7	200	28.13	–
17	DNNSA 0.0789 g	DOA 0.3882 g	CTA 0.1211 g	40	5	1 M HCl	7	200	20.32	–
18	DNNSA 0.0789 g	DOA 0.4667 g	CTA 0.1211 g	40	5	1 M HCl	7	200	5.34	–
19	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	50	26.86	–
20	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	100	33.80	–
21	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	150	41.40	–
22	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	200	45.80	–
23	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	250	43.57	–
24	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	300	46.94	–
25	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	350	46.22	–
26	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	5	1 M HCl	9	400	45.99	–
27	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	2	1 M HCl	9	200	33.26	–
28	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	3	1 M HCl	9	200	39.62	–
29	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	4	1 M HCl	9	200	44.15	–
30	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	4.5	1 M HCl	9	200	44.87	–
31	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	5.8	1 M HCl	9	200	26.95	–
32	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	40	6.5	1 M HCl	9	200	19.47	–
33	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	10	5	1 M HCl	7	200	4.23	–
34	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	20	5	1 M HCl	7	200	11.30	–
35	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	30	5	1 M HCl	7	200	24.27	–
36	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	50	5	1 M HCl	7	200	36.91	–
37	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1 M HCl	7	200	37.02	–
38	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	70	5	1 M HCl	7	200	24.99	–
39	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	80	5	1 M HCl	7	200	20.25	–
40	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	90	5	1 M HCl	7	200	17.54	–
41	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	100	5	1 M HCl	7	200	13.64	–
42	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	120	5	1 M HCl	7	200	10.03	–
43	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	160	5	1 M HCl	7	200	1.27	–
44	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1 M H_2SO_4	7	200	38.29	–
45	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1 M HNO_3	7	200	36.29	–

(continued)

No.	Carrier concentration	Plasticizer	Polymer	Initial ion concentration (mg L^{-1})	pH of source phase	Receiving phase	Time (h)	Aqueous phase mixing rate (rpm)	*E* (%)	Nano-particle
46	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	EDTA at pH = 5.5	7	200	2.00	–
47	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	0.25 M H_2SO_4	7	200	16.54	–
48	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	0.5 M H_2SO_4	7	200	21.55	–
49	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	0.75 M H_2SO_4	7	200	26.85	–
50	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	7	200	41.41	–
51	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.5 M H_2SO_4	7	200	41.91	–
52	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.5 M H_2SO_4	7	200	41.77	–
53	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	2 M H_2SO_4	7	200	41.56	–
54	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	2.5 M H_2SO_4	7	200	41.69	–
55	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	1.5	200	13.83	–
56	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	3	200	22.33	–
57	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	4.5	200	33.17	–
58	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	6	200	41.00	–
59	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	7.5	200	46.33	–
60	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	9	200	50.50	–
61	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	10.5	200	53.17	–
62	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	12	200	56.67	–
63	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	24	200	85.83	–
64	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	25.5	200	86.33	–
65	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	27	200	87.50	–
66	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	28.5	200	88.5	–
67	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	30	200	89.67	–
68	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	31.5	200	91.5	–
69	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	33	200	93.17	–
70		DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	34.5	200	94.17	–
71	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	36	200	95.00	–
72	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	48	200	95.5	–
73	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	50	200	97.33	–
74	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	52	200	97.17	–
75	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	54	200	97.77	–
76	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	10	200	61.9	–
77	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	10	200	61.6	–
78	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	10	200	62.3	–
79	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	10	200	61.4	–
80	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	10	200	62.1	–
81	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	10	200	61.9	–
82	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	10	200	60.8	–
83	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	10	200	62.1	–
84	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	10	200	60.4	–
85	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	10	200	61.3	–
86	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	24	200	91.2	SiO_2
87	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	24	200	89.1	TiO_2
88	DNNSA 0.0789 g	DOA 0.3263 g	CTA 0.1211 g	60	5	1.25 M H_2SO_4	24	200	85.4	Fe_3O_4