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Recovery of Zn (II) from its EDTA complexes by electro-membrane process

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ABSTRACT

Factors affecting the efficiency of electrochemical recovery of Zn (II) from its ethylenediaminetetraacetic acid (EDTA) complexes were systematically examined using three types of cation-exchange membranes in a two compartment electrolysis cell. In these experiments, the catholyte contained an equimolar amount of Zn (II) and EDTA, and the anolyte contained 0.1 M $NaNO_3$. The platinium and stainless steel were used as an anode and a cathode, respectively. The effect of current densities, metal concentration, the type of the cation-exchange membrane on the recovery of metals were determined. It was found that recovery of Zn (II) increased with increase of current density, concentration of catholyte solution, concentration ratio between metal—chelate and changed with the type of membrane in CMB>CMS>CMX order. The obtained numerical results showed that electrodeposition seems to be applicable method for the recovery of metals under appropriate conditions.

Keywords: Electrodeposition; Zinc; EDTA; Cation-exchange membrane

1. Introduction

The streams containing strong chelating agents such as ethylenediaminetetraacetic acid (EDTA), Nitrilotriacetic acid (NTA) and citrate were often encountered in remediation washing of heavy metal-contaminated soils [1–4]. These constituents were not only present in the process or waste effluents of manufacturing printed circuit boards for electroless copper plating and of some metal finishing industries [5,6] but also they have been used in many industrial applications such as water softening, photography, textile processing and industrial cleaning, etc., and bind with metal cations, preventing them from forming insoluble salts or other process problems. Furthermore; they complicate the treatment of industrial polluted effluents by reducing the efficiency of metal removal using traditional chemical precipitation ion exchange and other processes [7,8]. EDTA, NTA and citrate may make the chemical precipitation methods involving hydroxides and sulfides less effective, even with relatively high levels of metals. Moreover, the high buffer capacity provided by the complexing agents requires excessive amounts of chemicals to neutralize the alkalinity. These problems and restrictions warrant investigations to other recovery alternatives [9].

The recovery methods, which depend greatly on the particular chelating agent and metals as well as their concentrations, are generally grouped into three categories as chemical, physical and electrochemical. Among them, electrochemical method seems to be advantageous particularly for concentrated solutions. In these methods, the main concern becomes the recovery and reuse of metals and complexing agents [10,11]. Regardless of which concentration method is being used, however, the chelated metals can not be destroyed and the final step should be aided via electrolysis operation types [12,13]. For diluted solutions, ion exchange resins, adsorption onto activated carbon, inorganic materials and functional polymers have been tried [5,14–17]. In addition to these facilities, some problems can occur such as the oxidation of EDTA into many compounds.

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Thus, simultaneous recovery of metals and chelating agents is not possible using common electrolytic methods. On the other hand, one of the most important technique in these electrolytic methods, electrodeposition, has been usually applied for the recovery of metals from waste water or electroplating [18]. Electrodepositon is an electromembrane process in which ions are transported through ion permeable membranes from one solution to another under the influence of a potential gradient and deposited on the electrode surface. The electrical charges on the ions allow them to be driven through the membranes fabricated from ion exchange polymers. Although various separation membranes such as membranes for microfiltration, nanofiltration, ultrafiltration, reverse osmosis, pervaporation, gas separation and liquid membranes, etc. have been studied and industrially used, the ion-exchange membrane is one of the most advanced separation materials 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.

In this work, attention was paid to examine the recovery of zinc from its complexed solutions by using commercial cation-exchange membranes with electrodeposition method. Experiments were carried out by taking at equimolar Zinc (II)-EDTA as a function of current density, types of membranes, metal concentration.

2. Experimental details

2.1. Materials

All chemicals were purchased from Merck and were reagent grade. The catholyte solution was prepared by dissolving of Zinc (II) from sulfate form and EDTA in deionized water at equimolar. The anolyte solution was 0.1 M $NaNO_3$. The cation-exchange membranes selected in this work were Neosepta CMB, CMS and CMX kindly offered from Eurodia Co. They are homogeneous films comprising cross-linked sulfonated co-polymers of vinyl compounds on synthetic reinforcing fabric as listed in Table 1 [19].

2.2. Experimental procedures and chemical analysis

The apparatus for electrodeposition experiments is illustrated in Fig.1, which is made of from polyamide. Two chambers 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 30 mm 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. A stainless steel and Pt were used as a cathode and anode, respectively and their active dimensions were 30 mm. The flow of solutions was performed by peristaltic pump (913 Mity Flex, double-way). The power supply used in elelectrolysis experiments was capable of supplying a potential of up to 32 volt and a direct current of up to 2 amp.

An equal volume (250 mL) of the anolyte and the catholyte solution was filled in the respective chamber. The experiments were carried out at the constant current by changing the cell voltage according to the variation of the current. As expected, vigorous mixing reduced the thickness of the double layer adjacent to the electrodes, thereby enhancing mass transfer of the chelates toward to the cathode [7]. For this reason, the stirring speed of 500 rpm was selected to prevent the formation of a serious vortex in the electrolytic cell. Samples were taken at time intervals (for 15 min) from the cathode chamber and also from the anode chamber in the beginning and finishing time of the experiment to observe whether metal ions transport to the anode chamber or not. The concentration of Zn (II) ion was analyzed by an atomic absorption spectrophotometer (Unicam 929). The experiments were performed at $25 \pm 1^{o}C$. Each experiment was duplicated under identical conditions.

The following steps were conducted for all membrane samples (7,065 cm^2): Prior to use, all membranes were treated with distillated water at $70^{o}C$ for 1 h, 0,1 M HCl and 0.1 M NaOH at $50^{o}C$ for 1 h respectively to remove inorganic impurities. The resulting membranes were finally immersed in 1 M HCl solutions to transform membranes to their hydrogen form for 24 h and were used for electrodeposition experiments.

Table 1
Properties of the cation-exchange membranes.

Membrane	CMB	CMS	CMX
Functional group	Polysulphone	Polysulphone	Polysulphone
Ion-exchange capacity (meq/g)	2,7–2,8	2,0–2,5	1,5–1,8
Thickness (µm)	220–260	140–170	170–190
Water content (%)	33–41	35–45	25–30
Burst strength (Ω cm^2)	3,0–5,0 Ω-cm^2	1,5–3,5 Ω-cm^2	2,0–3,5 Ω-cm^2

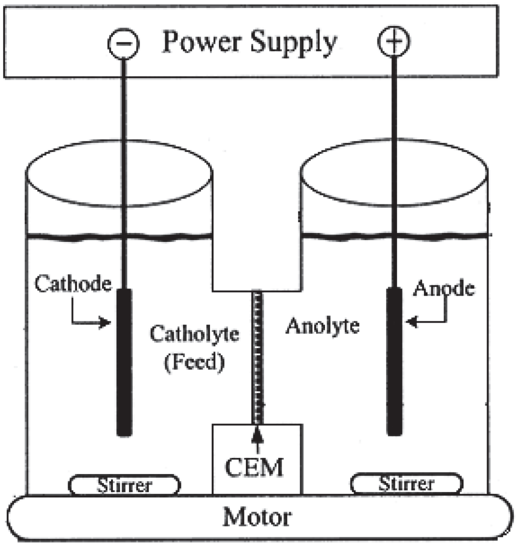

Fig. 1. The diagram used for Electrodeposition experiments.

3. Results and discussion

3.1. Reactions involved in the electrodeposition cell

EDTA is all polyprotic acid (H_xL) which can exist in many protonated forms in aqeous solutions. It can form stable chelates with most divalent metals in a 1:1 molar ratio over a rather wide pH range [20].

The catholyte pH increased during electrolysis due to the production of OH^- at the cathode in the reaction 8; in addition to this H^+ is generated at the anode such in reaction 1, as a result of this the pH of anolyte solution decreased during the experiment. Hence, when a current is applied, the following reactions may occur at the anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^0 = -1.229\ \text{V} \tag{1}$$
$$H_2O \rightarrow H^+ + OH^- \qquad E^0 = -0.828\ \text{V} \tag{2}$$
$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \qquad E^0 = -0.401\ \text{V} \tag{3}$$
$$2OH^- \rightarrow H_2O_2 + 2e^- \qquad E^0 = -0.547\ \text{V} \tag{4}$$
$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \qquad E^0 = -0.682\ \text{V.} \tag{5}$$

Whereas at the cathode:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad E^0 = 0.401\ \text{V} \tag{6}$$
$$2H^+ + 2e^- \rightarrow H_2 \qquad E^0 = 0\ \text{V} \tag{7}$$
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E^0 = -0.828\ \text{V} \tag{8}$$
$$Zn^{+2} + 2e^- \rightarrow Zn^0 \qquad E^0 = -0.764\ \text{V.} \tag{9}$$

Evidently the evolutions of O_2 and H_2 gases are the main side reactions at the anode and cathode, respectively, which would reduce the current efficiency [7]. In addition to this the binding affinity of the Zn (II)–EDTA complexes can not fully explain the fact that of percent of recovery values. This indicates that a small amount of electric energy is needed to destroy the complexes. Most of the energy is consumed to facilitate side reactions, migrate the chelated anions towards the anode, or transfer Na^+ across the membrane [10]. It appears that the reduction tendency of metal ions plays an important role; that is the reaction of equation (10) occurs in two steps:

$$ML^{2-} + 2e^- \rightarrow M(s) + L^{4-} \tag{10}$$

1. $ML^{2-} \rightarrow M^{2+} + L^{4-}$ (by virtue of applied cell voltage) Step 1

2. $M^{2+} + 2e^- \rightarrow M(s)$ Step 2

The standart reduction potential in step 1 can change due to the metal. The present results imply that the chelated anions are destroyed (step 1), possibly on the outside of electric double layer of the cathode, before the metals are deposited onto the cathode [21].

3.2. Equations used in calculations

Some equations were used for estimations to evaluate the experiment results.

Here as recovery value of the metal; R was calculated from the following equation:

$$R\ (\%) = 100 \times \frac{\text{actual amount of metal deposited onto the cathode}}{\text{Initial amount of metal in the catholyte}} \tag{11}$$

Here, η is commonly defined as: [22]

$$\eta\ (\%) = 100 \times \frac{\text{actual amount of metal deposited onto the cathode}}{\text{amount of metals deposited based on the Faradays law of electrolysis}} \tag{12}$$

It is found that η monotonously decreases with increasing current density, which agrees with the result obtained previously [23]. The lower η at a higher current density was a result of the larger extent of side reactions such as the evolution of O_2 and H_2 gases. When a current was applied to the electrolysis cell, the anolyte provided Na^+ to carry the current through the cation-exchange membrane into the cathode chamber and to regenerate EDTA to its sodium form. To maintain the electroneutrality in the anolyte, the loss of Na^+ must be accompanied with a generation of other cations, that is, H^+ via the oxidation of water (Eqs. 1, 2 and 5). At a higher current density, the more Na^+ was transferred and therefore the more H^+ was required, which reduced η to a more extent.

In the discussion of feasibility of electrolytic processes, it is accepted that the energy efficiency, defined as the energy consumed to produce an amount of product (kWh/kg), should be taken into account. In particular, it is of great importance for electrolysis in diluted electrolyte solutions and the operation using cells having membrane separator or diaphragm [13]. Owing to the constant-current operation in our study, the energy efficiency was not easily presented because the cell voltage significantly changed during electrolysis.

3.3. Effect of current density on electrodeposition

The effect of current density on Zn (II) recovery, R_{Zn}, from aqueous EDTA solutions is shown in Fig. 2. It was found that R_{Zn} increases with increasing electrolysis time and current density. As it is seen from the Fig. 2 that the recovery value of Zn (II) increased in that order: 45 mA >30 mA>15 mA but the assay of this augmentation varied with type of metal in the catholyte solution [24]. For example, when the metal of catholyte solution is copper in our previous studies, the recovery value of copper was 23.07% after 180 min at the current density of 35 mA. The corresponding values at the current density of 25 and 15 mA were 19.19 and 8.47, respectively [24,25].

The effect of the stirring speed was not examined because a more vigorous mixing reduces the thickness of the double 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 [12].

3.4. Effect of membrane types on electrodeposition

The cation-exchange membranes selected in this study were CMB, CMS, CMX and their properties are presented in Table 1. The effect of membrane types on recovery of Zn (II) from EDTA is shown as a graph in Fig. 3. As it is seen from the Fig. 3 that the amount of Zn (II) depozited onto the cathode increased in that order: CMB>CMX>CMS. The differences in the results of these experiments were explained with the structure of the membranes (Table 1). Although for three types of the cation-exchange membranes functional groups were same, they have some differences from the point of view ion exchange capacity, thickness, water content and burst strength. By the way in the results of the membrane type, there was a significant variation between the membrane types due to these differences especially as a result of their ion exchange capacity. Among these membranes the best membrane for the recovery of Zn (II) was found as CMB because CMB membrane has max ion-exchange capacity than the others. This comment can be made for the other membrane types. The results that were obtained from our previous studies it can be easily understood that, this membrane arrange is the same; as an example, the variations of slopes between the CMB and CMS membranes are 0.0289; 0.0211 and 0.0596 for copper, nickel and cobalt, respectively [25].

3.5. Effect of catholyte concentration on electrodeposition

The experiments were performed using catholyte solution having different concentrations (0.001; 0.003; 0.005 M) although the Zn (II)–EDTA concentration ratio was 1:1. Fig. 4 shows the effect of Zn (II)–EDTA catholyte concentration on electrolysis. For example; for the concentration of catholyte solution as 0.001, it means that [Zn (II)] = [EDTA] = 0.001 because the ratio between the metal and the chelate is 1:1, this ratio does not change for the concentration experiments of this study. By the way increasing in the concentration of catholyte means increasing in the metal concentration. Although the metal-chelate concentration was remained, it was clear that the amount of metal was rised in unit volume because of this recovery of metal value increased.

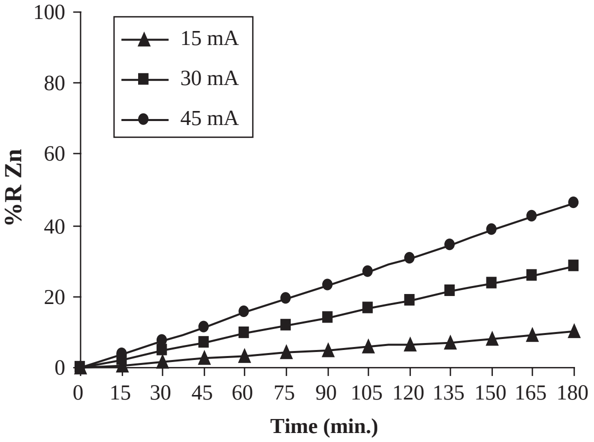

Fig. 2. The effect of current density on R_{Zn} from EDTA at 45 mA with CMB membrane.

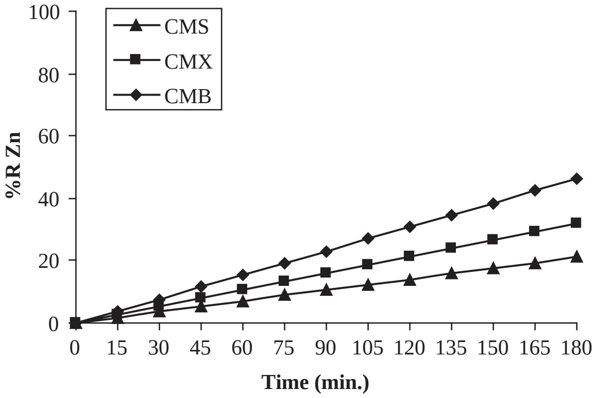

Fig. 3. The effect of the membrane type on R_{Zn} from EDTA at 45 mA.

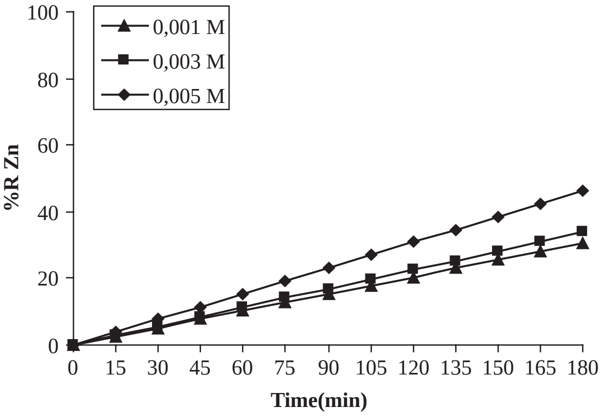

Fig. 4. The effect of the catholyte concentration on R_{Zn} from EDTA at 45 mA with CMB membrane.

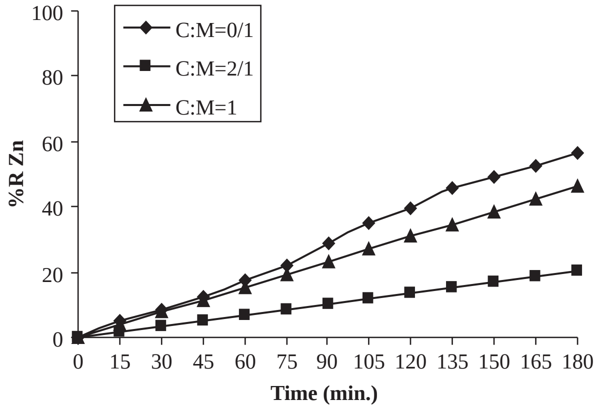

Fig. 5. The effect of the M:C concentration ratio on R_{Zn} from EDTA at 45 mA with CMB membrane.

3.6. Effect of the concentration ratio of Zn (II): EDTA on electrodeposition

Different concentration ratio of Zn (II)–EDTA was also examined in order to compare the effect of the chelates to the deposition of Zn (II) onto the electrode. The recovery values of Zn (II) as a graph is demonstrated in Fig. 5. In general, increasing of Metal concentration (M): Chelate concentration (C) causes to increase the driving force for mass transfer and thus facilitates the deposition of metal onto the 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 is occurred in different metal-chelate concentration ratio, 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, amount of the metal, recovered on the cathode, was decreased due to the permission of the chelate to metal to transport toward to surface of cathode. If the previous studies results compared with each other in their own field, the distinction between the different ratio of M:C concentration changed according to the type of metal. For example; while the difference of slopes between M:C = 1 and M:C = 1/2 is 0.0144 for copper, this difference varied as 0.0167 for nickel [25].

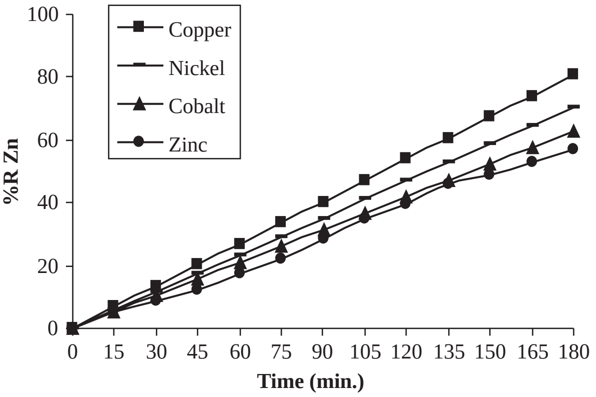

Fig. 6. The effect of the type of the metal on R_{metal} without chelating agent at 45 mA with CMB membrane.

3.7. Effect of the type of metal on electrodeposition

The experiments were performed to compare of the effect of the type of the metal without chelating agents to the deposition of metal onto the cathode under the optimum conditions. The results obtained from these experiments are shown in Fig. 6. In electrodeposition experiments of metals without chelating agents, the obtained results show that the recovery of copper was more than not only recovery of cobalt but also recovery of nickel and zinc because of its standart reaction potential.

4. Conclusion

The factors affecting for the recovery of metals from complexed solutions were systematically examined. About the mechanism of the growth of metal electrodeposition onto the cathode, it is basically a net result of the follwing three processes: (i) transfer of metal ions (including hydrated and chelated) toward to the cathode surface due to diffusion, convection and migration, (ii) transfer of electrons toward the cathode surface to form an adatom and (iii) diffusion of adatom into the crystal lattice after sliding along the cathode surface. The drawback of using the special two compartment cell for Zinc metal was demonstrated: recovery increased with increase of current density, concentration of catholyte solution and concentration ratio between metal and chelate. In these experiments, the least value as percent recovery of metal was found approximately 10%. This value increased due the type of the experiments upon to 85% for zinc. For this reason the obtained results show that this membrane technique is applicable method for the recovery of metals.

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