

Influence of Initial Feed Concentration and Ph on The Removal of Copper, Lead And Nickel Ions From Solutions in Electrolysis Process

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ABSTRACT

Influence of operating parameters of pH and initial concentration of feed solution were investigated on separation of divalent heavy metals (Cu^{2+} , Ni^{2+} and Pb^{2+}) from feed solutions using electrolysis (ED). The comparison of these operating parameters was determined using mathematical equations such as current efficiency, specific electrical energy consumption and removal efficiency. When the initial metal concentrations were examined, it was determined that the amount of removed matter increased as the concentration of feed solution increased. However, the efficiency of separation was decreasing. Effect of initial pH of the feed solution were examined, most appropriate recovery rates encountered in pH 6. More acidic pH values leads to a decrease in current efficiency and consequently an increase in energy consumption. The study represents that in an electrolysis process, it is necessary to select the most suitable operating parameters considering the factors such as limiting current density, electrical energy consumption, recovery efficiency, effluent quality and lifetime of membranes.

Keywords : Current Efficiency, Electrolysis, Heavy Metal Removal, Operational Parameters.

I. INTRODUCTION

Existence of heavy metals in effluent waters is an important problem for water pollution due to their high toxicity and non-biodegradability [1]. Plating, mining, automobile manufacturing, dyeing, and metal processing are most prominent industrial applications which releases heavy metal concentrations to environment [2]. Heavy metals can cause serious damages to the central nervous system and have adverse effect on kidney, skin, teeth, liver and lungs [3]. For the separation of heavy metal ions from wastewater, processes like adsorption, chemical precipitation, ion exchange etc. have been applied over years. These methods have advantages and also some disadvantages [4]. Among these methods ED comes to the forefront with short residence times, small installation area, minimal sludge production

advantages [5], high water recovery, highly selective desalination, less addition of chemicals and the possibility of a stop-and-go operation [6].

A typical ED stack is a whole of, anion and cation exchange membranes, electrodes, frames, gaskets and water inlet and outlet nozzles. With electrical current, ionized species migrates through membranes as cations transport toward the cathode crossing cation exchange membranes and vice versa [7]. Since 1950's ED processes has been applied in industrial scale [8].

ED processes has been used for recovery of useful products from waste water, salt and acid separation from food processes, treatment of the medical solutions, desalination of sea water, acid and base production from salts, acetic acid recovery, acid recovery from juices, purification of proteins,

regeneration of photographic chemicals [9], ultra-pure water production, demineralization of organic acids and sugar, treatment of amino acids and blood, decomposition of the electrolytes, preparation of isotonic solutions, wine stabilization [10], wastewater purification with mineral and metal ion recovery [5]. Heavy metal removal/recovery with electrodialysis has been studied with lead separation [6], remove of silver ions [11], lithium and cobalt separation [12], removal of copper cations [5] and gold (III) recovery [13].

Performance of an ED treatment system is depended on membrane properties, cell properties, operation mode and operational parameters like flow rate, pH of feed solution, applied voltage (or current), initial concentration of feed solution etc. [6]. Main industries that are discharging copper, lead and nickel ions are electroplating and metal surface treatment processes, printed circuit board manufacturing, wood processing industry and petroleum refining [14]. Because of these wide heavy metal discharging industries, removal of aforementioned heavy metals from wastewater become prominent. The objective of this study is to present the effects applied voltage, initial feed solution concentration and feed solution pH on the removal of certain metal ions in comparison with removal efficiency (RE %), current efficiency (CE %) and specific electrical energy consumption (SEEC) values.

II. METHODS AND MATERIAL

A. Experimental Setup

The electrodialysis cell used in the experiments was Microflowcell which is obtained from ElectroCell A/S. ED cell has got platinum covered titanium electrodes on both edges. The active electrode area for each electrode is 0.01 m². The electrodialysis system exists, three peristaltic pumps to circulate feed and electrolyte (anolyte and catholyte) solution, a direct current power supply for electrical demand and an electrodialysis stack consist of one anion exchange

membrane and one cation exchange membrane. Figure 1 shows the experimental setup used in the study.

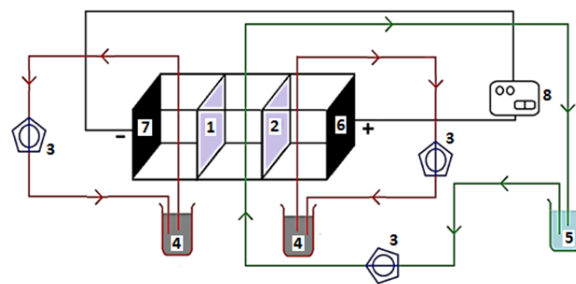


Figure 1. Experimental Setup (1-cation exchange membrane, 2-anion exchange membrane, 3-peristaltic pumps, 4-electrolyte solutions, 5-feed solution, 6-anode, 7-cathode, 8-DC power supply)

Nafion 117 was used as cation exchange membrane and Neosepta ACM was used as anion exchange membrane. Hence the electrodialysis stack has three compartments, one anion and one cation exchange membrane were installed to the stack.

Synthetic water was used as feed solution in all experiments that are prepared from lead (II) nitrate ($\text{Pb}(\text{NO}_3)_2$), nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), copper (II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) chemicals. For the electrolyte solution, desired mole of solutions from sodium chloride (NaCl) was prepared. Batch flow regime was applied and 0.5 L of electrolyte solutions and feed solution containing different heavy metal concentrations recirculated to ED stack for six hours of residence time in altered flow rates. For pH adjustments HCl and NaOH were used.

B. Analysis

Six hours of ED process were conducted to each waste water and samples were obtained in 10th, 30th and 60th minutes in first hour and in each hour after. If needed, samples were diluted with ultra-pure water and analyzed in Atomic Absorption Spectrophotometer (Thermo Scientific AAS ICE 3300) with appropriate calibration curves.

Removal efficiency (RE %) has been calculated with the following equation [7];

$$RE \% = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where, C_0 ; initial concentration of metal ion, C_t ; concentration of metal ion at time t ; The calculation of current efficiency (CE %) was performed with Eq. 2 [15].

$$CE \% = \frac{z F \Delta n}{N I \Delta t} \times 100 \quad (2)$$

Where, z is valency of the ion, F is Faraday constant which is $96485 \text{ A s mol}^{-1}$, Δn is the number of moles removed in time t (mol), N is the number of compartment in ED stack, I is the electrical current applied (A) and Δt is the time interval (s).

Specific electrical energy consumption (SEEC) has been calculated with Eq. 3. [16]

$$SEEC (\text{W h mg}^{-1}) = \frac{E \int_0^t I dt}{n} \quad (3)$$

Where E applied voltage (V), I is the electrical current (A), t is the time interval (h) and n is the amount of ions removed during time t (mg).

III. RESULTS AND DISCUSSION

Before applying different operational parameters to the reactor, limiting current density (LCD) has to be determined. LCD is called as the highest amount of current that can pass through a membrane area and exceeding the LCD value means wasting current that leads to energy losses [17]. For operational parameters of electrolyte solution concentration of 0.05 M NaCl; flow rate of 200 mL/min; pH of ≈ 6 which is natural pH of wastewater and 2 mg/L of feed concentration. LCD values for nickel, copper and lead containing feed solutions have been determined in between 0.034 – 0.037 mA/cm² for an applied voltages of 0 to 60 V. Figure that shows voltage – current curves and indicates the limiting LCD value can be seen on Fig. 2. Exceeding LCD value creates hydrolysis of water on

the surface of the membranes [18]. Also Lee G (2012) recommends 70 ~ 90% of the cell voltage corresponding to LCD for the applied voltage [19]. Due to these facts 45 V has been chosen and applied to electrochemical cell during the experiments.

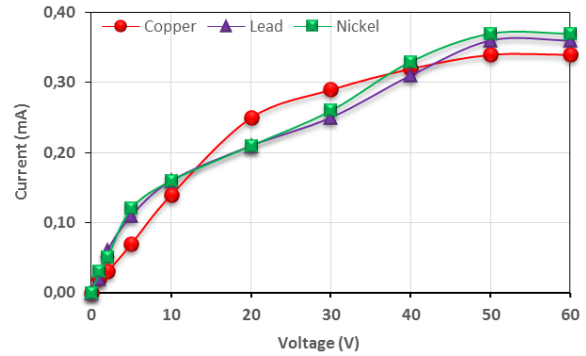


Figure 2. Determination of Limiting Current Density (Voltage – Current Curves)

A. Effect of Initial Feed Concentration

Initial feed solution concentration in an ED system is an important operational parameter to observe the effect on separation. Feed solutions containing copper, nickel and lead with initial concentrations of 1, 2, 5 and 10 ppm has been treated with constant operational parameters of 45 V of voltage, 0.05 M NaCl electrolyte solutions, natural pH and 200 mL/min flow rate to examine the effects.

Figure 3 shows the effect of initial concentration on removal and current efficiencies. For all types of metals, removal efficiencies has declined with increasing concentration. This situation can be explained as a result of concentration polarization [6] and membrane fouling [20] problems are more effective at higher concentrations. To reach a higher removal efficiency with increasing initial concentration, retention time of the wastewater has to be increased [21].

Adversely to removal efficiencies, increasing the concentration of feed solution proportionally increases the conductivity and ionic strength of

solution [21]. Which means an increase on current passing through electro dialysis stack. In example 1, 2, 5 and 10 mg/L copper containing wastewater have conductivities of 6.90, 10.96, 23.70 and 43.50 $\mu\text{S}/\text{cm}$ and these conductivities created currents such as 0.26, 0.35, 0.54 and 0.82 mA respectively. Depending on the Eq. 2 current efficiencies have to decrease with increasing currents but higher inlet concentrations leads higher amount of ions removed that makes positive impact on CE % values.

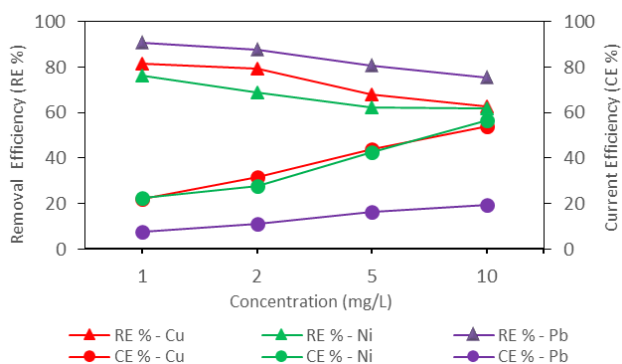


Figure 3. Effect of initial feed solution concentration on removal efficiency (RE %) and current efficiency (CE %) (Voltage: 45 V ; electrolyte solution: 0.05 M NaCl; flow rate: 200 mL/min; pH: \approx 6)

Amount of ions removed in mg depending on the feed concentration has also been examined with for altered concentrations and shown in Table 1. As the concentration rises quantity of matter removed rises. When examining the SEEC values, energy consumption per mg of removal had decreased with increasing initial concentration. This event depends on nature of the Eq. 3. Increased concentration may increase current passing through the stack and in constant voltage this situation had additive effect on electrical energy consumption. But increased concentration also had a positive impact on amount of matter removed which makes a decreasing impression on SEEC and lowered the values that makes EC process more efficient and more cost effective.

Table 1. Effect of initial feed solution concentration on SEEC and amount of ions removed (Voltage: 45 V ; electrolyte solution: 0.05 M NaCl; flow rate: 200 mL/min; pH: \approx 6)

Ion	Parameter	Concentration (mg/L)			
		1	2	5	10
Cu^{2+}	SEEC (W.h/mg)	0.173	0.121	0.087	0.071
	RM (mg)	0.41	0.79	1.69	3.15
Pb^{2+}	SEEC (W.h/mg)	0.153	0.106	0.072	0.060
	RM (mg)	0.45	0.88	2.02	3.77
Ni^{2+}	SEEC (W.h/mg)	0.184	0.150	0.097	0.073
	RM (mg)	0.38	0.69	1.56	3.09

B. Effect of pH

Initial pH of feed stream has been examined to determine the effect on removal efficiencies, current efficiencies and specific electrical energy consumptions. Experimental conditions were, feed solution concentration of 2 mg/L, applied voltage of 45 V, electrolyte solution concentration of 0.05 M with NaCl and flow rate of 200 mL/min for the pH's of 3, 5, 6 and 7. There are several reasons for the choice of the feed cell as neutral and acidic. One of these reasons is instability of Neosepta ACM in base mediums. One other reason is the form heavy metal in aqueous solution. Davis et al. (1997) had reported that solution composition and pH determines the nature of the ionic species that migrated across the membrane [22]. If a pollutant is not in form of ion, it cannot be treated in electro dialysis system. Ayres et al. (1994) [23] has reported the precipitation of metals with pH in form of metal hydroxides. Solubility of metal ions depends on pH, copper starts to precipitate in form of copper hydroxide around pH 6, nickel shows precipitation feature around pH 7.5 and lead starts to precipitate around pH 8 related to concentrations.

Figure 4 shows the effect of feed solution pH has been monitored for pH values of 3, 5, 6 and 7. With decreasing the pH of a solution, the ions and ionic strength of this solution increases by introducing the H⁺ ions into the medium. For pH 3, 5, 6 and 7 conductivities have been measured as 5391, 1350, 16.60 and 7.72 $\mu\text{S}/\text{cm}$ respectively. Although the ionic strength of the system has raised, inversely to pH, removal efficiencies have been decreased. This situation can be explained as the transport of H⁺ ions through cation exchange membrane with current instead of divalent metal ions. For pH's of 3 and 5 this assumption can be verified by measuring pH of catholyte solution. Catholyte solution's pH has been decreased from 6.12 to 4.26 value for pH 3 of feed solution containing lead. Also initial pH of 5 has showed the same trend. Adversely to this fact pH 7 has the lowest removal efficiency because of its low conductivity. In contrast to all these suggestions optimum removal efficiency has been obtained in pH 6 value which is the actual pH of feed solution. When considering the current efficiencies, low pH values has decreased the current efficiencies too much. Reason for this result is the currents passing through the stack. For pH's of 3, 5, 6 and 7 average currents monitored during EC were 9.14, 5.04, 0.35 and 0.24 mA respectively. The amount of ions removed could not response to increasing current values and CE % values has decreased drastically with decreasing pH. For pH 6 and 7 the difference in CE % values were not so significant.

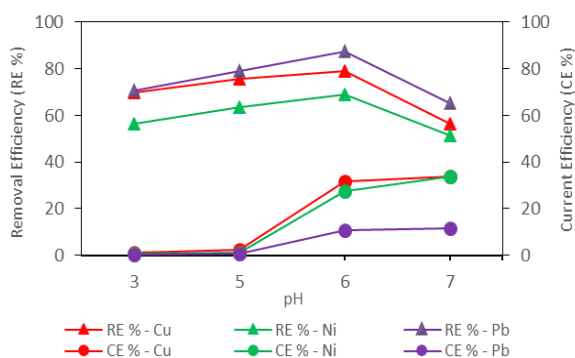


Figure 4. Effect of pH on removal efficiency (RE %) and current efficiency (CE %) (Feed solution conc.: 2

mg/L; voltage: 45 V; electrolyte solution: 0.05 M NaCl; flow rate: 200 mL/min)

Table 2 indicates the amount of removed matter in mg and SEEC values. Removed amount of ions in mg has optimal value in pH 6 because as mentioned in RE % values, not only current passing through the stack is significant but the types of species passing through the membranes is still an issue. For low pH values H⁺ ions flows with electrical current limits the removal of metal ions and decreases the amount of removed pollutants. As can be seen on Table 2 removed amount of matter in mg increasing until pH 6 and decreased in pH 7. The selectivity of cations with pH has an impact on removed amount of heavy metal ions but this action turned aside in pH 7 because at this pH value reduction of conductivity takes over the migration of ions and limited the removed amount of matter. When examining Table 2 specific electrical energy consumptions has very high distinctions with pH. Especially in low pH values with increasing ionic strength of the feed solutions by addition of HCl to adjust pH has enhanced the conductivity of the solution. Increasing conductivity of the feed solution boosted current passing through the system and this phenomena caused SEEC values to rise excessively. In ED process, the SEEC value is found to increase as the pH value of the feed solution decreases [24], furthermore ED process is not economical when pH of the feed solution is smaller than 3 [16]. If it is desired to increase the current passing through an ED system, this process must be achieved by increasing the ionic strength of the feed solution concentration with increasing concentration of the substance to be removed rather than by changing the pH value.

Table 2. Effect of pH on SEEC and amount of ions removed (Feed solution conc.: 2 mg/L; voltage: 45 V; electrolyte solution: 0.05 M NaCl; flow rate: 200 mL/min)

Ion	Parameter	pH			
		3	5	6	7
Cu ²⁺	SEEC (W.h/mg)	3.565	1.656	0.121	0.113
	RM (mg)	0.70	0.76	0.79	0.56
Pb ²⁺	SEEC (W.h/mg)	3.509	1.744	0.106	0.102
	RM (mg)	0.71	0.79	0.88	0.65
Ni ²⁺	SEEC (W.h/mg)	4.617	3.346	0.150	0.122
	RM (mg)	0.56	0.64	0.69	0.52

IV. CONCLUSION

Determination of LCD is an important indicator of how much current or voltage to be applied and to understand how efficiently the electrical energy used in the system. Applied voltages was chosen as 45 in experiments and the choice was made depending on LCD values.

Inlet feed solution concentration had reverse effect on removal efficiency because of intervention of concentration polarization phenomena. But adversely to RE % values, CE % values had raised with concentration. With increasing concentration, amount of metal ions passing to electrolyte solutions had increased and this fact enhanced current efficiency values despite increasing currents. Also increasing amount of ions removed has effected SEEC and lowered it.

pH of the feed solution has affected removal efficiency but especially current efficiency and SEEC values. Acidic medium leads higher ionic strength of the solution and creates higher current passing along ED stack. Adding H⁺ ions into feed solutions creates H⁺

ions to pass across the cation exchange membranes instead of divalent metal ions with electrical current and reduces the removal efficiency. pH > 8 feed solutions does not recommended because of precipitation of metal ions in form of metal hydroxides.

V. REFERENCES

- [1]. Zhou, G.Y., et al., A highly efficient polyampholyte hydrogel sorbent based fixed-bed process for heavy metal removal in actual industrial effluent. *Water Research*, 2016. 89: p. 151-160.
- [2]. Syukor, A.R.A., et al., Integration of phytogreen for heavy metal removal from wastewater. *Journal of Cleaner Production*, 2016. 112: p. 3124-3131.
- [3]. Huang, Y.F., et al., Removal of heavy metals from water using polyvinylamine by polymer-enhanced ultrafiltration and flocculation. *Separation and Purification Technology*, 2016. 158: p. 124-136.
- [4]. Han, W.J., et al., Studies on the optimum conditions using acid-washed zero-valent iron/aluminum mixtures in permeable reactive barriers for the removal of different heavy metal ions from wastewater. *Journal of Hazardous Materials*, 2016. 302: p. 437-446.
- [5]. Chang, J.H., et al., Copper cation transport and scaling of ionic exchange membranes using electro dialysis under electroconvection conditions. *Journal of Membrane Science*, 2010. 361(1-2): p. 56-62.
- [6]. Mohammadi, T., A. Razmi, and M. Sadrzadeh, Effect of operating parameters on Pb²⁺ separation from wastewater using electro dialysis. *Desalination*, 2004. 167(1-3): p. 379-385.
- [7]. Marder, L., A.M. Bernardes, and J.Z. Ferreira, Cadmium electroplating wastewater treatment using a laboratory-scale electro dialysis system.

- Separation and Purification Technology, 2004. 37(3): p. 247-255.
- [8]. Mier, M.P., R. Ibanez, and I. Ortiz, Influence of ion concentration on the kinetics of electro dialysis with bipolar membranes. *Separation and Purification Technology*, 2008. 59(2): p. 197-205.
- [9]. Scott, K., Overview of the application of synthetic membrane processes, in *Industrial Membrane Separation Technology*, K. Scott and R. Hughes, Editors. 1996, Springer Netherlands: Dordrecht. p. 8-31.
- [10]. Sadrzadeh, M., A. Rami, and T. Mohammadi, Separation of monovalent, divalent and trivalent ions from wastewater at various operating conditions using electro dialysis. *Desalination*, 2007. 205(1-3): p. 53-61.
- [11]. Guvenc, A. and B. Karabacakoglu, Use of electro dialysis to remove silver ions from model solutions and wastewater. *Desalination*, 2005. 172(1): p. 7-17.
- [12]. Iizuka, A., et al., Separation of lithium and cobalt from waste lithium-ion batteries via bipolar membrane electro dialysis coupled with chelation. *Separation and Purification Technology*, 2013. 113: p. 33-41.
- [13]. Sadyrbaeva, T.Z., Gold(III) recovery from non-toxic electrolytes using hybrid electro dialysis-electrolysis process. *Separation and Purification Technology*, 2012. 86: p. 262-265.
- [14]. Barakat, M.A., New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry*, 2011. 4(4): p. 361-377.
- [15]. Yu, L.X., et al., Recovery of acetic acid from dilute wastewater by means of bipolar membrane electro dialysis. *Desalination*, 2000. 129(3): p. 283-288.
- [16]. Abou-Shady, A., et al., Effect of pH on separation of Pb (II) and NO₃⁻ from aqueous solutions using electro dialysis. *Desalination*, 2012. 285: p. 46-53.
- [17]. Ravikumar, Y.V.L., S. Sridhar, and S.V. Satyanarayana, Development of an electro dialysis-distillation integrated process for separation of hazardous sodium azide to recover valuable DMSO solvent from pharmaceutical effluent. *Separation and Purification Technology*, 2013. 110: p. 20-30.
- [18]. Kanavova, N., L. Machuca, and D. Tvrznik, Determination of limiting current density for different electro dialysis modules. *Chemical Papers*, 2014. 68(3): p. 324-329.
- [19]. Lee, G., Effects of operating parameters on the removal performance of electro dialysis for treating wastewater containing cadmium. *Desalination and Water Treatment*, 2011. 35(1-3): p. 150-157.
- [20]. Lee, H.J., et al., Topiramate does not alter the kinetics of arachidonic or docosahexaenoic acid in brain phospholipids of the unanesthetized rat. *Neurochemical Research*, 2005. 30(5): p. 677-683.
- [21]. Kabay, N., et al., Separation of fluoride from aqueous solution by electro dialysis: Effect of process parameters and other ionic species. *Journal of Hazardous Materials*, 2008. 153(1-2): p. 107-113.
- [22]. Thomas A. Davis, J.D.G., Derek Pletcher, *A First Course in Ion Permeable Membranes* 1997, Romsey, England: The Electrochemical Consultancy.
- [23]. David M. Ayres, A.P.D., Paul M. Gietka, *Removing Heavy Metals from Wastewater* 1994, University of Maryland.
- [24]. Kabay, N., et al., Effect of feed characteristics on the separation performances of monovalent and divalent salts by electro dialysis. *Desalination*, 2003. 158(1-3): p. 95-100.