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INFLUENCE OF FLOW RATE ON THE REMOVAL OF COPPER, LEAD AND NICKEL FROM SOLUTIONS IN ELECTRODIALYSIS PROCESS

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Abstract

In electrodialysis (ED) of heavy metals such as copper, lead and nickel from solutions, one of the main operating parameter is the flow rate. The study focus on understanding the impact of different flow rates on removal efficiency, current efficiency, specific electrical energy consumption and removed amount of matter in mg. 70, 140 and 200 mL/min of flow rates has been applied to ED stack which has constant operating parameters of 0.05 M NaCl containing electrolyte solutions, 45 V of applied voltage, pH of 6 and dilute solutions with heavy metal concentrations of 2 mg/L. After 360 min. of ED process removal efficiencies of all types of metals has shown an increment trend. As an opposite effect, current efficiencies has been declined. When examining the removed amount of matter during process, parallel indications to removal efficiencies has been determined. Increasing flow rates has increased the amount of matter removed. Last findings on the removal of heavy metal depending on flow rates were specific electrical energy consumptions. Comparing flow rates of 70 and 200 mL/min, energy consumptions per mg of heavy metal removed has raised. These results *clearly points out that flow rate of dilute and electrolyte solutions in EC has an alternating effect on process. Further researches can be done for improving the removal efficiency and lowering the electrical energy consumption depending on other operational parameters on electrodialysis.*

Keywords

Current Efficiency, Electrodialysis, Flow Rate, Heavy Metal Removal

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1. Introduction

Accumulation of heavy metals to human body and environment can effect for long time periods (Zhou, Liu, Chu, Tang, & Luo, 2016). Basis of heavy metal pollution is from several industries and their occurrences has become a major risk nowadays (Ramteke & Gogate, 2016). Waste water treatment is the only way to reduce these risks. But when operating a waste water treatment system, environmental sustainability of the treatment plant and energy efficiency of the technologies used in treatment plant are important (Saha, Choudhury, & Majumder, 2017). Electrodialysis process can overcome these two important issues. Electrodialysis employs ion-exchange membranes and described as an alternative method to the treatment of wastewater containing metal ions (Marder, Bittencourt, Ferreira, & Bernardes, 2016). ED gains attentions with attractive advantages such as: simple, reliable, and cost-effective operation (Deghles & Kurt, 2016). Various treatment technologies and processes has been applied for the removal or recovery of heavy metals from different waste water types. These technologies and processes includes, adsorption (Shariful et al., 2017), chemical precipitation (Ku & Jung, 2001), electrocoagulation (Heidmann & Calmano, 2008), electroflotation (Khelifa, Moulay, & Naceur, 2005), ion exchange (He et al., 2016), biosorption (Cazon, Viera, Donati, & Guibal, 2013), phytoremediation (Favas & Pratas, 2015) and some other membrane filtration methods (Basumatary, Kumar, Ghoshal, & Pugazhenthi, 2016; Figoli et al., 2010; Mohsen-Nia, Montazeri, & Modarress, 2007). Also a novel type of membrane named modified polyamide thin film composite membranes (Ngo & Tran, 2017) has been introduced to membrane filtration methods.

Electrical potential applied to the system acts as the driving force in the separation of ions in the ED process. The mechanisms that are effective in ED are diffusion (concentration difference) and electrical potential. Configuration of the membrane cell determines the amount of ions to be removed. Membrane cell can be vertical or horizontal (Valero, Barceló, & Arbós, 2011). Parameters influencing the performance of ED, the number of cell pairs, the length of the solution path in the cell, applied voltage, flow rate and the concentration of the feed solution. Feed solubility quality indicators such as hardness and organic pollution also affect the performance of the ED process by influencing factors such as membrane fouling (Kanavova, Machuca, & Tvrznik, 2014).

Influence of flow rate on the removal/recovery of different pollutants or production of some chemicals has been studied by different researchers. In a study aims to produce CO_2 (Iizuka et al., 2012) has shown that increasing flow rate has a positive effect on CO_2 production. But this impact was limited. Conversely, as the flow rate of lead removal from wastewater increases, the performance of the cell is lowered, or even at very high speeds, it is observed that the separation ceases completely (Mohammadi, Razmi, & Sadrzadeh, 2004). So effect of flow rate on electrodialysis has diversity depending on the system used.

With the study presented, the effect of flow rate on performance criteria’s such as removal efficiency, current efficiency, specific electrical energy consumption and removed amount of matter in ED has been investigated for the removal of copper, lead and nickel containing solutions.

2. Materials and Methods

2.1. Experimental Setup

The electrodialysis stack used in the experiments was Microflowcell obtained from ElectroCell A/S. Two platinum covered titanium electrodes are installed to the edges of the stack. The ED system consists, three peristaltic pumps to circulate dilute and electrolyte (anolyte and catholyte) solution, a direct current power supply and an electrodialysis stack including of one anion exchange membrane and one cation exchange membrane. Fig. 1 shows the experimental setup used in this study.

Figure 1: *Experimental Setup*

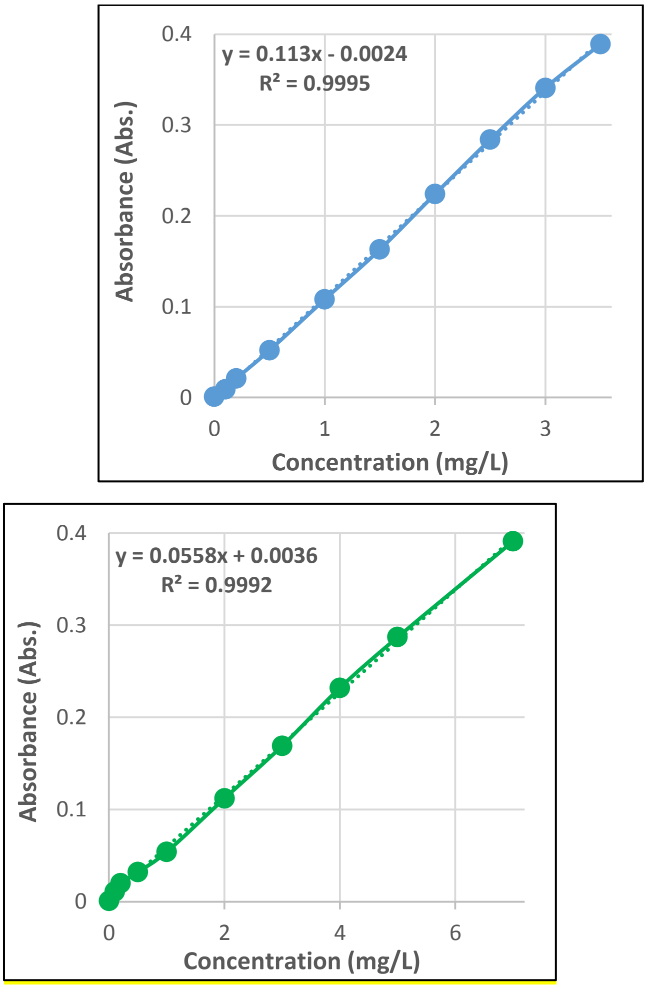
Nafion 117 and Neosepta ACM was used as cation exchange membrane as anion exchange membrane respectively. The electrodialysis stack has three compartments so one anion and one cation exchange membrane were installed.

Synthetic solutions was used in all experiments that are prepared from lead (II) nitrate ($Pb(NO_3)_2$), nickel (II) nitrate hekzahydrate ($Ni(NO_3)_2.6H_2O$), copper (II) sulfade pentahydrate ($CuSO_4.5H_2O$) for dilute solution. Batch flow regime was applied with 0.5 L of electrolyte concentration of 0.05 M NaCl and dilute solutions recirculated to ED stack.

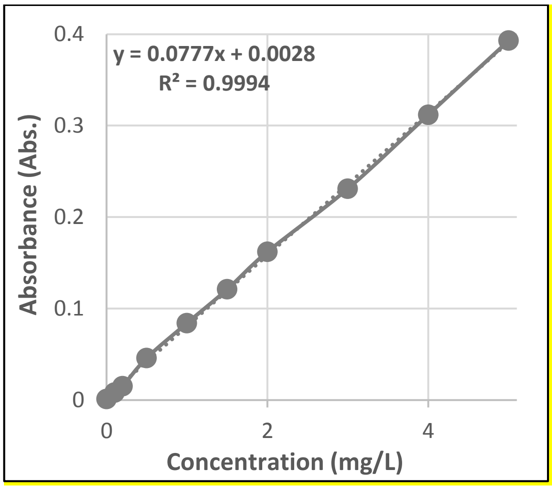
2.2. Analysis

Six hours of treatment 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.

Calibration curves were prepared from 1000 ppm stock solutions with different dilutions depending on maximum absorbances that Atomic Absorption Spectrophotometer can measure. The calibration curves used in the experiments shown in Figure 2 for (a) copper, (b) lead and (c) nickel.



(a) (b)



(c)

Figure 2: *Calibration curves used to determine the concentrations* ***(a)*** *copper,* ***(b)*** *lead,* ***(c)*** *nickel*

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

$$RE\ \% = \frac{C_0 - C_i}{C_0}\ x\ 100 \text{ (Marder, Bernardes, \& Ferreira, 2004) (1)}$$

Where C_0 the initial concentration of metal ion is, C_i is the concentration of metal ion at time t.

The calculation of current efficiency (CE %) was performed with Eq. 2.

$$CE = \frac{z\ F\ \Delta n}{N\ I\ \Delta t}\ x\ 100 \text{ (Yu, Guo, Hao, \& Jiang, 2000) (2)}$$

Where z is valency of the ion, F is Faraday constant which is 96485 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.

$$SEEC\ (W\ h\ mg^{-1}) = \frac{E \int_0^t I\ dt}{n} \text{ (Abou-Shady, Peng, Almeria, \& Xu, 2012) (3)}$$

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).

3. Results and Discussions

The constant operational parameters used in the experiments were 0.05 M NaCl electrolyte concentration, 45 V applied potential, 2 mg/L initial metal concentration, and the feed solution's natural pH which was ≈ 6 for flow rates of 70, 140 and 200 mL/min.

Fig. 3 shows the effect of flow rate on removal and current efficiencies for all three types of heavy metals.

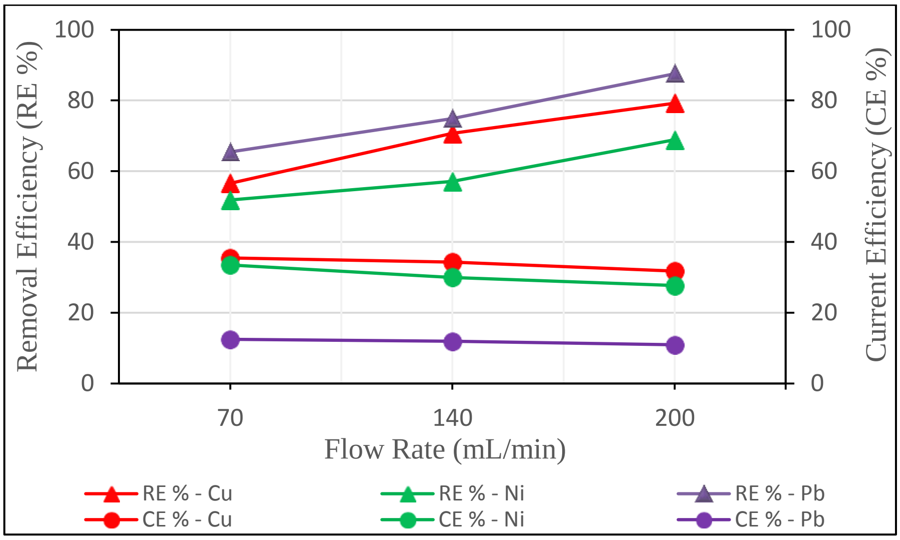


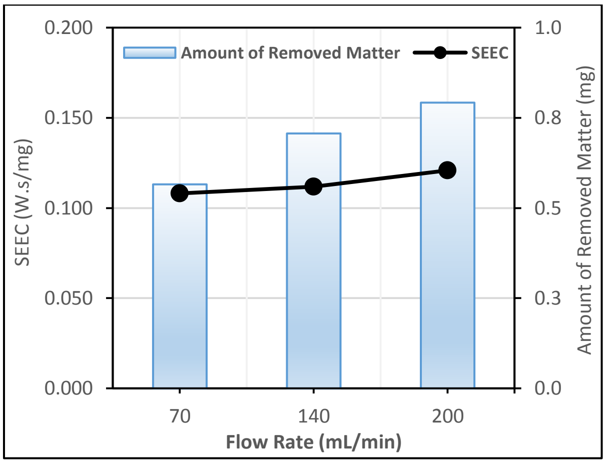
Figure 3: Effect of flow rate on removal and current efficiencies *(Dilute Conc.: 2 mg/L; Electrolyte Conc.: 0.05 M NaCl; Applied Voltage: 45 V; pH: ≈ 6)*

In an ED system, although the influence of the flow rate on the amount of matter removed is directly proportional, there are also some limitations. First limitation is the operating range for the ED system, maximum flow rate specified in the user manual is set to 15 L/h or 250 mL/min. If the system is operated above these flow rates, the increase in water pressure can damage the system. In addition, at very high flow rates, deterioration or rupture of the membrane surface can occur. The flow rate should be kept at an optimum value considering such adverse effects. So with these limitations flow rates has been chosen as 70, 140 and 200 mL/min.

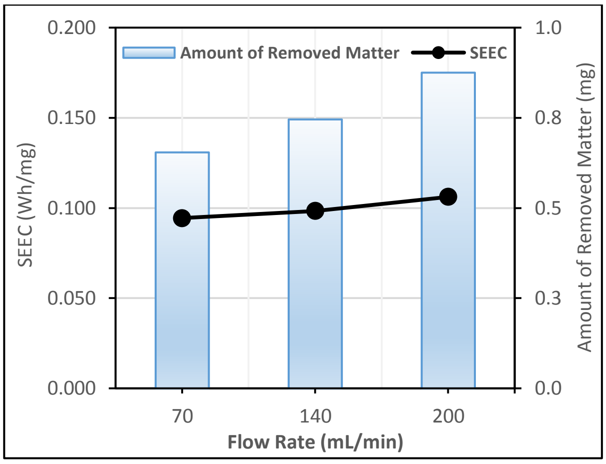
Results indicated that for all three ion types higher flow rates led to an increase in removal efficiency. For copper, nickel and lead containing wastewaters, removal efficiencies has been increased from 56.59 %, 51.83 % and 65.45 % to 79.25 %, 68.85 % and 87.56 % respectively for studied flow rates. This behavior can explained as slimming of the liquid film layer formed between the membrane surface and the liquid adjacent to the membrane at high flow rates and accordingly an increase of ion transport (Wang & Yang, 2001). Also thinning liquid film raises the mean current values passing through the ED module during process. Furthermore, with rising flow rates, concentration polarization phenomena decreases and ion transport between the phases increases (Gherasim, Krivcik, & Mikulasek, 2014). The increase in flow rate led to a decrease in current efficiency. Rising mean currents passing through the ED stack caused the system to operate with lower current efficiency. One other fact influencing current efficiency is the number of moles removed. Current efficiency values has been monitored for flow rate of 70 mL/min as 35.44 % for copper, % 33.49 for nickel and 12.45 for lead. When flow rate of 200 mL/min was applied removal efficiencies were calculated as 31.73 % for copper, 27.66 % for nickel and 10.89 % for lead. All three metal ions worked out in study have same concentration but their molecular weights are impressing current efficiency calculations depending on Eq. 2.

It can be seen with Fig. 3 that removal efficiencies of lead, copper and nickel ions are different. Reason for different removal efficiencies depends on the hydration energies of ions. The hydration energy is the energy change that occurs as a result of the hydration of one mole of ion in gas form (Whitten, Peck, Stanley, Davis, & Keeney-Kennicutt, 2009). It is stated that an ion with lower hydration energy has higher removal efficiency (Greben & Rodzik, 2005). The hydration energies of nickel, copper and lead metal ions are 2105, 2100 and 1481 Kj mol^{-1} respectively (Smith, 1977).

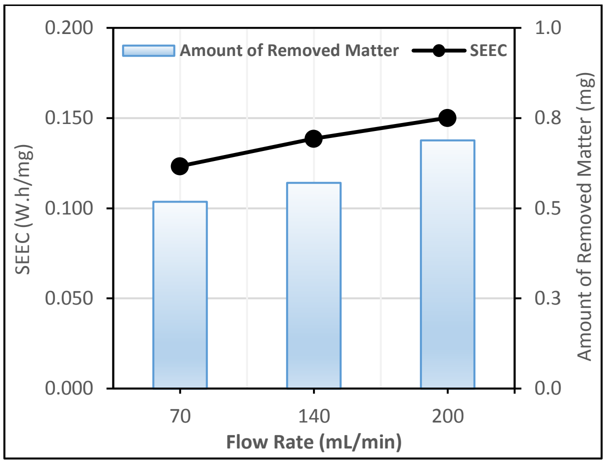
The effect of flow rate on specific electrical energy consumption and removed amount of matter in mg can be seen on Fig 4. for (a) copper (b) lead and (c) nickel containing solutions.



(a)



(b)



(c)

Figure 4: Effect of flow rate on Amount of matter removed and SEEC **(a)** copper, **(b)** lead and **(c)** nickel *(Dilute Conc.: 2 mg/L; Electrolyte Conc.: 0.05 M NaCl; Applied Voltage: 45 V; pH: ≈ 6)*

Fig. 4 indicates that the amount of removal is directly proportional to the flow rate and can be explained as reducing effect of flow rate on concentration polarization and liquid film. Amount of removal in mg has raised from 0.566 mg to 0.792 mg for copper, 0.655 mg to 0.876 mg for lead and 0.518 mg to 0.689 mg for nickel. SEEC values increased with the raising flow rates. Although the expectation with more amount of matter removed is depreciation on SEEC but depending on Eq. 3, the raise in the current passing with increasing flow rate has more effected the calculated SEEC values. Adverse effect of flow rate on the SEEC values can be recognized. Increasing flow rate increases specific electrical consumptions like for copper 0.108 $W.h.mg^{-1}$ has raised to 0.121 $W.h.mg^{-1}$ as the flow rate increases and same trends for lead and nickel containing wastewaters.

4. Conclusions

Flow rate along with other operational parameters such as applied voltage, pH, initial concentration, current density etc. has a huge impacts on an ED system. Before applying different flow rates, flow limits for the ED cell has to be considered.

One of the positive effects of increasing flow rate of dilute and electrolyte solutions is on the removal efficiencies and on the amount of matter removed. Increasing flow rates directly increases the removal efficiencies and amount of removal which is related to the effect of decreasing liquid film layer formed between the membrane surface and the liquid adjacent to the membrane and decreasing concentration polarization. However, on the contrary, raising of flow rate reduced the current efficiency and increased the energy consumption because there was not enough increment in the amount of the material removed despite an increase in mean current passing through the stack which are undesirable in an electrodialysis process.

Further researches can be conducted to understand the impact of operational parameters rather than flow rate to improve the removal efficiency values and to lower the electrical energy consumptions.

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