



Transport of selected transition metal ions across heterogeneous membranes in ED enhanced with complex formation

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ABSTRACT

In this work, the effectiveness of electro dialysis enhanced with complex formation for selective zinc ions removal from simulated zinc electroplating bath contaminated with copper and iron was investigated. The effect of the chelating agent (citric acid) addition and pH of examined solutions were discussed. The selectivity coefficients of iron, copper and zinc ions were determined. Maximum values of selectivity coefficients equaled to 4.5 for Zn^{2+}/Cu^{2+} and 35 for Zn^{2+}/Fe^{3+} system. The electro dialysis enhanced with complexation appeared to be a viable method for selective removal of zinc from waste electroplating baths and similar industrial effluents.

Keywords: Electro dialysis; Complex formation; Transition metals; Electroplating bath

1. Introduction

Effluents containing heavy metals can be generated by several industries. One of the most hazardous industrial process is electroplating. The electroplating baths become contaminated during the regular electroplating operation. The main sources of their pollution are impurities removed from the surface of processed metallic elements, especially during acidic baths [1–3].

The common methods applied in removal metals from the industrial effluents are chemical precipitation, ion exchange, electrolysis, adsorption and flotation [1,2,4]. Chemical precipitation is most widely used for transition-metal removal from inorganic effluents, but the main disadvantage of this method is the generation of large amount of solid wastes [5]. The process of ion exchange also has its drawbacks. The conventional methods of transition-metal salts elimination from industrial sewage are expensive and complicated [1,6,7]. One of these methods, dedicated to zinc, nickel, copper, iron and other toxic metals removal from industrial wastewater

is electro dialysis (ED). It is a membrane technique based on the separation of ions across membrane. The process involves the use of two different types of the ion-exchange membranes (IEM), that is, cation-exchange membrane (CEM) and anion-exchange membrane (AEM), which allow for selective passage of cations and anions, respectively. Nevertheless, ED method has also significant drawbacks such as relatively low selectivity, which makes an efficient separation and selective recovery of metals from mixtures of various ions impossible [7–12]. Cifuentes *L.* et al. conducted some investigations on the electro dialytic separation of copper and iron ions and recovery of water from the aqueous solution of $CuSO_4 \cdot H_2SO_4 - FeSO_4$. They proved that simple ED is not useful for effective separation of copper ions from iron salts [13]. Therefore, the selectivity of ED for metal salt removal can be substantially increased by the introduction of additives (ligands, complexing agents), which are known to create highly stable complexes with particular metal ions. Some results on three-compartment ED (more precisely membrane electrolysis) separation of calcium and cadmium ions in a system containing EDTA as the complexing agent were reported in [14].

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In the mentioned arrangement, cadmium preferably formed negatively charged complexes, while calcium remained in the positively charged EDTA-free form. At the applied electric field, calcium was transported across CEM (to the cathode compartment), while more than 90% of cadmium was removed across AEM to the anode compartment. Although the membrane arrangement presented in [14] differed from the classical ED. The results proved that complex formation affected the mass transfer rate. Similarly in [15], in which conditions for the selective removal of nickel from cobalt in aqueous solutions by ED revealing the greater stability of the EDTA complex with nickel were investigated. The Ni-(EDTA)²⁻ complex and hydrated Co²⁺ ions were removed from the feed solution to the anolyte and catholyte chambers. A three compartment cell was required to prevent the transfer of hydrated Ni²⁺ from the anolyte chamber as the applied EDTA was oxidized at the anode. Complete separation of nickel from cobalt was achieved, but there was a compromise between cobalt purity and cobalt yield.

The preferential transport of nickel and cupric ions across CEM in ED supported with a complex agent was reported in [16]. In this study, glycine and citric acid (CA) were used as complex agents. Authors stated that increase of stoichiometric ratio of a complex agent to metal ions, as well as increase of investigated solution pH, improved the value of permselectivity coefficient. In Huang and Wang's study [16], it was also demonstrated that ED enhanced with complex formation could be a useful method for metal separation from multicomponent solutions. The behavior of ED enhanced with complexing agents was also performed by Huang et al. in [17]. It was found that CA could be an effective chelating agent for cupric and ferric ions separation. However, the ratio of complexing agent to metal ions, solution pH and applied voltage had significant influence on the selectivity. In addition, ED combined with complex formation was applied by Cherif et al. to silver separation from copper and zinc using EDTA. Results presented in [18] showed that obtained metal

complexes had different charges, thus silver was recovered from investigated solution with satisfactory yield [18].

In this work, the applicability of ED enhanced with complex formation to selective separation of the most troublesome transition metal ions (Cu²⁺, Fe³⁺) from simulated zinc sulfate electroplating baths was investigated. The proposed method is a combination of ED process with the complex formation reaction, schematically shown in Fig. 1. In this system, metal ions which are selectively bound in the complex, are transported across the CEM at much lower rate than the co-existing non-complexed metals ions and are effectively removed from the process solutions. Moreover, ED enhanced with complex formation seems to be a promising method for the treatment of effluents contaminated with heavy metals to recover valuable compounds for consequent reuse [16–18].

The aim of this study was to verify the possibility of selective zinc removal from zinc sulfate electroplating bath contaminated with other metals, by ED enhanced with complex formation. The transport of iron, copper and zinc ions across heterogeneous AEM and CEM was investigated. The effects of the chelating agent (CA) addition and pH of investigated solutions were discussed. The selectivity coefficients of iron, copper and zinc ions were determined.

2. Materials and methods

The experiments were carried out in a five-compartment electrolysytic cell with a unit effective membrane area of 16 cm². In this arrangement, presented in Fig. 1, cations were transported from the diluate compartment through the CEM into the concentrate compartment, while anions were transported across the AEM into the auxiliary compartment. All of the process solutions such as diluate, concentrate and electrode-rinse solution as well as auxiliary solution were recirculated by Masterflex L/S peristaltic pump at a flow rate of 281.5 ml min⁻¹, that corresponded to linear flow velocity of 1 cm s⁻¹ inside the chamber. All experiments were carried out

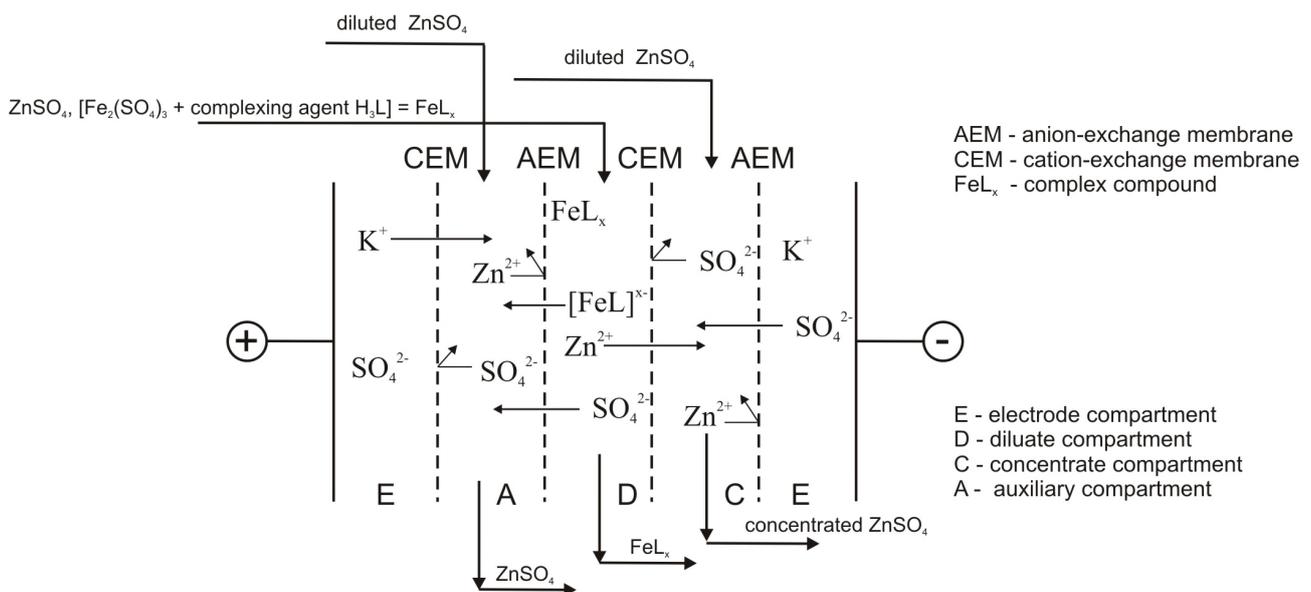


Fig. 1. The principle of the ED enhanced with complex formation method.

at 25°C. The cathode and the anode were made of platinized titanium, with the surface area of 16 cm². Heterogeneous membranes used in this work were AM(H) – CM(H) (Ralex, Czech Republic). The surface morphology of membranes was examined by scanning electron microscopy (SEM, Hitachi TM3000). Micrographs of tested membranes surface are shown in Fig. 2.

Experiments included a series of electrodialeses of two-component transition-metal salt solutions with addition of CA (complexing agent). The examined solutions contained copper, iron and zinc compounds. The copper was added to the test solution as CuSO₄·5H₂O, iron as Fe₂(SO₄)₃·24H₂O and zinc as ZnSO₄·7H₂O. All chemicals were of analytical grade.

The ED process solutions composition at the presence of particular salts is given in Table 1.

Separation experiments were performed at electric current density of 250 A m⁻². Electric current density was maintained constant during particular experiments. Duration of experiments was 1 h, that is, the time which was required to remove approximately 10% of zinc from the diluate. The summary of the experimental conditions is presented in Table 1. In the course of the experiment, samples of concentrate and auxiliary solutions were collected every 10 min and analyzed for iron, zinc and copper concentration using ICP-OES (Varian, Australia). Basing on slopes of molar

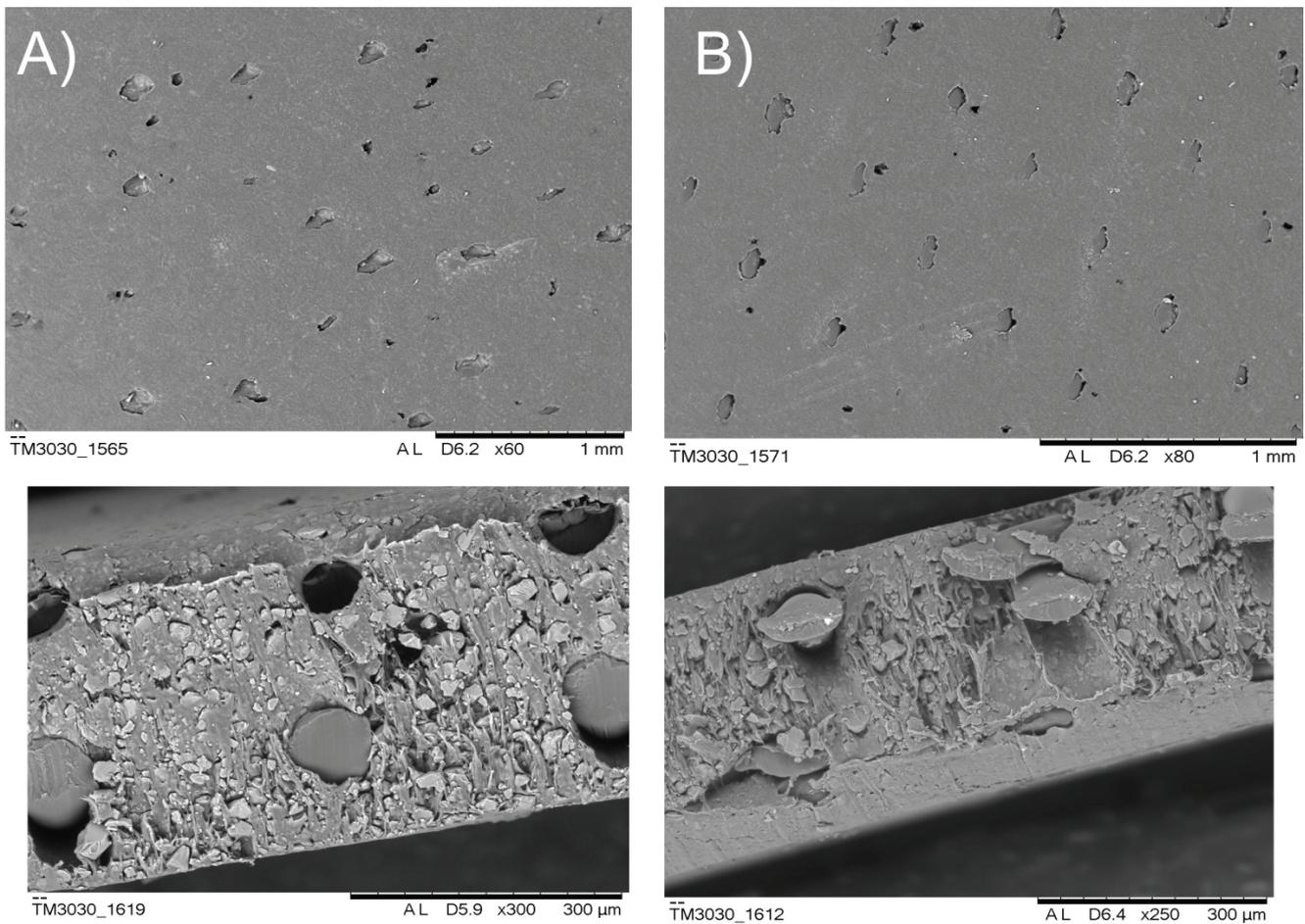


Fig. 2. Micrographs of the surface and cross section of (a) CM(H)-PES and (b) AM(H)-PES membranes.

Table 1
ED process solutions compositions and experimental conditions

j , A/m ²	t , min	Diluate solution	Citric acid/metal (Cu or Fe) molar ratio	Concentrate and auxiliary solutions	Electrode-rinse solution
250	60	0.748 M ZnSO ₄ ·7H ₂ O	1.5	0.1 M ZnSO ₄	0.5 M K ₂ SO ₄
		0.0157 M CuSO ₄ ·5H ₂ O	3		
		Citric acid	6		
		0.748 M ZnSO ₄ ·7H ₂ O	1.5		
		0.0806 M Fe ₂ (SO ₄) ₃ ·24H ₂ O	3		
		Citric acid	6		

concentration vs. time curves molar fluxes of iron, copper and zinc at a given electric current density were determined and selectivity coefficient was calculated as using Eq. (1):

$$\alpha_{Zn^{2+}/M^{n+}} = \frac{J_{Zn^{2+}}/J_{M^{n+}}}{C_{Zn^{2+}}/C_{M^{n+}}} \quad (1)$$

where $J_{Zn^{2+}}$ is zinc molar flux, $J_{M^{n+}}$ is a separated metal (Cu or Fe) molar flux, $C_{Zn^{2+}}$ is an initial concentration of zinc in the diluate, while $C_{M^{n+}}$ is an initial metal content in the diluate.

3. Results and discussion

3.1. The effect of an addition of a CA on Cu^{2+} ions transport across IEMs

The effect of addition of chelating agent, such as CA, on copper ions removal from simulated zinc electroplating bath

was investigated. The applied chelating agent contained three carboxylate groups, which allowed to create coordination compounds with metal cations (e.g., Cu^{2+} , Fe^{3+}) [19–21]. Experiments were performed at various CA to copper molar ratios in the range from 1 to 6. pH of examined solutions was 4. The results were evaluated in terms of relative metal fluxes and selectivity coefficients. Copper molar fluxes across CEM and AEM were determined. The results are summarized in Figs. 3–5.

In Fig. 3, the effect of CA/copper ions molar ratio on the copper molar flux across CEM and the zinc to copper ions molar fluxes ratio are presented. It was observed that zinc to copper molar flux ratio increased monotonously with CA/copper ions molar ratio, while copper ions molar flux across CEM decreased with addition of chelating agent. However, a significant transport of copper ions across AEM was also observed (Fig. 4). This effect can be explained by formation of negatively charged copper citrate ionic complexes, which can be transported across AEM, due to the fact that zinc

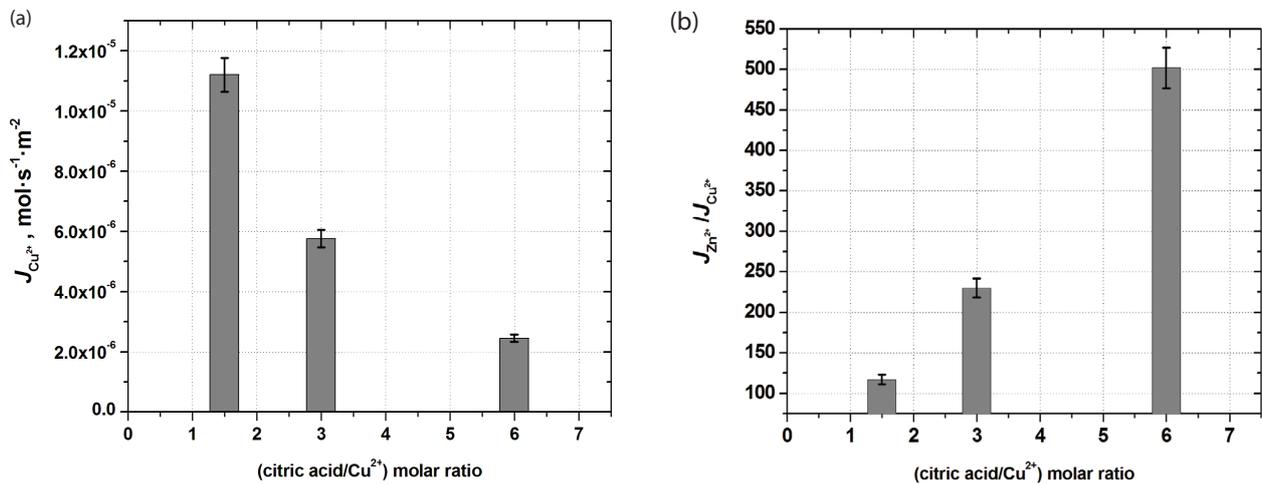


Fig. 3. The effect of complex agent/metal ion molar ratio on (a) copper ions molar flux across CEM and (b) zinc to copper ions molar fluxes ratio; $j = 250 \text{ A m}^{-2}$.

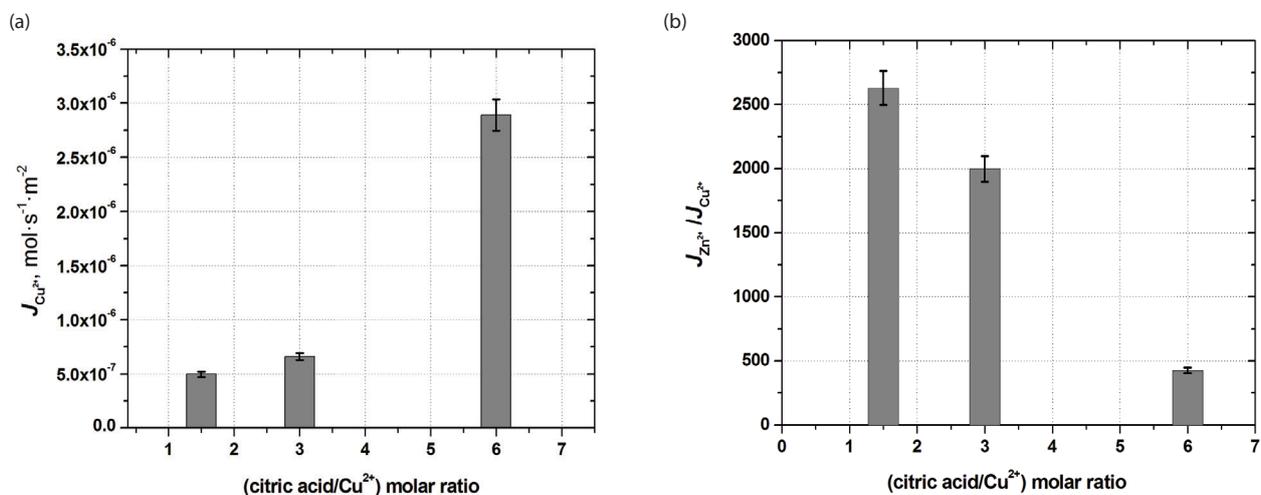


Fig. 4. The effect of complex agent/metal molar ratio on (a) copper ions molar flux across AEM and (b) zinc to copper ions molar fluxes ratio; $j = 250 \text{ A m}^{-2}$.

ions molar flux across AEM was negligible. Additionally, the transport of copper anionic species across AEMs to concentrate solution in the conventional ED stack with n membrane pairs is also very low. Hence, in Fig. 4(b), the effect of complex agent/metal ions molar ratio on zinc to copper ions molar fluxes ratio is presented. However, zinc ions molar fluxes applied corresponded to fluxes across CEM.

The effect of CA addition on the selectivity coefficient $\alpha_{Zn^{2+}/Cu^{2+}}$ is shown in Fig. 5. The selectivity coefficient increased from around 2.5 at CA/Cu²⁺ molar ratio of 1.5 to around 4.5 at CA/Cu²⁺ molar ratios of 3 and 6. It was found that the selectivity coefficients $\alpha_{Zn^{2+}/Cu^{2+}}$ for CA/Cu²⁺ molar ratios of 3 and 6 did not differ in significant manner. Such a behavior can be explained by formation of anionic copper citrate complexes, when CA/Cu²⁺ molar ratio was higher than 3 and pH was 4. These copper citrate complexes were transported through AEM to the concentrate.

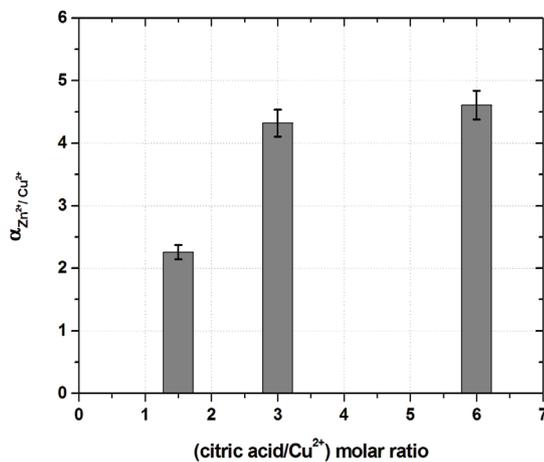


Fig. 5. The effect of complex agent/metal molar ratio on the $\alpha_{Zn^{2+}/Cu^{2+}}$ selectivity coefficient; $j = 250 \text{ A/m}^2$.

3.2. The effect of an addition of a CA on Fe³⁺ ions transport across IEMs

The effect of addition of CA on ferric ions transport through IEMs was also investigated. CA is known to create complexes with ferric ions, which are far more stable than citrate complexes with zinc. Complex formation constants for metal cation – CA complexes increase in the following order: Zn²⁺ < Cu²⁺ < Fe³⁺ [19–21]. Furthermore, at the presence of equimolar amounts of CA only Fe³⁺ ions should be coordinated [21]. In Fig. 6, the effect of CA/Fe³⁺ molar ratio on the ferric molar fluxes across CEM and the zinc to ferric molar fluxes ratio is presented. pH of examined solutions was 4. It was observed that in Zn²⁺/Fe³⁺ system, the amount of ferric ions in concentrate compartment decreased with the addition of CA (Fig. 6(a)). Therefore, zinc to iron molar flux ratio through CEM increased with increasing CA concentration in initial diluate solution (Fig. 6(b)). Moreover, for CA/Fe³⁺ molar ratio equaled to 3 and 6, respectively, the relative metal molar fluxes did not differ in significant manner. This effect can be explained by the formation of electrically neutral complex species, which in consequence affects the rate of their transport across CEM (Fig. 6).

In Fig. 7, the effect of complex agent/Fe³⁺ molar ratio on ferric ions molar fluxes across AEM and the relative zinc to ferric ions molar fluxes is presented. However, zinc molar fluxes used corresponded to fluxes across CEM. In general, zinc ions molar flux across AEM was negligible and anionic iron species could be transported to concentrate solution in conventional ED with n -membrane pairs. The values shown in Fig. 7 indicate that for CA/Fe³⁺ molar ratio equaled 3 and 6, respectively, ferric ions molar fluxes through AEM were close to value obtained for sample without chelating agent. These results proved a formation of electrically neutral ferric citrate complexes at pH 4 and CA/Fe³⁺ ratio of 3. The pH of examined solution had significant impact on Fe³⁺ molar flux through CEM and AEM (Table 2). It was observed that when pH of the investigated solution was equaled to 5 probably,

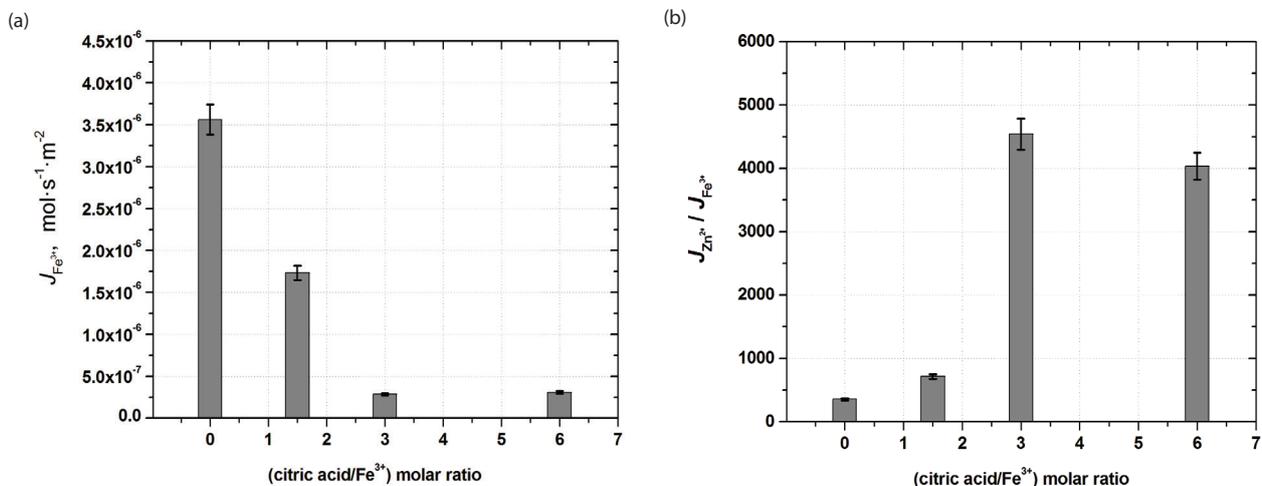


Fig. 6. The effect of complex agent/metal molar ratio on (a) ferric ions molar flux across CEM and (b) zinc to ferric ions molar fluxes ratio; $j = 250 \text{ A/m}^2$.

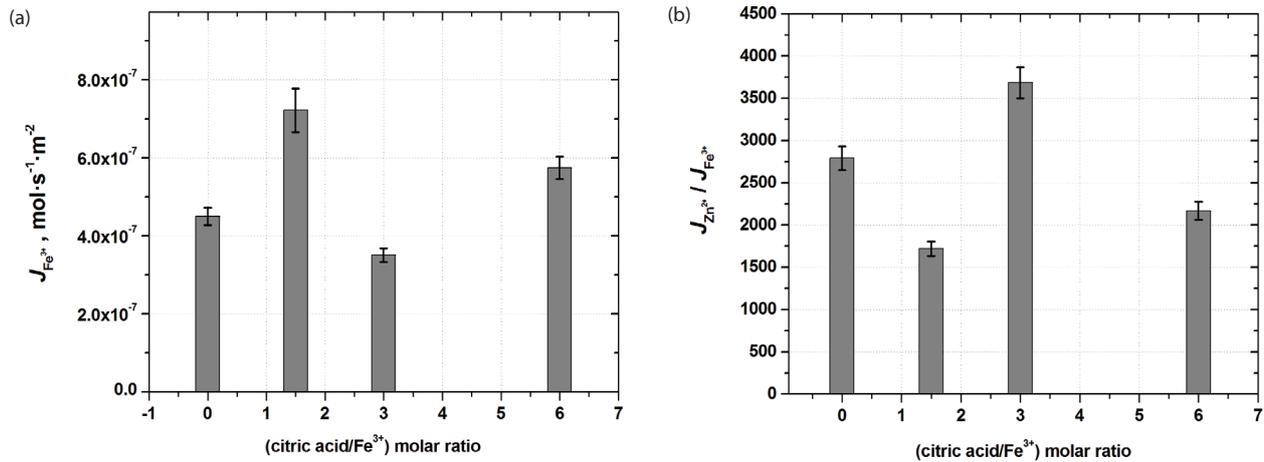


Fig. 7. The effect of complex agent/metal molar ratio on (a) ferric ions molar flux across AEM and (b) zinc to ferric ions molar fluxes ratio; $j = 250 \text{ A m}^{-2}$.

Table 2

Fe³⁺ and Zn²⁺ molar fluxes through IEMs (pH = 5, citric acid to Fe³⁺ molar ratio = 6)

$J_{Fe^{3+}} \cdot 10^7$ (across CEM), mol·s ⁻¹ ·m ⁻²	$J_{Fe^{3+}} \cdot 10^7$ (across AEM), mol·s ⁻¹ ·m ⁻²	$J_{Zn^{2+}} \cdot 10^7$, mol·s ⁻¹ ·m ⁻²
1.23	23.40	12,080

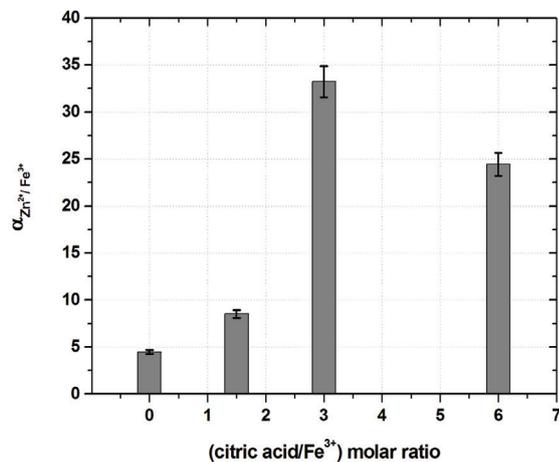


Fig. 8. The effect of complex agent/metal molar ratio on the $\alpha_{Zn^{2+}/Fe^{3+}}$ selectivity coefficient; $j = 250 \text{ A/m}^2$.

the anionic iron citrate complex firstly existed in a solution. In this case, the transport of negatively charged iron citrate complex across AEM was promoted.

The effect of complex agent/metal molar ratio on the selectivity coefficient is presented in Fig. 8. The selectivity coefficient of Zn²⁺/Fe³⁺ system increased from around 5 for solution without chelating agent to the around 35 at CA/Fe³⁺ molar ratio of 3. These results suggested that the separation efficiency could be improved, when CA/Fe³⁺ molar ratios equaled to 3 and 6, respectively.

4. Conclusions

In this paper, the applicability of ED enhanced with citrate complex formation for separation of copper and iron species from zinc was investigated. Results indicated that in performed experiments anionic as well as electrically neutral citrate complexes of copper and ferric were created. The effect of the chelating agent (CA) addition was examined. It was found that selectivity of ED in Zn²⁺ separation from Fe³⁺ and Cu²⁺ could be enhanced by the addition of chelating ligands, such as CA. The maximum values of selectivity coefficient for Zn²⁺/Cu²⁺ system observed in this work equaled to around 4.5 and 35 for Zn²⁺/Fe³⁺ system.

ED enhanced with complexation appears to be a viable method for removal of heavy metals from waste industrial effluents such as zinc electroplating baths. Analysis of results proves that ED with complex formation makes selective removal of zinc sulfate from the studied solutions possible.

Heavy metal removal from industrial effluents by ED enhanced with complex formation requires further investigations. Especially, the impact of membrane type (i.e., homogeneous or heterogeneous membrane), initial concentration of contaminating heavy metals in diluate, as well as type of chelating compounds such as lactic acid or malic acid, on selected transition metal ions transport across membranes should be investigated.

Symbols

$\alpha_{Zn^{2+}/M^{n+}}$	—	Selectivity coefficient
$J_{Zn^{2+}}$	—	Zinc ions molar flux, mol·s ⁻¹ ·m ⁻²
$J_{Cu^{2+}}$	—	Copper ions molar flux, mol·s ⁻¹ ·m ⁻²
$J_{Fe^{3+}}$	—	Iron ions molar flux, mol·s ⁻¹ ·m ⁻²
$C_{Zn^{2+}}$	—	Initial concentration of zinc ions in the diluate, mol·dm ⁻³
$C_{Cu^{2+}}$	—	Initial concentration of copper ions in the diluate, mol·dm ⁻³
$C_{Fe^{3+}}$	—	Initial concentration of iron ions in the diluate, mol·dm ⁻³

Acknowledgments

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