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Separation of nickel from cobalt using cation exchange membranes in the presence of chelating agents

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ABSTRACT

Selectivity of metals from aqueous solutions containing chelating agents such as EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid) and citrate was studied in a two-chamber cell separating with a commercial cation-exchange membrane (CEM). In the experiments, equimolar solutions of metal and chelating agent as an anolyte and acid solutions as a catholyte were used, the effect of current density, type of solvent, concentration of catholyte and anolyte solution, type of chelating agent, type of the cation-exchange membrane on the selectivity for metals were determined. The obtained results show that this membrane technique, classified as electrodeposition and electrodialysis, seems to be an applicable method for the selectivity of metals under appropriate conditions.

Keywords: Separation; Chelating agent; Cation-exchange membrane; Electrodialysis; Electrodeposition

1. Introduction

Various separation membranes such as membranes for microfiltration, nanofiltration, ultrafiltration, reverse osmosis, pervaporation, gas separation and liquid membranes, etc. are generally studied and industrially used. The ion-exchange membrane is one of the most advanced separation membranes among these separation membranes. The essential property of the cation-exchange membrane and anion-exchange membrane is to selectively permeate cations or anions through the membrane. Since the first publication of the preparation of the ion-exchange membrane, more than half a century has passed. The performance of the ion-exchange membranes has been extremely improved during this period due to extensive studies [1,2]. The ion-exchange membrane is generally used in the solutions containing multi-ions: electrodialytic concentration of seawater to produce sodium chloride, desalination of saline water to produce potable water, demineralization of whey, acid and alkali recovery from waste acid [3] and alkali solutions [4] by diffusion dialysis, etc. In addition to this; ion-exchange membranes having monovalent ion permselectivity were developed and have been industrially used [5]. Separation of specific ions from the mixture by electrodialysis is also important in hydrometallurgy together with acid recovery by membranes [6]. Electrodialysis using ion-exchange membranes can be continuously operated and do not require any acids, alkalis and organic solvents. Permselectivity among cations through cation-exchange membranes in electrodialysis is also governed by the affinity of the cations with the membranes and the difference of the migration speed of the respective cations in the membrane phase [7].

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In this work, attention was paid to separation of nickel from cobalt. The separation of cobalt and nickel is difficult because of the similarities in their properties. The methods in use also do not tend to be more efficient in removing nickel from cobalt. Most of them are based on differences in the solubilities or the kinetic or the thermodynamic stabilities of their chemical compounds. But it was determined by some researchers that the use of electrodialysis for separation of cobalt and nickel has been achieved using ion-exchange membranes in the presence of EDTA exploiting a difference in the solubility constants of Ni-EDTA and Co-EDTA complexes [8].

From the point of this view, this study combined the two possibilities in its body: separation and electrodeposition. For this aim; binary complexed solutions of Co(II) and Ni(II) with EDTA, NTA and citrate were selected. Experiments were carried out by taking at equimolar chelating agents — metals as a function of current densities, type of solvent, concentration, type of chelating agent, the type of the cation-exchange membrane.

2. Experimental

2.1. Materials

All chemicals were purchased from Merck and were reagent grade. The anolyte solution was prepared by dissolving the sulphate salts of nickel ($NiSO_4.6H_2O$) and cobalt ($CoSO_4.7H_2O$) and chelating agent in 0.01 M H_2SO_4 at equimolar per metal ion (1 mM) and 2 mM for chelating agent. The pH of resulting anolyte solution was between 1.18–1.94 when the acid solution used as a solvent. The catholyte solution is 0.01 M H_2SO_4 but when the effect of pH was studied, KCl and NaOH were tried as a catholyte solution and its pH changed from 1.36 to 11.79. The cation exchange membranes selected in this work were Neosepta CMB, CMS and CMX kindly offered from Eurodia Co. The properties of these cation-exchange membranes are given in Table 1 [9]. All membrane samples (7.065 cm^2) were applied due to the pretreatments which were mentioned in our previous works [10–14].

2.2. Electrodialysis using a two-compartment cell

The apparatus for electrodeposition experiments is illustrated in Fig. 1, which was made of polyamide. This cell consisted of two chambers which were attached by means of inserting two screws on their flanges with a cation-exchange membrane in between. The membrane was cut as a circle with a diameter of 3 cm and glued into the inner mounting wall of the two chambers with silicone rubber sealant to prevent any leakage between the chambers. The electrodes were fitted in the inner wall of apparatus and were symmetrically separated about 65 mm from the membrane surface. Stainless steel and Pt were used as a cathode and anode, respectively and their active dimensions were 19.625 cm^2. The flow of solutions was performed by peristaltic pump (913 Mity Flex, double-way). The power supply used in elelectrodialysis experiments was capable of supplying a potential of up to 32 V and a direct current of up to 2 Å.

250 mL solutions for both of the part of the cell were presented and circulated during the experiments via us-

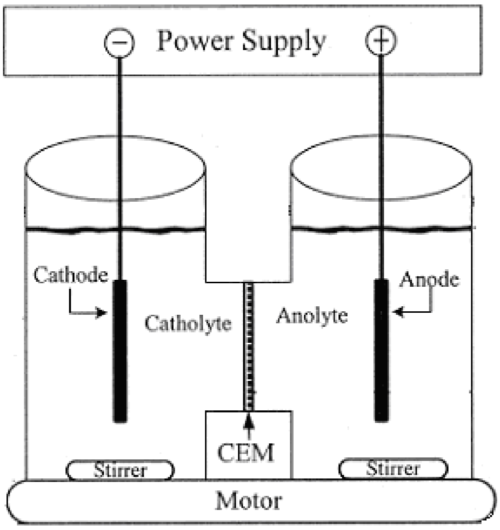

Fig. 1. The diagram used for electrodialysis experiments.

Table 1
Properties of the cation exchange membranes

Membrane	CMB	CMS	CMX
Type	Strongly acidic cation permeable	Strongly acidic cation permeable	Strongly acidic cation permeable
Characteristics	High mechanical strength (Na form)	Mono-cation permselective (Na form)	High mechanical strength (Na form)
Ion exchange capacity (meq/g)	2.7–2.8	2.0–2.5	1.5–1.8
Water content (%)	33–41	35–45	25–30
Thickness (mm)	220–260	140–170	170–190
Burst strenght (Ω-cm^2)	3.0–5.0	1.5–3.5	2.0–3.5

ing pump in order to provide 40 mL solution for anodic and cathodic cell. The experiments were carried out at the constant current by changing the cell voltage according to the variation of the resistance. The pH values of the anolyte and the catholyte solutions were measured with Orion EA 940 pH meter. Samples were taken as 5 mL and diluted to 25 mL at time intervals (for 15 min) from the anode chamber. The concentration of Ni(II) and Co(II) ions was analyzed by an atomic absorption spectrophotometer (Unicam 929). The actual amount of metal deposited onto the cathode was determined by calculation from the actual metal concentrations in the solution changed with time. The experiments were performed at 25±1°C. Each experiment was duplicated under identical conditions.

3. Results and discussion

3.1. Reactions involved in the electrodialysis cell

Citric acid, NTA and EDTA are all polyprotic acids (H_xL) which can exist in many protonated forms in aqeous solutions. They form stable chelates with most divalent metals in a 1:1 molar ratio over a rather wide pH range [15].

The catholyte pH increased during electrodialysis due to the production of OH^- at the cathode. In addition, H^+ is generated at the anode. Hence, when a current is applied, the following reactions may occur at the anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^0 = 1.229\ \text{V} \tag{1}$$

Whereas at the cathode:

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^0 = 0.00\ \text{V} \tag{2}$$

$$Co^{2+} + 2e^- \rightarrow Co^0 \qquad E^0 = -0.277\ \text{V} \tag{3}$$

$$Ni^{2+} + 2e^- \rightarrow Ni^0 \qquad E^0 = -0.250\ \text{V} \tag{4}$$

Evidently the evolution of H_2 is the main side reaction at the cathode.

3.2. Effect of current density on electrodialysis

A two-compartment cell was used to determine the effect of current density to the nickel separation from cobalt using cation-exchange membranes among the EDTA complexes in H_2SO_4. Equimolar solutions of metals (1.10^{-3} M for each metal) and chelating agent (2.10^{-3} M) in 1.10^{-2} M H_2SO_4 as an anolyte and 1.10^{-2} M acid solutions as a catholyte were used in the electrochemical cells that was separated with CMB membrane. The results obtained from these experiments are given in Table 2. It was found that recovery of metals increased with increasing electrodialysis time and current density. Here as recovery value of the metal R was calculated from the following equation:

Table 2
The effect of current density on RCobalt and RNickel from EDTA at 45 mA with CMB membrane

Current density	Co	Ni
	Slope (%R/min)	
15 mA	0.1862	0.1388
30 mA	0.2842	0.2333
45 mA	0.5288	0.4166

$$R(\%) = 100 \times \frac{\text{Actual amount of metal depodited onto cathode}}{\text{Initial amount of metal in anolyte}} \tag{5}$$

In our previous studies it was easily seen that the recovery value of metal or the transported amount of metal ions increased with increasing current density but the assay of this augmentation varied with the other parameters such pH, type of metal, chelating agent or membrane [10–14,16].

The results obtained from this study show that the cobalt recovery percent in the cathode chamber was 33.52% after 180 min at the current density of 15 mA. The corresponding values at the current densities of 30 and 45 mA were 51.16% and 94.10% respectively. The $\%R_{\text{cobalt}}/\%R_{\text{nickel}}$ ratio in the cathode chamber decreased from 1.3419 to 1.2548 at the current densities of 15 and 45 mA, respectively.

The effect of the stirring speed was not examined because a more vigorous mixing reduces the thickness of the diffusion layer adjacent to the electrodes, enhancing mass transfer of the chelates and the deposition of metals onto the cathode, by the way recovery of metals increase with increasing the stirring speed. [17].

3.3. Effect of membrane types on electrodialysis

The cation-exchange membranes selected in this study were CMB, CMS and CMX in order to determine the effect of the membrane type to the permeability of cation-exchange membranes for Co(II) and Ni(II) among the EDTA complexes of Co and Ni metals in H_2SO_4. Equimolar solutions of metals (1.10^{-3} M for each metal) and chelating agent (2.10^{-3} M) in 1.10^{-2} M H_2SO_4 as an anolyte and 1.10^{-2} M acid solutions as a catholyte were used in the application of 45 mA to the electrochemical cell. The effect of membrane types to permeability of cation-exchange membranes and recovery of metal ions from EDTA are given as the slope of the graph of %R vs. time of results of the experiment in Table 3. But the similar cases were obtained when the other chelating agents such as NTA and citrate were used. The differences in results of these experiments were explained with the structure

Table 3
The effect of the membrane type on R_{cobalt} and R_{nickel} from EDTA at 45 mA with CMB membrane

Membrane types	Co	Ni
	Slope (%R/min)	
CMB	0.5288	0.4166
CMX	0.3031	0.2388
CMS	0.2114	0.1666

of the membranes which are presented in Table 1. The highest recovery was realized with having the highest ion-exchange capacity of the cation-exchange membrane. As it is understood from Table 3, the amount of nickel depozited onto the cathode increased in the order: CMB > CMX > CMS.

3.4. Effect of anolyte concentration on electrodialysis

In order to determine the effect of anolyte solution concentration to the metal amount transported from the anode chamber to the cathode chamber, the experiments were performed using anolyte solution having different concentration ratios of metals and EDTA in 0.01 M H_2SO_4 in the usage of the CMB membrane and application of 45 mA to the system. Table 4 shows the effect of concentration of anolyte solution on the experiment results. In these experiments, 0.01 M H2SO4 was used as a catholyte in the same technical conditions. In general, increasing metal:chelate concentration (M:C) causes the increase of the driving force for mass transfer and thus facilitates deposition of metal onto cathode. This reduces the occurrence of side reactions and increases the total amount of species recovered rather than recovery of metals. In the experiments that were performed in different metal–chelate concentration ratios, different results were obtained due to the effect of the amount of chelates onto the unit volume of metal. Increasing with the concentration of chelating agent or decreasing with the ratio of M:C concentration, the amount of metal recovered on the cathode decreased due to the permission of the chelate to metal to transport toward to surface of cathode. The distinction between the different ratios of M:C concentration changed according to the type of metal, for example, R% values are 81.04 and 98.21 for Ni and Co respectively, while the anolyte solution did not contain a chelating agent. These values changed as 36.72 and 58.41 for the same order for M:C = 1/2.

3.5. Effect of types chelates on electrodialysis

In order to determine the effect of the type of chelating agents on the permeability of cation-exchange membranes for Co(II) and Ni(II) among the three types of complexes of Co and Ni metals in H_2SO_4, equimolar solutions of metals (1.10^{-3} M for each metal) and chelating agent (2.10^{-3} M) in 1.10^{-2} M H_2SO_4 as an anolyte and 1.10^{-2} M acid solutions as a catholyte were used. The effects of complexing agents on the permeability of membranes were found to be different according to their complex formation constants with metals. The recovery values of metals in the presence of different chelating agents are presented in Table 5. According to the experiment results of types of chelating agents, it can be said that the chelating agents' effects on the recovery of metals have variation which depends on their complex formation constants with metals. Recovery of nickel value is ordered like that: from EDTA chelate < NTA chelate < citrate chelate because of the complex formation constant order; K_{fNi}-EDTA > K_{fNi}-NTA > K_{fNi}-citrate. The results and the comments obtained from the experiments made with cobalt are the same as for the complexes of nickel.

3.6. Effect of type of the solvent on electrodialysis

The experiments were performed using anolyte solution having different solvents and due to these different catholyte solutions. The effect of the type of the solvent and catholyte solution on the transportation of metals was examined. Table 6 illustrates the effect of these parameters on transportation. It was expected from Eqs. (1) and (2) that while the anolyte pH would decrease after electrodialysis, the catholyte pH would increase due to the formation of hydroxyl ions in the cathode chamber. This idea was predicted with measuring the pH of the solutions at the end of the experiments. The types of the solvents were selected due to the different pH ranges. The pH effect was determined by using of 0.01 M KCl (for the

Table 4
The effect of the anolyte concentration on R_{cobalt} and R_{nickel} from EDTA at 45 mA with CMB membrane

Anolyte concentration	Co	Ni
	Slope (%R/min)	
Only metal	0.5456	0.4502
M:C=1:1	0.5288	0.4166
M:C=1:2	0.3245	0.2040

Table 5
The effect of the type of the chelating agent on R_{cobalt} and R_{nickel} at 45 mA with CMB membrane

Chelate types	Co	Ni
	Slope (%R/min)	
EDTA	0.5288	0.4166
NTA	0.5624	0.4277
Citrate	0.6744	0.5111

Table 6
The effect of type of the solvent on R_{cobalt} and R_{nickel} from EDTA at 45 mA with CMB membrane

Type of solvent	Co	Ni
	Slope (%R/min)	
H_2SO_4	0.5288	0.4166
KCl	0.4100	0.3222
NaOH	0.2145	0.1666

neutral medium), 0.01 M H_2SO_4 (for the acidic medium) or 0.01 M NaOH (for the alkaline medium) solutions as a catholyte and a solvent for anolyte solution. Increasing the acid concentration or decreasing the pH values resulted in a slight increase in the total nickel (or cobalt) transferred to the catholyte chamber and gave a significant increase in the metal purity. The results obtained from these experiments were the long hoped for theoretical knowledge. From this point of view, as it is known in the basic media Co and Ni have became a hydroxyl compound and their solubility product is close to each other for nickel and cobalt. Because of this for this study basic and neutral media were not suitable.

3.7. Effect of type of acidic solvent on electrodialysis

The experiments were performed using anolyte solution having different solvents and due to these different catholyte solutions. The effect of solvent on the transportation of metals was examined. Table 7 demonstrates the effect of acidic solvent on transportation. This effect was examined by using of HNO_3 (as the monoprotic acid), H_2SO_4 (as the diprotic acid) or H_3PO_4 (as the poliprotic acid) solutions as a catholyte and a solvent for anolyte solution. The differences of the results, obtained from the experiments that were made in order to determine the effect of solvent, are explained with the acidity constants of the solvents. The metal transportation and their deposition could be formed in the acidic medium.

Table 7
The effect of type of the acidic solvent on R_{cobalt} and R_{nickel} from EDTA at 45 mA with CMB membrane

Type of acidic solvent	Co	Ni
	Slope (%R/min)	
H_2SO_4	0.5288	0.4166
HNO_3	0.4956	0.3777
H_3PO_4	0.4642	0.3500

4. Conclusions

In this study the factors affecting the transportation of metals from the anode chamber to the cathode chamber were systematically examined. Due to the transportation of metals from the anolyte solution to the catholyte solution and to the applied potential, deposition could be materialized on the cathode surface. The drawback of using a special two-compartment cell for mixed metals as complexes was demonstrated: the recovery increased with the increase of current density, concentration ratio between metal–chelate, changed for the type of membrane in CMB > CMS > CMX order, for the type of the chelating agent in citrate > NTA > EDTA, for the pH in acidic > neutrall > alkaline medium, for the solvent $H_2SO_4 > HNO_3 > H_3PO_4$ order. In these experiments the least value as percent recovery of cobalt was found to be approximately 33.5%. This value decreased due the type of the experiments to 25% for nickel. The results obtained from a two-compartment cell showed that very little separation could be achieved using a single cation exchange membrane. The fact that EDTA was destroyed at the anode surface meant that uncomplexed Ni(II) was released and this permitted the transfer of free Ni(II) towards the catholyte chamber in order to reduce at the cathode surface. For this reason all the data presented are sets of straight lines of percent recovery value of nickel against time.

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