Elimination of nickel and chromium (VI) ions from industrial wastewater by electrodialysis/characteristics/impact of parameters

Hossein Kamani[1], Mehrnaz Hosseinzehi[1], Hossein Abdipour[2]*, Mohammad seyf[2], Hossein Moein[1] and Zeynab Moradian Haft Cheshmeh[3]

[1]Infectious Diseases and Tropical Medicine Research Center, Research Institute of Cellular and Molecular Sciences in Infectious Diseases, Zahedan University of Medical Sciences, Zahedan, Iran

[2]Student Research Committee, Department of Environmental Health Engineering, Hamadan University of Medical Sciences, Hamadan, Iran
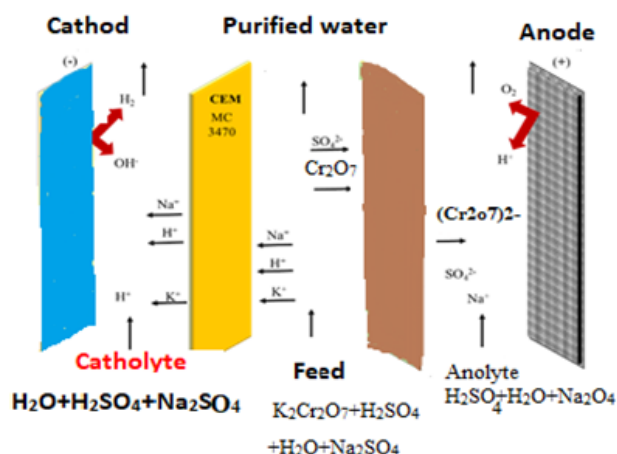
[3]Department of Epidemiology, School of Public Health, Iran University of Medical Sciences, Tehran, Iran

Graphical abstract

Abstract

Healthy water is a concern for the world due to rapid population growth and technological advancement. The entry of heavy metals into water as a result of various activities causes water pollution that has persistent effects. In this study, a specially designed electrodialysis cell was used to remove chromium (VI) and nickel ions from wastewater. The chambers were partitioned by Ionac MC 3470 cation exchange and Ionac MA 3475 anion exchange membranes. The cathode and anode were made of carbon fiber and stainless steel, respectively. The effects of voltage, initial pH, time, Na_2SO_4 concentration, feed flow rate and metal ion concentration on metal removal efficiency, energy consumption, current efficiency, current density and flux were investigated. Optimum values for 98.5% removal of 80 mg/L Cr (VI) ion in 90 min voltage 30 V, pH=3, addition of Na_2SO_4 0.5 g and feed flow rate 52. 8 ml/min, as observed. At the end of this period, concentration 1 mg/L, energy consumption 40 W/L, flow efficiency 30% and flux 12 x 10^{-5} mol/m2s were calculated. Optimum values of 25 V, pH=3, addition of Na_2SO_4 0.2 g and Qf = 42.6 mL/min were observed for 94.3% removal of 50 mg/L Ni^{2+} ions in 90 min. At the end of this period, the nickel ion concentration was 4 mg/L, the energy consumption was 34 Wh/L, the flow efficiency was 96.51%, and the flux was calculated as 40×10^{-5} mol/m2s. This study shows that the electrodialysis method can be effectively used to elimination chromium (VI) and nickel (II) ions from dilute wastewaters.

Keywords: Industerial wastewater, electrodialysis, chromium (VI), nickel (II), heavy metal elimination, ion exchange membranes

1. Introduction

Population growth, urbanization and industrial development all play an important role in the crisis of dehydration and lack of safe water (Lin *et al*. 2021; Jahangiri *et al*. 2023). Development is meaningless without adequate access to water (Dai *et al*. 2022). Water stress and the water health crisis affect the whole world and cause outbreaks of infectious diseases Several factors have led to the water recovery approach (Kamani *et al*. 2023; Kamani *et al*. 2023; Saleh *et al*. 2019), including water stress, lack of safe and sanitary drinking water sources, and excessive water consumption in agriculture and industries that consume a lot of water (Abdipour *et al*. 2023; Asgari *et al*. 2023; Kamani *et al*. 2023).

The increasing trend towards water shortages has a number of adverse effects on economic development, people's livelihoods and the quality of the global environment (Duruibe *et al*. 2007; Kamani *et al*. 2024). The periodic table of metals in groups 3 to 16 from period 4 onwards is referred to as heavy metals (Liang *et al*. 2021). These metals are inorganic compounds that are recognised for their high density and toxicity at low concentrations and have a special weight that is 4 to 5 times the weight of water (Liu *et al*. 2008; Miranzadeh *et al*. 2011). Heavy metals can find their way into water reservoirs via various natural and artificial pathways (Raikwar *et al*. 2008). Artificial pathways include the burning of fossil fuels, mining, agricultural wastewater,

factory wastewater and transport, while natural routes include soil erosion, precipitation and the dissolution of soluble salts (Liu *et al*. 2018; Farokhneshat *et al*. 2016). Various industries like tanning, textiles, battery manufacturing, electroplating, paper manufacturing, dying, metal smelting, mining and other industries result in the release of these metals into the environment (Remoundaki *et al*. 2016). As a result of interaction with heavy metals, problems such as cancer, stomach disorders, skin disorders, and visual impairment not only occur, but also lead to further death (Karamanis *et al*. 2007; Babaji *et al*. 2004). Heavy metal pollution causes serious damage to the entire ecosystem (Nachana'a, 2019). Nickel, one of the heavy metals, is a occurring metallic element in nature (Dong *et al*. 2022). Because of its chemical and physical properties, it is widely used its compounds in industry (Hu *et al*. 2022). It is used in zinc casting, silver refineries, and batteries (Parmar *et al*. 2013). And is also a versatile finishing process with a wide range of applications such as nickel electroplating, engineering, and decorative (Li *et al*. 2023). On the other hand, nickel is a carcinogenic metal and also causes pulmonary and reproductive toxicity with prolonged and repeated exposure (López *et al*. 2022). Chromium is one of the most essential elements for humans and animals. But this element in excess quantities, particularly in the +6 capacity, is harmful to health and can cause diseases like lung and bowel cancer (Balali-Mood *et al*. 2021; Islam *et al*. 2023). Therefore, it is found in the relevant factory wastewater, and since Cr (VI) is included in the group of carcinogenic chemicals, it should definitely be removed (Kırmızı *et al*. 2023; Xia *et al*. 2020). Chromium in wastewater is very dangerous from an environmental point of view (Chen *et al*. 2020). Cr (VI) accumulation in living tissues can also cause serious problems in the liver and kidneys (Sharma *et al*. 2022). It can cause skin irritation, eye diseases, and respiratory problems in humans (Zeng *et al*. 2019).

It is important to note that heavy metals such as cobalt and chromium can cause various health problems in humans. Some of the health issues include skin irritation, respiratory problems, and eye diseases (Chang *et al*. 2022). However, recent studies have shown that electrodialysis can be an effective method to remove heavy metals such as cobalt, nickel, and chromium from water.

There are various methods to remove heavy metals from wastewater, but electrodialysis using ion exchange membranes and electric current as a separation device is an effective process for removing heavy metals from wastewater (Li *et al*. 2023). The process has advantages such as high separation quality, easy scaling, easy operation, and removal of ions and salts in water and wastewater without the use of chemicals (Wang *et al*. 2020).

This study aims to investigate the removal of chromium (VI)and nickel (II), from model solutions by using a specially designed electrodialysis cell made of Teflon, silicone, and polyethene materials. The electrodialysis cell will be assembled in the laboratory and tested for stiffness to provide a cost-effective ED cell. The experiments will focus on investigating the effects of voltage, pH, sodium sulfate as a supporting electrolyte, flow rate, and metal concentration. Additionally, the study will evaluate the performance of electrodialysis in the removal of heavy metals by calculating the removal efficiency (RE), energy consumption (EC), current efficiency (CE), current density, and molar flux. The study is significant since previous studies have not adequately addressed the removal of heavy metals in wastewater, and it will be conducted to remove nickel, and 6-valent chromium from the wastewater of various industries by the electrodialysis method.

2. Materials and methods

2.1. Electrodialysis cell

The design of electrodialysis cell chambers was done with AutoCAD, these chambers were made of Teflon and polyethylene plates. which was assembled from cheap equipment. The structure of this cell consists of inlet and outlet for anolyte, catholyte and feed solutions. There are six liquid inlet and outlet compartments. Teflon inner frame and polyethylene outer frame were used, and washers were used to separate different parts, which are silicone and considered insulating. Part of the anode is made of carbon fiber and the cathode is made of stainless steel, which is exposed to the liquid that is the active area, 18 cm^2(40 mm $\times$ 45 mm).

2.2. Ion exchange membranes

In the electrodialysis cell, Ionac MA 3475, and Ionac MC 3470 anion and cation exchange membranes are used, which have three chambers. The anion exchange membrane has a permeability of 99% and a resistance of about 18 Ω cm^2, while the cation exchange membrane has a permeability of 95% and a resistance of about 16 Ω cm^2. The membranes were placed in distilled water at 75°C for 45 minutes. It was important to use 0.01 M sulfuric acid after each test.

2.2.1. Material and chemical products

A pH meter was used to adjust the pH value of the solution. A peristaltic pump ensured the flow of the nutrient solution and the electrolyte liquids, and a special lamp served as a direct current source. The metals were analysed using an Aquamate spectrophotometer for the ultraviolet-visible range. The metal ion sources included nickel (II) nitrate hexahydrate (Ni (NO$_3$)$_2$.6H$_2$O) and potassium dichromate (K$_2$Cr$_2$O7). Sodium sulphate (Na$_2$SO$_4$) was used as conductivity improver and supporting electrolyte. Diphenyl carbazide (C$_{13}$H$_{14}$N$_4$O) and diethyldithiocarbamic acid (C$_5$H$_{10}$NNaS$_2$.3H$_2$O, sodium salt trihydrate) were used as indicators for the UV spectrophotometric analysis of chromium (VI) and nickel (II) ions, respectively. The pH of the solution was adjusted with sulphuric acid (H$_2$SO$_4$) and sodium hydroxide (NaOH). Merck provided all chemicals.

2.3. Laboratory parameters and metal analysis

The electrodialysis cell consists of a dilution chamber and two electrolyte chambers separated by anion and cation exchange membranes. A solution of distilled water with

pH adjusted to 3 using H_2SO_4 is used as the electrolyte solution, with 7 mm sodium sulphate added. The solution is fed into the chamber and contains metal ions that are diluted. Other parameters are adjusted for each experiment.

Different experiments are conducted to investigate the effects of pH (2 to 4.59 for chromium and 2 to 5.67 for cobalt and nickel), supporting electrolyte addition (3.5 to 21.1 mm), flow rate (30 to 60 ml/min), and voltage (5 to 30) on efficiency, energy consumption, and flow efficiency. The wastewater with a metal ion concentration of 60 mg/L (separately) is used for these experiments.

To determine the limiting current density, gradual increases in voltage values are applied, and the current values flowing through the cell are observed. The removal of all three metals is observed for 90 minutes, with a 30 A sample being taken every minute. Cobalt and nickel are analyzed using diphenylcarbazide at a wavelength of 540 nm, while chromium is analyzed using diethyldithiocarbamic acid at a wavelength of 395 nm by atomic absorption spectroscopy (AAS) in the ED cell. Separate model solutions of cobalt and nickel are prepared from $K_2Cr_2O_7$ and nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), respectively. The feed solution volume is 100 mL in each experiment.
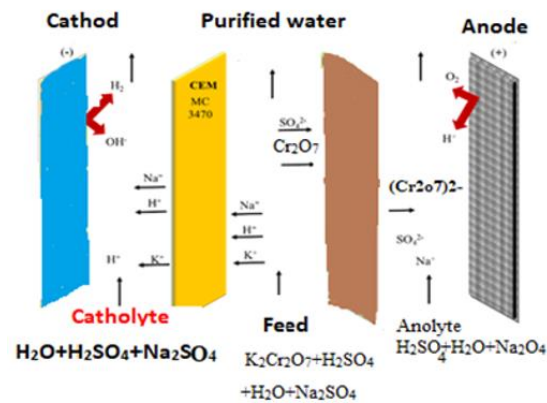

Figure 1. Batch operation for chromium

The ED system is studied in batch recirculation mode at constant potential (potentiostatic), and corresponding current values are recorded under constant voltage with an externally connected power supply. The galvanostatic mode is another method that could be used. However, it may not be possible to develop high voltages at very low concentrations. Therefore, the potentiostatic method is more convenient and reliable. When an electric current is supplied to the ED cell through a DC power supply, nickel and dichromate ions in the middle chamber go through the cation and anion exchange membranes, respectively, and are directed to the cathode or anode (as illusterate in Figures 1 and 2).

Hydrogen gas and oxygen are released at the anode during water electrolysis.

$$2\,H_2O \rightarrow O_2 + 4\,e^- + 4\,H^+ \tag{1}$$
$(E^0 = 1{,}299\ V;\ 25^{\circ}C,\ 1\ atm)$
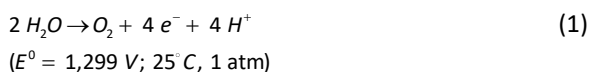
At the cathode, hydrogen ions which are positively charged, undergo reduction and as a result, hydrogen gas is produced.

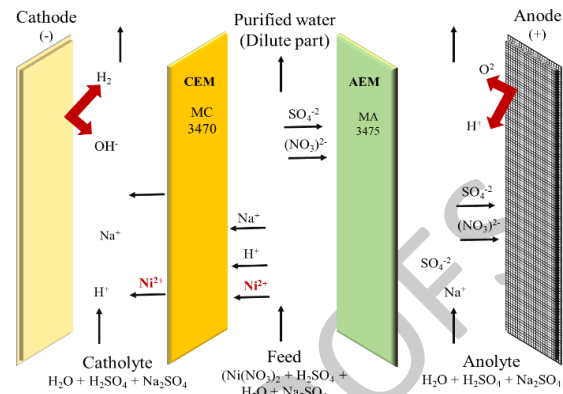$$H^+ + 2\,e^- \rightarrow H_2 \tag{2}$$
$(E^0 = 0\ V;\ 25^{\circ}C,\ 1\ atm)$

Figure 2. Batch operation for Nikel

During the cathodic reduction of nickel ions, these reactions occur at the anode and cathode.

$$Ni^{2+} + 2e^- \rightarrow Ni^+ \tag{3}$$
$(E^0 = 0{,}24\ V;\ 25^{\circ}C,\ 1\ atm)$

2.4. Theorical calculation equations

To quantitatively evaluate the performance of the ED system, three key parameters were computed: removal efficiency, energy consumption, and current efficiency. Removal efficiency (RE) indicates the percentage of heavy metal in the wastewater that is removed by the ED cell at the end of the experiment. By analyzing these parameters, we can determine how different experimental conditions affect the overall performance of the ED system.

$$RE\ (\%) = \frac{(C_i - C_d)}{C_i} \times 100 \tag{4}$$

The equation to calculate outlet concentration in a dilute solution at time t is given by Cd, where Ci represents the initial feed concentration in mol/m3. The energy consumed (EC) in an electrodialysis cell is directly proportional to the applied voltage, time, current intensity, and the volumetric amount used. The time is measured in minutes, and the current is measured in amps.

$$EC\,(Wh/L) = \frac{W \times t}{V} \tag{5}$$
$(W = Current \times Voltage)$

Where W is the power (watt), t is the time (hour), and V is the volume (L).

3. Results and discussion

The study aimed to determine if the current density limit is reached during the current source's operating range for both metal ions. Subsequently, the effects of applied potential, flow rate, supporting electrolyte concentration, pH, and metal ion concentrations on the feed's removal percentage (RE), energy consumption (EC), and current

efficiency (CE) were examined. An attempt was made to determine the most suitable treatment conditions. In all experiments, a peristaltic pump circulated distilled water with a pH of 3 containing 7 mm Na_2SO_4 in the electrode chambers at a rate of 33.6 mL/min.

3.1. Limiting current density

The electrodialysis system principle relies on understanding the limiting current density, which is a crucial parameter. This value provides information about the amount of current and electrical resistance, and it is determined by the number of ions present in the initial stage of the experiment. As voltage is applied to the system, ion migration begins and the amount of current increases. Eventually, the system reaches the point where ion migration stops, which is known as the limiting current density. At this point, the current becomes stable and will not increase even if the voltage continues to rise.
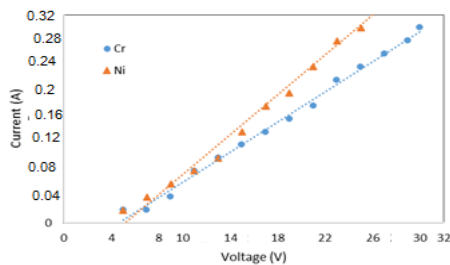
**Figure 3.** Limiting current density; current-voltage curve

An experiment was conducted to determine the limiting current density. In this experiment, separate voltages ranging from 5 to 30 volts were applied to Cr (VI) and Ni (II) solutions having a concentration of 50 mg/L and adjusted to pH 3. Current values were recorded at every 5-minute interval as the voltage was increased by two units. However, despite minor fluctuations, the limit current value could not be reached even when the voltage was increased up to 30 volts. Figure 3 shows that the graph is almost linear, indicating that the current-voltage curves are in the ohmic region. Therefore, we can conclude that the current density does not reach the limiting current density for this ED cell in the 0-30 V range.

### 3.2. The impact of applied voltage

During an experiment, the purpose was to determine the limiting current density. Two solutions of Cr^{6+} and Ni^{2+} with a concentration of 50 mg/L and pH 5 were used. The experiment involved applying separate voltages ranging from 5 to 30 volts to each solution. As the voltage increased by two units, current values were recorded at every 5-minute interval. However, even after increasing the voltage up to 30 volts, the limit current value could not be reached, despite minor fluctuations. According to Figure 3, the graph is almost linear, indicating that the current-voltage curves are in the ohmic region. Thus, we can conclude that the current density did not reach the limiting current density for this ED cell in the 0-30 V range.

The amount of ions transported across a membrane is directly proportional to the current density or electric current. As the voltage increases, the current density also increases, which in turn, increases the number of transported ions, or flux. Therefore, metal ion removal is expected to increase with time and voltage. However, the effect of electrical potential varies depending on the ions and their properties such as charge, hydrated radius, or ionic mobility. It has been found that the ED cell's selectivity for both ions decrease after a certain voltage value (Figure 4).
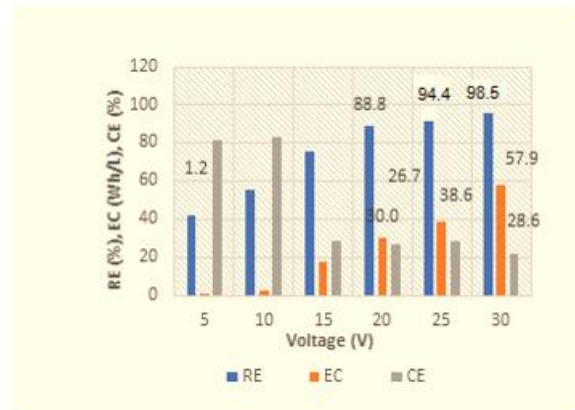
(a)
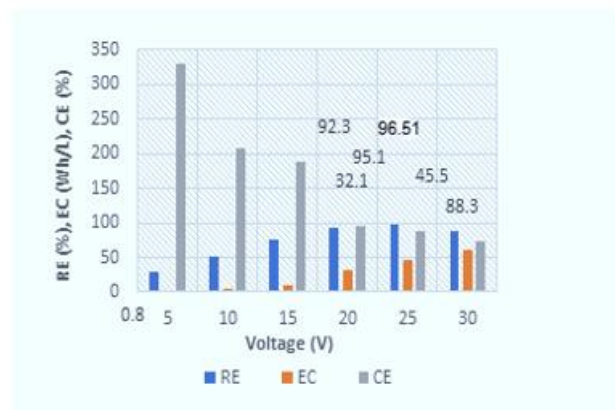
(b)

Figure 4. The impact of voltage on RE, EC and CE for (a) Cr (VI), (b) Ni (II) (t= 90 min, C_i=50 mg/L, pH=3, Na_2SO_4=7 mM, Q_f = 40.3 mL/min)

When considering energy consumption, a consistent increase in voltage is observed. Low energy consumption and high removal efficiency are crucial in separation systems to minimize costs. Therefore, a voltage of 25 volts is suitable for chrome removal and 20 volts for nickel removal. The energy consumed increases with the voltage value as the current increases. Several studies show that energy consumption increases as voltage increases.

Apart from low energy consumption, high current efficiency is also critical. High current efficiency was observed at low voltage values for the removal of Cr (VI) and nickel ions. However, the current efficiency decreases as the voltage increases. At 5 and 10 volts, the highest current efficiency was observed. Concentration polarization may cause a significant decrease in current efficiency after 10 V. Contamination in the ED system is possible because OH- ions can combine with cations in the

chamber due to electrodialysis. The resistance of ion exchange membranes is slightly low, but the resistance is high in the dilute chamber with low ion concentration. As the voltage value increases, the ions are transported faster due to the increasing current. However, as time progresses, metal ions are depleted in the dilute chamber, and the electrical resistance of the chamber increases. Thus, lower current efficiency is obtained at high voltage values compared to low voltages. In the removal of nickel ions, current efficiency values exceeding 100% were obtained. This demonstrates that the electrodialysis method works in nickel ion removal not only with the potential difference driving force but also with the concentration difference control.

The amount of flux is also expected to increase due to the ion transfer to the anode and cathode compartments as the voltage value increases. Since the limiting current density was not reached, no decrease in flux was observed. When the limiting current density is reached, an increase in voltage or current will not make sense since there are no ions to be transported in the medium. Figure 5 shows the variation of flux for different voltage values. It was observed that the voltage and flux with time increased, especially in the range of 5-15 V.
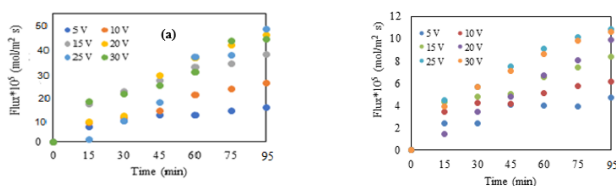

Figure 5. The variation of molar flux with time and voltage (a) Cr (VI), (b) Ni (II) (Ci=50 mg/L, pH=3, Na₂SO₄ =7 mM, Qf = 40.3 mL/min)

During the experiment, it was noticed that the flux values were quite similar, particularly in the range of 20-30 V, after 90 minutes for both nickel and chromium. The molar flux of Ni (II) in the designed ED cell was about four times higher than that of Cr (VI). The increase in voltage resulted in an increase in driving force due to ion migration, leading to higher flux values in both cases. However, the difference in the hydrated radii of the two ions could account for the variance in their respective performances and flux values. The size of the ionic and hydrated radii of each ion has a unique effect on ion migration and flux. Ions with larger hydrated radii also tend to have higher fluxes, which means a faster ion migration rate. This difference could be attributed to W Ye *et al*. (2019).

The presence of sodium sulfate in the solution means that sodium and sulfate ions are also present in the environment. This means that the current in the cell is carried not only by metal ions but also by sodium and sulfate ions. Therefore, excessive use of the supporting electrolyte will reduce metal ion transport. Furthermore, a study conducted by Wu *et al*(38). found that the rate of increase in conductivity decreased after 2 M sodium sulfate. When evaluating the removal percentage, current efficiency, and energy consumption together, it was determined that adding 7 mM Na₂SO₄ is sufficient for the

effective removal of both metal ions. This amount corresponds to a very low amount of 1 g per 1 L waste stream. There have not been many studies on chemicals used as electrolytes or conductivity enhancers. The current values show that sodium sulfate significantly increases conductivity in studies using electrolytes and synthetic wastewater, but the use of high dosages does not have a great effect. Additionally, the effect of using chemicals other than sodium sulfate can be investigated to provide clearer data. In a study, the effect of using NaCl, Na₂SO₄, H₂SO₄, and NaNO₃ chemicals as electrolytes was investigated. It was found that sodium sulfate is more effective in separating nitrate than the other three chemicals within the selected processing time and provides lower energy consumption(39).
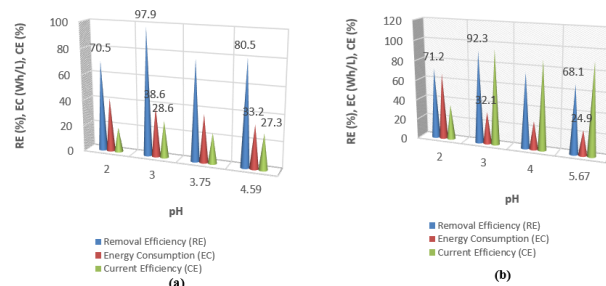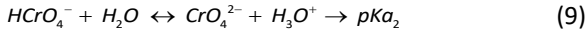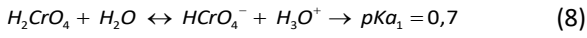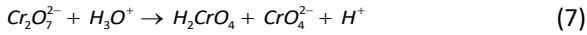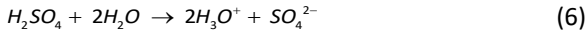

Figure 6. The effect of pH on RE, EC and CE (a) Cr (VI), (b) Ni (II) (t= 90 min, Ci=50 mg/L, Qf = 43 mL/min, Na₂SO₄=7 mM, Voltage=30 V for Cr (VI); 20 V for Ni (II))

### 3.3. The effect of pH of feed solution

It is seen from Figure 6 that the removal increases with the increase of the pH value from 2 to 3, but decreases at values after 3. Maximum removal was achieved at pH 3 for both metal ions. The difference in the amount of removal with a pH change may be caused by the hydrogen ions. The amount of acid used to lower the original pH of the solution from 4.59 to 3.0 is much less than the amount of acid added to lower the pH from 3.0 to 2. Apart from this, the presence of dichromate species can also affect the system. There are different types of chromium (VI), and they are affected by certain pH values and redox reactions. Chromium (VI) is only present at high pH values. Chromium (VI) species are given in Figure 16 (Pourbaix 1974). Chromium (VI) in aqueous solutions exists as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), hydrogen chromate ($HCrO_4^-$), dihydrogen chromate (chromic acid, H_2CrO_4), hydrogen dichromate ($HCr_2O_7^-$), trichromate ($Cr_3O_{10}^{2-}$) and tetrachromate ($Cr_4O_{13}^{2-}$). Hydrogen dichromate ($HCr_2O_7^-$), trichromate ($Cr_3O_{10}^{2-}$) and tetrachromate ($Cr_4O_{13}^{2-}$) are found in solutions where the chromium concentration is greater than 1 M and the pH value is less than zero. Dichromate ($Cr_2O_7^{2-}$) and hydrogen chromate ($HCrO_4^-$) can be found together in their aqueous solutions according to the pH range, this range is between pH = 2 and 6 according to Tandon *et al*. (1984) and between pH = 0.75 and 6.45 according to Pourbaix (1974). Accordingly, we can attribute the decrease and increase in the removal of chromium (VI) ions, which is maximum at pH = 5, up to pH = 3, to the existence of different chromium (VI) forms, as seen in Figure 6. Therefore, hydrogen chromate ions can also be

found in the medium in the pH 3–4.59 range. This can be explained by the following equations:

$$H_2SO_4 + 2H_2O \rightarrow 2H_3O^+ + SO_4^{2-} \qquad (6)$$

$$Cr_2O_7^{2-} + H_3O^+ \rightarrow H_2CrO_4 + CrO_4^{2-} + H^+ \qquad (7)$$

$$H_2CrO_4 + H_2O \leftrightarrow HCrO_4^- + H_3O^+ \rightarrow pKa_1 = 0,7 \qquad (8)$$

$$HCrO_4^- + H_2O \leftrightarrow CrO_4^{2-} + H_3O^+ \rightarrow pKa_2 \qquad (9)$$

$$pH = pKa + \log \frac{[HCrO_4^-][H_3O]}{[H_2O][H_2CrO_4]} \qquad (10)$$

When sulfuric acid is dissolved in water, it releases a hydronium ion, as shown in Equation (3.1). In an acidic medium, the dichromate ion dissolves in the hydronium ion, releasing chromic acid (H_2CrO_4) as given in Equation (3.2). The equilibrium reaction of chromic acid takes place in two steps, as shown in Equations (3.3) and (3.4). The pH values of the equilibrium reactions are also given in Sanchez-Hachair and Hofmann(40). The Henderson-Hasselbalch equation calculates the pH value, as shown in Equation (3.5) for Equation (3.3). The ratio of the concentration of the products to the concentration of the reactants should be a maximum of 1 or a minimum of -1. Therefore, in this case, the pH value of Equation (3.3) is close to 2, representing the abundance of hydrogen dichromate ions in the medium. This confirms the pH range mentioned by Tandon V *et al* (2019). The dichromate ion and the hydrogen chromate ion exist together in the same pH range, and the presence of hydrogen chromate may be responsible for the decrease and increase of the dichromate ion in analyses performed with feed solution samples at varying pH values.
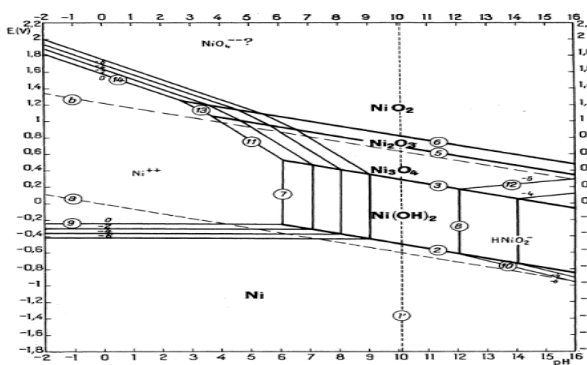
Figure 7. Potential-pH balance diagram for nickel-water system at 25°C

For the nickel ion, the amount of removal increased over time for each pH value. Energy consumption and current efficiency also increased over time for each pH value. The ion mobility in the medium affects the energy used and the current efficiency since the pH value changes with time for each pH value. At low pH values, conductivity is high due to the hydrogen ions in the medium, causing an excess of conductivity that increased the current. Increasing the current under constant voltage also increased the amount of energy used. At pH 2, the lowest current efficiency values were obtained for both metal ions. The acidity increases as pH decreases, resulting in an increase in the amount of hydrogen ions that use the majority of the current. The presence of H^+ and SO_4^{2-} ions in the medium as a result of the sulfuric acid added to the solution at low pH values is another reason for the decrease in current efficiency for both metal ions.

The pH value of 3 shows the highest removal efficiency. Although energy consumption is low at pH values of 4 and 5.67, pH=5 was observed to be the most appropriate value due to the high difference in removal efficiency. The removal decreases after reaching the optimum value of pH=3. At lower pH values, there are more hydrogen ions, which compete with the Ni^{2+} ions in the medium, resulting in less removal (Mohammadi *et al.* 2021). It is easier for hydrogen ions (with a mobility of 4) to pass through the membrane as compared to metal ions like Ni^{2+} (with a mobility of 0.267), Cr^{3+} (with a mobility of 0.25), and Cu^{2+} (with a mobility of 0.3) Bernardes *et al* (2019). stated that in their tests of purifying synthetic wastes in the ED cell, nickel ions had less separation due to their competition with hydrogen at low pH values. Therefore, in the case of nickel precipitation in wastewater with a pH value of 5, agitation with a magnetic stirrer is recommended (Segura *et al.* 2015).

Observations show that the concentration of nickel (Ni^{2+}) ions is present in specific amounts at the cathode, especially at 48 mg/L with a pH of 3. The pH values of the cathode chamber were measured and found to be 10 or higher in the basic medium due to the release of OH^- ions from the reduction of water molecules. Nickel (II) ions combine with hydroxide and precipitate at the cathode. The nickel ion reacts with the hydroxide ion formed in the basic medium, leading to precipitation. Consequently, instead of nickel reduction, nickel (II) hydroxide can be forme (Ash *et al.* 2020; Lekhlif *et al.* 2014). If the solubility limits are exceeded, nickel can be combined with the hydroxide (OH^-) ion. Figure 7 illustrates the pH balance diagram for the nickel-water system at 25 °C. According to the diagram, the nickel ion is present in the range of 6-7 pH, while the chemical Ni $(OH)_2$ exists in the pH range of 9–12. That is, in fact with the increase of pH, (Ni^{2+}) ions is in the cathode in the form of nickel hydroxide, and then by performing reactions in the cathode, it is formed in the form of safe nickel dioxide.

3.4. *The effect of flow rate to the feed solution*

The difference in removal efficiency for nickel ions is small for both flow rates used, resulting in low energy consumption. However, for chromium ions, a higher energy was required at a lower flow rate. Furthermore, the removal efficiency decreased for both ions as the flow rate increased, as shown in Figure 8.

Flow rate is an important factor in the electrodialysis process. It refers to the time the solution stays in the compartment. As the flow rate increases, the duration of the ions in the membranes decreases, which can lead to a decrease in removal efficiency. This happens because the ions do not have enough time to transfer between the membranes. Ions with high diffusion, such as nitrate and

fluoride, can take advantage of the residence time in the membrane. However, if the diffusion of the dichromate ion in water is low, like that of the chromate ion, low diffusion reduces the transfer to the concentrated compartment. This can also negatively affect the removal efficiency. The diffusion of ions in water can play an important role in the electrodialysis process. For instance, the diffusivity of nickel in water is 0.7×10^{-8} m^2/s, and the diffusion of chromate in water is 1.22×10^{-9} m^2/s.
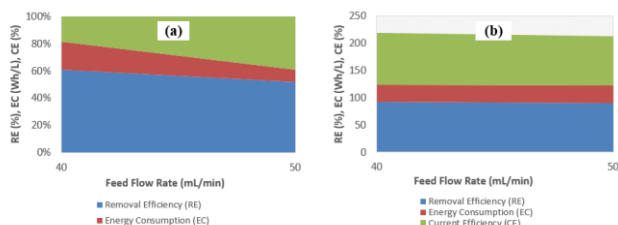
Figure 8. The effect of feed flow rate on RE, EC and CE (a) Cr (VI), (b) Ni (II) (t= 90 min, Ci=50 mg/L, Na$_2$SO$_4$=7 mM, Voltage=25 V for Cr (VI); 20 V for Ni (II))

Flow rate can reduce the concentration polarization phenomenon caused by the accumulation of substances in the membranes and increase efficiency. However, it can also negatively affect the removal efficiency by reducing the retention time in the membranes. Therefore, choosing the appropriate flow rate is crucial. The flow rate varies depending on the characteristics of each ion. Since the mobility of chromium (VI) (dichromate) ions is higher than that of nickel, it has been observed that the removal efficiency of chromium is higher at low flow rates. On the other hand, the energy consumption increases with the increase in flow rate due to the increasing current density in nickel removal. In contrast, chromium removal decreases as the current density decreases. The current efficiency decreases with the increase in flow rate for nickel ions, but it increases for chromium ions. This could be because the increase in ion transfer is more or less than the increase in current density.
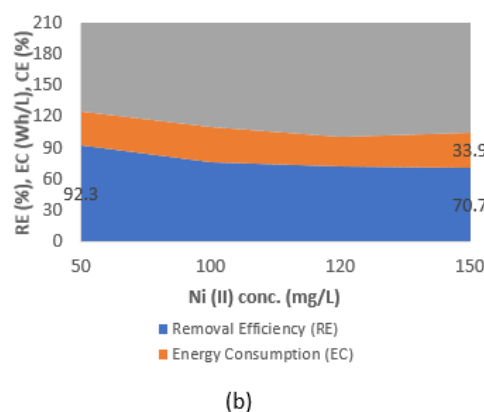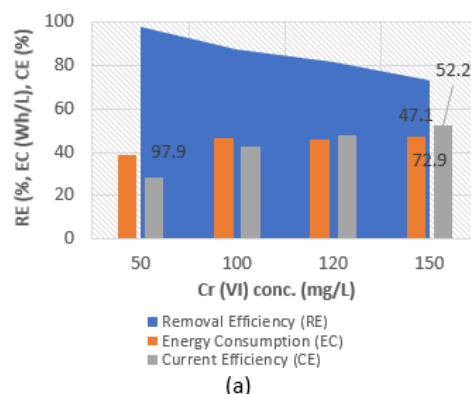
3.5. The impact of initial metal concentration in the feed solution

As the concentration increases, a decrease in the removal efficiency and an increase in the current efficiency and energy consumption are observed. The reason for this can be explained by the abundance of Cr (VI) ions in the medium.

The high current efficiency indicates the presence of many ions in the medium, which carry the current, making the process efficient. During the 90-minute experiment, an increase in the concentration of ions caused a decrease in the removal efficiency, despite the increase in conductivity. This decrease can be attributed to concentration polarization and the limited separation capacity of the membranes. Excess ions can accumulate and cause pollution, resulting in the accumulation and stratification of the membranes, leading to decreased removal efficiency (Figure 9).

As the concentration increased, counter-ion competition also increased, which can reduce the removal efficiency.

Previous studies have shown that removal efficiency decreased due to counterions. Additionally, an increase in energy consumption was observed with an increase in concentration. The energy consumed is low at 100 mg/L concentration for both ions, but it increases as the concentration increases (Figure 10).

(a)

(b)

Figure 9. The effect of initial metal concentration on RE, EC and CE (a) Cr (VI), (b) Ni (II) (t= 90 min, Qf=40 mL/min, Na$_2$SO$_4$=7 mM, Voltage=30 V for Cr(VI); 20 V for Ni(II))
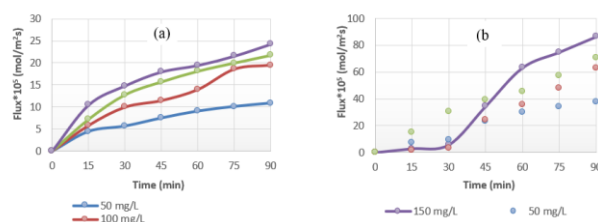
Figure 10. The variation of molar flux with time and concentration (a) Cr (VI), (b) N$_i$ (II) (pH=3, Na$_2$SO$_4$=7 mM, Q$_f$ = 40.3 mL/min)

The current efficiency increased with an increase in the concentration of both ions. The decrease in electrical resistance of the solutions and the increase in ion transfer result in higher current efficiency. For concentrations between 50 mg/L and 150 mg/L, the increase in ion transfer is much higher than the increase in current density, leading to increased current efficiency. In summary, the removal efficiency is higher at lower concentrations regardless of nickel and chromium.

The mobility of chromium ions is high, which causes them to adhere less to the membrane and move away from the medium. On the other hand, nickel ions behave in the opposite direction. Chromium and nickel ions are used in

varying concentrations across many industries. Therefore, research was conducted using a feeding solution with concentrations of 50, 100, 120, and 150 mg/L for both ions. It was observed that the removal efficiency decreased with increasing concentration. At high concentrations, removal of ions becomes more difficult due to excess ions in the medium (increased conductivity) or concentration polarization, which in turn reduces efficiency. Additionally, the abundance of ions in the medium necessitates longer time and higher energy consumption to ensure removal. This is undesirable both in laboratory-scale systems and industrial activities. Based on the test results, a concentration of 50 mg/L is suitable for both ions, although there is a concentration difference besides the electrical potential in nickel. Literature studies show that a removal efficiency of almost 100% can be achieved at a concentration of 10 mg/L.

4. Conclusion

The study investigates the effectiveness of electrodialysis for removing nickel and chromium ions from water. These heavy metals are notorious for causing environmental issues. The study examines the impact of various parameters such as applied voltage, treatment time, metal concentration, pH value, and feed solution circulation rate on removal efficiency, energy consumption, and molar flux in this electrochemical separation process. The optimal operating conditions for efficient removal were determined.

The study found that pH is highly effective in removing nickel and chromium ions and lowering energy consumption. The ED cell should be operated at pH 3 for the removal of both ions, rather than at low or high pH values. Specific pH conditions can be set for each compartment, based on the chemical properties of chromium and nickel. The study also found that chemicals used as electrolytes or conductivity enhancers have not been widely researched. Sodium sulfate was found to increase conductivity significantly in studies with electrolytes and synthetic wastewater. However, when used in high doses, it had little effect on removal efficiency.

Flow rate is an essential parameter in electrodialysis. While it can reduce concentration polarization caused by the accumulation of substances in the membranes and increase efficiency, it can also negatively affect removal efficiency by reducing retention time in the membranes. Therefore, selecting the appropriate flow rate is crucial. The flow rate varies according to the characteristics of each ion. Chromium (VI) ions have higher mobility than nickel ions. It was observed that the removal efficiency of chromium was higher at low velocities. On the other hand, as flow rate increased, the removal efficiency of nickel was higher than that of chromium. High ion mobility made chromium adhere less to the membrane and move away from the medium. Nickel behaved in the opposite direction.

The study found that removal efficiency decreased with increasing concentration. High concentrations of ions in the medium caused either more conductivity or concentration polarization, which makes removal difficult and lowers efficiency. Moreover, due to the abundance of ions in the medium, it takes longer to ensure removal, and energy consumption increases.

The study found the most suitable parameters for efficient removal of 80 mg/L of Cr(VI) and Ni^{2+} ions. The optimal values for the removal of 80 mg/L of Cr(VI) ions in 90 minutes were 30 volts, pH=3, 7 mM sodium sulfate in feed solution, 0.2 g sodium sulfate in electrolyte solutions, 52.8 mL/min electrolyte solution flow rate, and 50.38 mL/min feed solution flow rate. The study achieved 98.5% removal of chromium ions with an energy consumption of 40 Wh/L and current efficiency of 30%. For the removal of 80 mg/L of Ni^{2+} ions, 20 volts, pH 3, 0.1 g feed solution sodium sulfate, 0.2 g electrolyte solution sodium sulfate, 52.8 mL/min electrolyte solution flow rate, and 42.6 mL/min feed solution flow rate were optimal. The study achieved 92.31% removal of nickel ions with an energy consumption of 34Wh/L and current efficiency of 96.51%. The study demonstrated the cost-effectiveness of the laboratory-scale cell design.

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