Removal of Chromium (VI) ions from Aqueous Solutions using Electrocoagulation System

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ABSTRACT

Access to freshwater resources has been dwindling in recent years, owing in part to the rising population, industrial expansion, and the uncontrolled discharge of various contaminants into waterways. Chromium-containing wastewater, in particular, is one of the major environmental contaminants; it is an exceedingly hazardous metal in the form of Cr(VI) that causes serious environmental and health issues. As a result, the goal of this study was to remove chromium ions from an aqueous solution utilizing cost-effective and environmentally friendly electrocoagulation technology with iron and aluminium electrodes, as well as to assess its treatment capacities under a variety of parametric conditions.

Under identical conditions, the chromium removal efficiency of iron and aluminium electrodes were evaluated. First, the results shows that removal efficiency improves with increasing agitation in the reaction tank and at an optimum electrode distance of 2 cm under both acidic and basic conditions. At optimum conditions (chromium concentration of 25 mg/L, electrode distance of 2 cm, 1.5 g electrolyte (NaCl), 9 V, and stirring speed of 400 rpm); an iron electrode removed 95% of the chromium ion at pH 8, while an aluminium electrode removed ~100% of the chromium ion at pH 3 in 60 minutes. To treat 200 mL of the aqueous solution containing 25 mg/L of chromium ions, the Fe and Al electrodes demonstrated 81.5% and 92.4% Faraday electrode efficiencies and consumed 7.2 kWh and 13.5 kWh electrical energy, respectively. The operating costs to treat an aqueous solution containing 200 mL of chromium ion were \$ 1.26 per m^3 for Al and \$ 0.68 per m^3 for Fe electrode, when considering the electrical energy consumed and the cost of electrodes.

When the removal efficiencies, treatment duration, and treatment cost are considered, it can be stated that the electrocoagulation approach used here is efficient, cost-effective, and simple to manage and maintain. In addition, using the adsorption approach, the sludge produced can be reconditioned and utilized as an adsorbent for water treatment.

Keywords: Chromium ion removal; electrocoagulation technique; heavy metal pollution; wastewater treatment.

ÖZ

Kısmen artan nüfus, endüstriyel genişleme ve çeşitli kirleticilerin su yollarına kontrolsüz deşarjı nedeniyle tatlı su kaynaklarına erişim son yıllarda azalmaktadır. Özellikle krom içeren atık su, başlıca çevresel kirleticilerden biridir; ciddi çevre ve sağlık sorunlarına neden olan Cr(VI) formundaki son derece tehlikeli bir metaldir. Sonuç olarak, bu çalışmanın amacı, demir ve alüminyum elektrotlarla uygun maliyetli ve çevre dostu elektrokoagülasyon teknolojisini kullanarak sulu bir çözeltiden krom iyonlarını uzaklaştırmak ve ayrıca çeşitli parametrik koşullar altında arıtma kapasitelerini değerlendirmektir.

Aynı koşullar altında, demir ve alüminyum elektrotların krom giderme verimliliği değerlendirildi. İlk olarak, sonuçlar, hem asidik hem de bazik koşullar altında, reaksiyon tankında artan çalkalama ile ve 2 cm'lik bir optimum elektrot mesafesinde çıkarma verimliliğinin arttığını göstermektedir. Optimum koşullarda (25 mg/L krom konsantrasyonu, 2 cm elektrot mesafesi, 1.5 g elektrolit (NaCl), 9 V ve 400 rpm karıştırma hızı); bir demir elektrot pH 8'de krom iyonunun %95'ini çıkarırken, bir alüminyum elektrot pH 3'te krom iyonunun ~%100'ünü 60 dakikada uzaklaştırdı. 25 mg/L krom iyonu içeren 200 mL sulu çözeltideki krom giderimi için Fe ve Al elektrotları sırasıyla %81.5 ve %92.4 Faraday elektrot verimliliği gösterdi ve yine sırasıyla 7,2 kWh ve 13,5 kWh elektrik enerjisi tüketti. 200 mL krom iyonu içeren sulu bir çözeltiyi işlemek için işletme maliyetleri, tüketilen elektrik enerjisi ve elektrotların maliyeti göz önüne alındığında, Al için m^3 başına 1,26 $ (dolar) ve Fe elektrot için m^3 başına 0,68 $ (dolar) olarak hesaplanmıştır.

Giderim etkinliği, giderim süresi ve giderim maliyeti göz önüne alındığında, burada kullanılan elektrokoagülasyon yaklaşımının verimli, uygun maliyetli, yönetimi ve bakımı basit olduğu ifade edilebilir. Ek olarak, adsorpsiyon yaklaşımı kullanılarak üretilen kalıntı, yenilenebilir ve su arıtımı için bir adsorban olarak kullanılabilir.

Anahtar Kelimeler: Krom iyonu giderme; elektrokoagülasyon tekniği; ağır metal kirliliği; atık su arıtma.

DEDICATION

I dedicate this work to Almighty Allah, my family and friends for their love, care, and constant support.

ACKNOWLEDGMENT

Alhamdulillah, all praises to Almighty Allah (S.W.T) for the strength and His blessing in completing this thesis.

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LIST OF ABBREVIATIONS

Al	Aluminium
CD	Current Density
Cd	Cadmium
COD	Chemical Oxygen Demand
Cr	Chromium
Cu	Copper
EC	Electrocoagulation
Fe	Iron
Ni	Nickel
TiO_2	Titanium Dioxide
Zn	Zinc
$Zn_3(PO_4)_2$	Zinc Phosphate

Chapter 1

INTRODUCTION

1.1 Water Pollution

Water is sometimes referred to be a universal solvent since it dissolves not just numerous compounds but also more pollutants than any other liquid, making it particularly vulnerable to contamination. Water pollution is a growing global challenge that threatens economic progress and the health of several millions of people. The reduction in the quality and quantity of water these days is a result of the increase in population, change in climate, industries and growing demand for food that has a large environmental impact [1]. According to the International Initiative on Water Quality (IIWQ) report, an average of 350 megatons of industrial waste is dumped into water bodies each year. In addition, tons of millions of polluted water and other effluents are released into the world's water each day, causing global water quality to deteriorate.

Hospitals and pharmaceutical effluents, residential releases, agricultural run-offs, sewage releases, oil pollution, radioactive substances, marine and river dumping, and manufacturing industries are all sources of water pollutants in the environment [2]. By increasing the quantity of highly toxic chemicals and heavy metals in the water, these contaminants will have an impact on marine life and plant growth, as well as potentially reduce dissolved oxygen [3].

1.1.1 Heavy Metal in Wastewater

Metals like chromium, cadmium, lead, nickel, iron, and mercury are commonly used in industry and are often released into the environment. The majority of these heavy metal ions are hazardous and can migrate into a variety of water sources. In addition, these heavy metal ions can accumulate and be bio-augmented [4,5]. Their toxicity has the potential to cause everything from minor discomfort to a serious life-threatening illness, as well as irreversible damage to vital body systems. This is due to their non-biodegradability, high toxicity, and potential carcinogenicity.

Chromium (Cr) is among numerous metals used in industrial applications like electroplating, metallurgy, chemical catalyst, printing inks, leather making, cement production, photography, and dyeing. Chromium's chemical and toxicological properties are determined by its oxidation state: trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). Hexavalent chromium is highly soluble in water and has high mobility in the environment, whereas trivalent chromium solubility in water is low and in alkaline or even slightly acidic condition easily precipitates as $Cr(OH)_3$ [1]. Although trivalent chromium is an important nutrient for humans[5], its toxicity to living cells is 500–1000 times lower than hexavalent chromium and being exposed to Cr(III) for a long time may have certain negative health consequences[6].

As a result of increased discharge by various industries that make use of chromium for different purposes, the amount of chromium ions discharged into the environment is rising, posing environmental and health risks [7]. Exposure to fatal doses of chromium ions; in particular, can cause health problems such as liver damage, stomach ulcers, kidney damage, reproductive issues, lung and nasal cancer, irritation of the skin, and oedema.

As a result, developing a cost-effective and highly viable approach for reducing chromium ions in industrial effluent before its release into the environment is very important [8].

1.2 Conventional Wastewater Treatment Techniques

Heavy metal ions from various industrial effluents can be removed as efficiently as possible via several techniques. Figure 1 depicts these processes, with some being explained below:

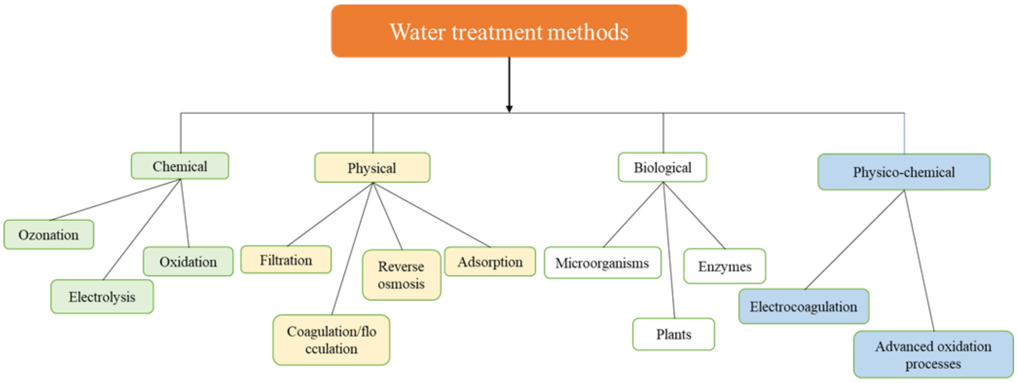

Figure 1: Various water treatment technologies

1.2.1 Biological Treatment Method

Bacteria, nematodes, and other microscopic organisms are used in biological treatment to break down organic wastes through natural processes. Biological treatment is widely employed since it is both effective and cost-efficient. It involves using two processes:

Aerobic process —Microorganisms convert organic substrates and other contaminants to carbon dioxide (CO_2) and water (H_2O) in the presence of oxygen.

Anaerobic process— Microorganisms convert the organic substrate and other pollutants to methane (CH_4) and carbon dioxide (CO_2) without the presence of oxygen.

These processes can be sensitive to both the chemical and physical properties of some compounds which reduces the effectiveness of the treatment [9]. The drawbacks of this method include maintenance of the microorganisms, certain molecules like dyes have low biodegradability and it is a very slow process.

1.2.2 Coagulation and Flocculation

Are common pre-treatment processes for separating dissolved and suspended substances from water. In the coagulation process, aluminium or iron salts is added to the water. These substances are known as coagulants, and they carry a charge (positive) that nullifies the negative charge of the dissolved solids and suspended particles in the water. This reaction causes the particles to bind together or coagulate (sometimes also called flocculation). The heavier bigger particles, known as floc, settle at the bottom of the water supply rapidly and this process is known as sedimentation. Figure 2 illustrates the basic reactions and processes that occur during coagulation.

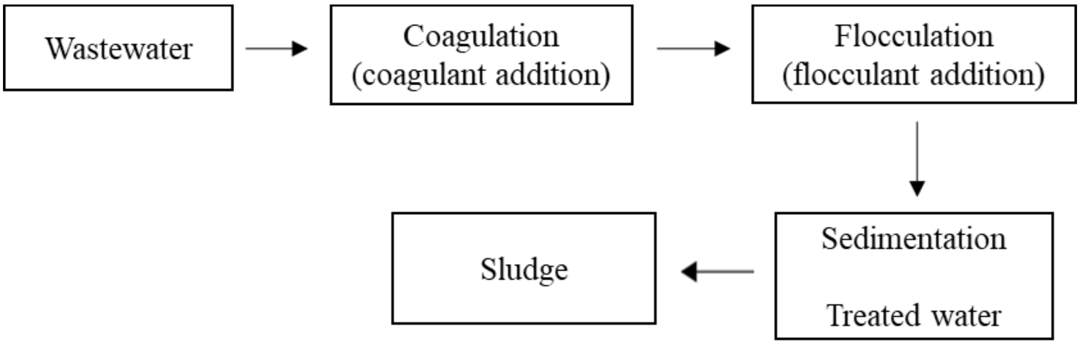

Figure 2: Coagulation, Flocculation and Sedimentation

1.2.3 Filtration

Filtration removes suspended particles from water through slow or quick filtration by using a granular medium like sand. Sand is the most common filter medium; however, other minerals are sometimes employed for specific purposes. For the purification of water, slow sand filters have been employed since the Roman era.

The water sample is filtered via a layer of fine sand with an extremely low velocity forming a gelatinous layer on the sand's surface, removing turbidity, colour, taste, and odour through a combination of filtration and biological activity. Slow sand filtering removes bacteria, protozoa, and viruses, resulting in practically clean water, however, a disinfectant should still be used as a precaution. Rapid gravity filters remove suspended materials with coarse sand; however, they do not remove bacteria, protozoa, or viruses.

1.2.4 Membrane Separation Processes

This procedure separates specified materials from an aqueous solution by passing water under high pressure via a semi-permeable membrane. One of the benefits of the membrane separation method is that it is based on physical separation and chemicals are not needed [10]. Various membrane processes with different separation mechanisms include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), forward osmosis (FO) and reverse osmosis [10]. The permeability of the membrane, the pressure exerted, and the size of the pores varies in these separation processes, but the mechanism is the same. This method is flexible, easy to scale up, and cheap in energy use. Although the process is susceptible to membrane fouling, it consumes a lot of energy and is expensive in terms of equipment and cleaning.

1.2.5 Adsorption

Sorption is a method of separating dissolved material (sorbate) from a liquid state to a solid phase (sorbent). Adsorption is a common method for removing organic materials in water treatment. Activated carbon is the most often used adsorbent, this is because its porous property is high and has a larger surface area to which pollutants may adsorb. Surface forces such as Van der Waals forces and hydrogen bonding keep adsorbate molecules on the adsorbent's surface in this process.

This process is often of simple design and easy to operate and maintain and the downside of this process is the relatively high cost [11].

1.2.6 Advanced Oxidation Processes

This is a process that generates highly reactive oxidizing species (such as hydroxyl radicals, persulfate radicals, holes) during the treatment of water to oxidatively destroy the target pollutants. According to Glaze et al [12], advanced oxidation processes is "the formation of OH in adequate quantity to enable the purification of water. Aromatics, pesticides [13], petroleum components, and volatile organic compounds are all examples of biologically hazardous and non-degradable chemicals that can be removed via the AOP technique. The contaminating materials are mostly transformed into an organic compound that is stable like water, CO_2, and salts, i.e., they are subjected to mineralization by oxidation reactions with hydroxyl radicals (OH) and other strongly oxidizing species [12]. This procedure uses little or no chemicals, produces no sludge and can remove certain heavy metals in the form of precipitated $M(OH)_X$. One of the major downsides of AOPs is the high operational costs.

1.2.7 Electrocoagulation

Is the technique of introducing an electrical current into an aqueous medium to destabilize suspended, emulsified, or dissolved pollutants? The electrochemical technique involves electrolytically oxidizing a sacrificial anode generally made of Fe or Al by a DC or AC power source to release metal ions which acts as coagulants, destabilizing impurities, and breaking emulsions. The flocculants produced by this coagulation float to the top and are easily removed. The pH, together with the current density and the material of the electrode, are the most key parameters to be considered when using the EC treatment [14,15]. The electrocoagulation approach is inexpensive, simple to use, and produces less sludge [15].

The theory of EC involves chemical and physical phenomena, and it is divided into three stages; (i) Electrolytic oxidation of sacrificial electrodes, often Fe or Al, which results in the formation of coagulants (ii) Contaminant destabilization, including particle suspension and break up of emulsion (iii) Aggregation of destabilized phases to form flocs: The coagulants provide an active surface for the contaminated species to adhere to. These flocs entrap and bridge the remaining coagulants in the aqueous medium. Electrolyzed water at the cathode produces hydrogen while the anode produces small oxygen bubbles. Flocculated particles are attracted to the bubbles and float them to the surface [16].

1.3 Aim and Objectives of This Thesis

This work was done with the following main objectives:

- ✓ To treat synthetic water contaminated with chromium (Cr) ions by electrocoagulation.
- ✓ To study the effect of process variables such as pH, current density, treatment time, spacing between electrodes and the rotating speed for different types of electrode pairs (Al and Fe) for EC removal of hexavalent chromium in other to determine the optimum pollutant removal.

The limitations of this work are.

- ✓ The work is laboratory-scale experimentation on synthetic wastewater and was not performed on actual industrial effluents.
- ✓ Assess various electrodes to try out various electrode combinations and designs.

Chapter 2

LITERATURE REVIEW

2.1 Theory of Electrocoagulation

("Electro" means applying an electrical charge to water, and "Coagulation" refers to the process where the surface charge of a particle is changed causing suspended materials to agglomerate). This technique can remove suspended solids, split emulsions such as oil and grease or latex, also oxidizing and eliminating heavy metals from water using electrical current without the use of filters or adding separate or expensive chemicals.

Vik et al [17] proposed electrocoagulation for the first time in 1889, which described the first sewage treatment system established in London, where electrocoagulation treatment was used by mixing household wastewater with saline water [18]. In the United States in 1909, J.T. Harries got a license to use electrolysis to treat wastewater employing Al anode and Fe anode [17]. The 'Electronic Coagulator,' described by Matteson et al [19], which dissolves Al from the anode electrochemically into the solution reaction, producing aluminium hydroxide by reacting with the OH ions generated at the cathode which purifies the water.

EC has become more widely employed lately for the treatment of metal-containing industrial effluent such as food processing, metal processing, dye processing, hospital, pulp and paper, textile, oil refinery industries [20].

The theory of electrocoagulation involves a conglomeration of many chemical and physical phenomena. It entails the three stages listed below.

a) Oxidation of the sacrificial electrodes (often Fe or Al) electrolytically, which results in the formation of coagulants. The anode acts as dissolution of respective ions and is called a sacrificial electrode.

b) Contaminant destabilization includes suspension of particle and breaks up of emulsion.

c) Formation of flocs by the aggregation of destabilized phases: The coagulants provide an active surface for the contaminated species to adhere to. These flocs entrap and bridge the remaining coagulants in the aqueous medium. Water electrolyzed at the cathode generates hydrogen, whereas water electrolyzed at the anode generates tiny oxygen bubbles. Flocculated particles are attracted to the bubbles and float them to the surface [16].

Bazrafshan et al [21] investigated the effect of operating parameters on effluent from a diary which was treated by EC process using an Al electrode and potassium chloride (KCl) as the electrolyte. They reported that as the voltage and reaction time was increased, there was also an increase in the efficient removal of chemical oxygen demand (COD), biological oxygen demand (BOD), and total suspended solids (TSS). In 60 minutes at 60 V, they achieved 98.84% COD, 97.95% BOD, 97.75% TSS, and >99.9% bacterial indicators removal which shows that the EC process is efficient.

Un and Ocal [22] studied the EC method for removing Cd, Cu, and Ni from synthetic wastewater. The effects of varying the operating factors on removal efficiency, such as starting pH (3, 5, 7), current density (30, 40, 50 mA/cm^2), and initial concentration (10, 20, 30 ppm), were investigated.

The maximum Cd, Ni, and Cu removal rates of 99.78%, 99.98%, and 98.90% were achieved respectively after 90 minutes of EC process at pH 7, 30 mA/cm^2 and electrolyte, according to the data (0.05 M Na_2SO_4). The results of the experiments showed that these heavy metal ions could be removed using an electrochemical cell.

The EC technique was investigated by Al-Shannag et al [23] for the heavy metal ions removal from an effluent from metal plating, specifically Cu^{2+}, Cr^{3+}, Ni^{2+}, and Zn^{2+}. In this experiment, a total of six monopolar electrodes made of carbon steel were used. Three electrodes were labelled as cathodes, while the remaining three were marked as anodes. The results obtained revealed that as the EC reaction time and direct CD are increased, the efficiency of heavy metal ion removal improves. By using an EC treatment with a CD of 4 mA/cm^2, a pH of 9.56, and 45 minutes EC time, over 97% of heavy metal ions were effectively eliminated. These operating conditions resulted in specific energy consumption of 6.25 kWh/m^3 and a dissolved electrode of roughly 1.31 kg/m^3. Metal plating removal with EC uses very little energy, rendering it cost-effective and scalable.

Using an electrocoagulation process with both iron and Al electrodes, Kobya et al [24] investigated the influence of CD on Zn removal from water emanating from a $Zn_3(PO_4)_2$ coating process in an automotive assembly facility. For a reaction period of 30 minutes, adjusting the CD from 1 mA/cm^2 - 6 mA/cm^2 significantly improved Zn efficiency removal from 4.8% to 97.8% using Fe electrodes and from 28% to 96.7% using Al electrodes.

Gao et al [25] studied chromium removal without the use of a filter using an electrocoagulation-electrofloatation technique. The parameters like pH effect, the effect of surfactants, and power consumption were studied using an Fe electrode. The EC process containing 100 mg/L solution was treated with 98% efficiency at a CD of 1.2 mA/cm^2 within a duration of 9 minutes.

Adhoum et al [26] employed EC to treat electroplating wastewater and achieved a 94% copper removal efficiency at 480 mA/cm^2 CD, anode surface area of 50 cm^2, within a duration of 5 minutes. The ideal pH was discovered to be somewhere around 4 and 8, with a CD of 80–480 mA/cm^2 consuming 32 kWh/m^3 of energy.

EC was utilized by El-Ashtoukhy et al [27], to estimate the maximal copper removal. At pH 5, and a CD of 31 mA/cm^2, 80% copper removal was attained in 6 minutes. Also, lowering the starting concentration of copper from 3 mg/L to 1 mg/L reduced the removal effectiveness from 91% to 73%. Another study indicated that using Al electrodes, the best pH was between 4 and 6 for removing copper.

Sharma et al [28] examined the use of Fe electrode in the EC process for treating electroplating effluent. The initial chromium (Cr) and lead (Pb) concentrations were 55.3 and 3.5 mg/dm^3, respectively. A CD of 73.5 mA/cm^2 and pH 3.5 was reported to be the best with four-plate configurations. Maximum Cr(VI) removal of 91.7% and Pb removal of 91.3% were achieved in 90 minutes under these working conditions. The results of the study revealed that EC treatment can successfully treat oriented wastewater containing heavy metals and is also very effective in treating actual wastewater at a low cost.

According to Zaroual et al [29] using Al anodes to treat Cr(III) with EC can achieve a removal efficiency of 91% at a pH of 4.23, 9.14 voltage and 10 minutes treatment time. The authors reported that the process consumed 3.536 kWh/m^3 energy.

2.2 Advantages of Electrocoagulation Process

Because of its significant advantages over other wastewater treatment processes, EC has rapidly expanded in popularity [18,32]:

1. EC technique is simple and easy to operate.
2. EC usually requires low capital, maintenance, energy consumption, and treatment expenses.
3. Water from EC treated wastewater is odourless, transparent, and colourless.
4. The EC procedure generates little sludge. Sludge produced by EC is mainly made of metallic oxides/hydroxides.
5. No chemical is needed in the EC process.
6. Filtration can easily separate EC flocs because they are more stable.
7. It also generates valuable substances such as hydrogen gas.
8. During electrolysis, gas bubbles lift pollutant particles to the surface of the solution formed where they are easily separated.

2.3 Disadvantages of Electrocoagulation Process

1. Due to oxidation, the sacrificial anodes dissolve into the solution and must be replaced regularly.
2. The wastewater suspension must have a high conductivity.
3. In some instances, viscous hydroxide may solubilize.
4. In some places, electricity may be scarce and expensive.
5. Oxide film formation on the cathode diminishes the electrocoagulation efficiency.

2.4 Mechanism and Principle of Electrocoagulation

EC is a complicated process involving the generation of ionic coagulant species in the reaction mixture through the oxidation of metallic electrodes [23].The ionic coagulants generated permeate the mixture, destabilizing the emulsion and facilitating the production of clusters from dissolved or suspended pollutants [31].The following seven stages can be used to simplify the complicated physical and chemical changes that occur in the EC process [23]:

1. The "sacrificial electrode" is oxidized to produce positive ionic coagulants.
2. Water molecule is reduced on the negative electrode, resulting in hydroxyl ions (OH^-) and some oxygen as well as hydrogen gas bubbles.
3. The ions that are produced move to the electrodes with opposite charges. This migration destabilizes the contaminants and particle suspension, causing the emulsion to break down.
4. The positive ion reacts with the OH^- to generate metallic hydroxides with strong adsorption properties.
5. Pollutants adhere to hydroxide structures, forming bigger aggregates.
6. Redox processes can be used to convert pollutants into less hazardous forms.
7. The aggregates formed are subsequently removed by flotation, which involves oxygen and hydrogen bubbles moving upward in the liquid phase or precipitating if their density is too high compared to the medium.

Figure 3 illustrates an EC cell showing the essential reactions involved in the EC process. The anode material determines which oxidation reactions occur on the sacrificial electrode which is usually composed of Al or Al alloy [32], Fe, and stainless steel (SS). Some researchers also make use of magnesium or magnesium-based alloy anode [33], copper [34], and zinc [35].

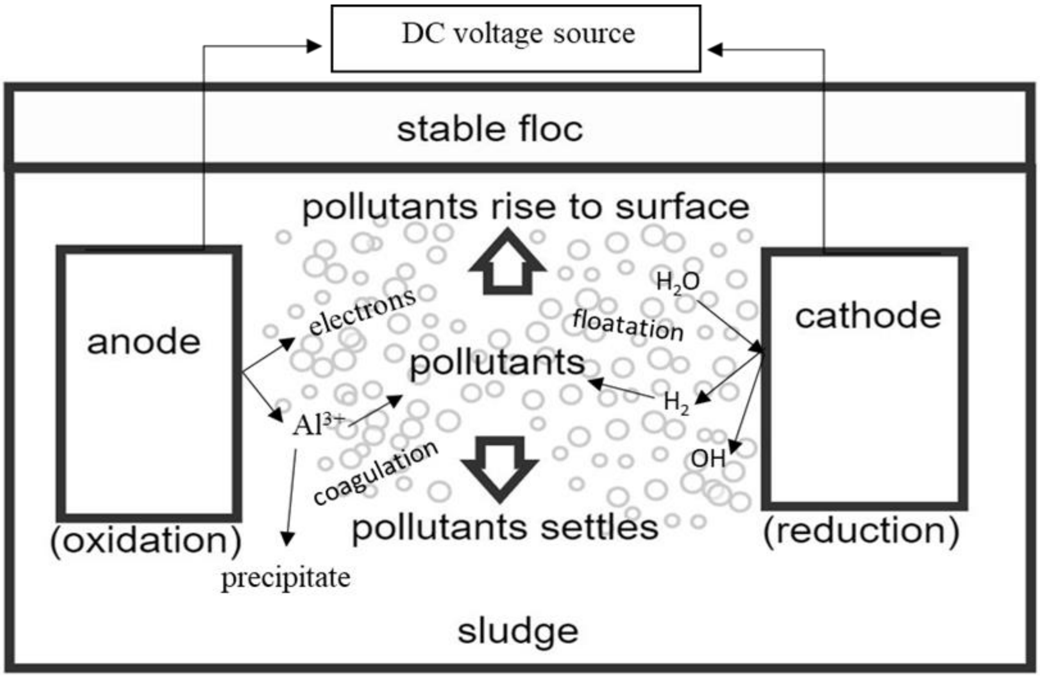

Figure 3: EC cell showing the essential reactions involved in the EC process

2.4.1 Possible Reactions When the Iron Anode is Used

Depending on the oxidation state of iron, iron anode generates iron hydroxide, Fe(OH)n where n can either be 2 or 3. When n is 2,

At the anode (oxidation): $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$

At the cathode, hydroxide ions and hydrogen gas are released.

Cathode (reduction): $2H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2_{(g)}}$

Overall reaction: $Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2_{(s)}} + H_{2_{(g)}}$

However, when n is 3,

At the anode (oxidation): $Fe_{(s)} \rightarrow Fe^{3+}{}_{(aq)} + 3e^{-}$

$$4Fe^{2+}{}_{(aq)} + 10H_2O_{(l)} + O_2 \rightarrow 4Fe(OH)_{3_{(s)}} + 8H^{+}_{(aq)}$$

While cathode (reduction): $8H^{+}{}_{(aq)} + 8e^{-} \rightarrow 4H_{2_{(g)}}$

Overall reaction: $4Fe_{(aq)} + 10H_2O_{(l)} + O_{2_{(g)}} \rightarrow 4Fe(OH)_{3_{(s)}} + 4H_{2_{(g)}}$

2.4.2 Possible Reactions When the Aluminium Anode is Used

Anode reaction (oxidation): $Al_{(s)} \rightarrow Al^{3+}{}_{(aq)} + 3e^{-}$

Cathode reaction (reduction): Here, OH^- ion and H_2 gas is formed

$$3H_2O_{(l)} + 3e^{-} \rightarrow 3OH^{-}{}_{(aq)} + \frac{3}{2}H_{2_{(g)}}$$

Overall reaction: $Al_{(s)} + 3H_2O_{(l)} \rightarrow Al(OH)_{3_{(s)}} + \frac{3}{2}H_{2_{(g)}}$

According to complex precipitation kinetics, these electrochemically generated metal cations (Fe^{2+}, Fe^{3+}, or Al^{3+}) will react spontaneously and produce hydroxide or poly hydroxide.

The various monomeric species of Fe^{3+} and Al^{3+} convert into $Fe(OH)_3$ and $Al(OH)_3$, respectively. By electrostatic attraction followed by coagulation, these insoluble $Fe(OH)_3$ and $Al(OH)_3$ persist in the aqueous medium destabilizing the pollutants. Contaminants are destabilized primarily using two methods.

1. The products of cationic hydrolysis neutralize negatively charged colloids.
2. Sweep flocculation: Contaminants are trapped and removed in the form of amorphous hydroxide precipitate.

H_2 and O_2 gas bubbles cling to agglomerates generated at the electrode surfaces during electrolysis and bring them to the water surface [36]. The amount of metal that is deposited is dependent on the amount of electricity that is passed through the electrolytic solution.

2.5 Effects of Operational Parameters on EC Process

Understanding the effect of various operational factors on the EC process is important to achieve optimum removal efficiency in the shortest electrolysis time with the lowest operational cost. The EC process parameters include electrode arrangement, electrolysis time, pH effect, inter-electrode distance, electrode materials, current density and many more.

2.5.1 Electrode Arrangement

An EC system can have one or more anode-cathode pairs coupled in either a monopolar or bipolar mode.

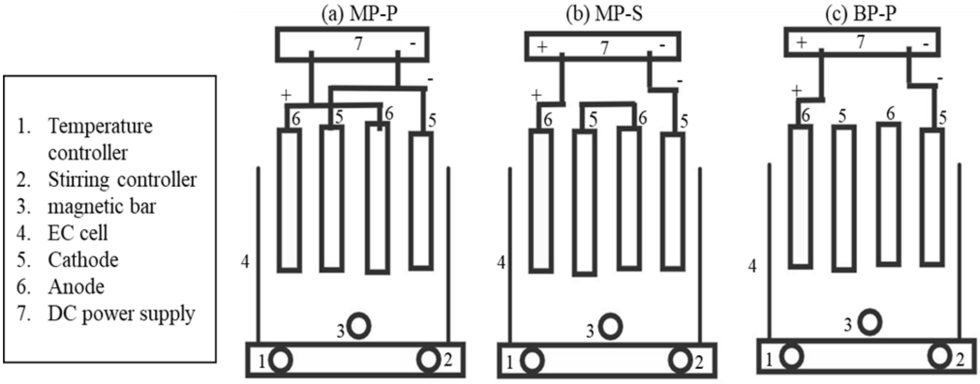

Figure 4: Different mode of connecting electrodes (a) Monopolar parallel (MP-P) (b) Monopolar series (MP-S) (c) Bipolar parallel (BP-P)

In the monopolar mode of parallel connection (MP-P), a current is divided among all electrodes based on their resistance. As compared to the monopolar mode of series connections (MP-S), each pair of sacrificial electrodes is internally connected as illustrated in Figure 4. While in the bipolar mode of parallel connection (BP-P), sacrificial electrodes are placed with no electrical connection between the two parallel electrodes. During electrolysis, the positive sides of electrodes undergo anodic reactions, whereas the negative sides undergo cathodic reactions [37].

Al-Shannag et al [23] investigated the heavy metal ions removal from metal plating effluent, specifically Cu^{2+}, Cr^{3+}, Ni^{2+}, and Zn^{2+}. In this experiment, a total of six monopolar electrodes made of carbon steel were used. Three electrodes were labelled as cathodes, while the remaining three were marked as anodes. The results obtained revealed that as the EC reaction time and direct CD are increased, the efficiency of heavy metal ion removal improves. By using an EC treatment with a CD of 4 mA/cm^2, a pH of 9.56, and 45 minutes EC time, over 97% of heavy metal ions were effectively eliminated.

2.5.2 Effect of Electrolysis Time

The electrolysis time has a considerable impact on the efficiency of pollutant removal. It states the number of coagulants produced as well as the process's cost. An increase in electrolysis time up to the optimum level improves pollutant removal efficiency, but not beyond the optimum level [38]. Bejankiwar [39] observed a 56% in chemical oxygen demand (COD) and an 84% in biological oxygen demand (BOD) removal from cigarette manufacturing wastewater at a current of 3.5 A for 5 hours utilizing Fe electrode while Deshpande et al [40] achieved 72% COD removal efficiency with an improvement in COD/BOD ratio from 0.18 to 0.3 following 2 hours of treatment with Fe electrodes from pharmaceutical wastewater.

2.5.3 Inter Electrode Distance

Inter-electrode distance is an important factor in the EC process. Pollutant removal effectiveness is maximized when the spacing between electrodes is optimal. When the inter-electrode spacing is kept to a minimum, the efficiency of pollutant removal is high. The generated ions move more slowly as the inter-electrode distance increases giving the ions enough time to form floc for the coagulation of pollutants [41]. Whereas an increase in the inter-electrode distance above the optimal value reduces anodic dissolution, hence, increasing the distance the ions must travel to create flocs, lowering electrocoagulation efficiency [42].

Sengil et al [43] eliminated 98% of the colour of a dye at 100 mg/L concentration, pH of 5, a CD of 45.75 mA/cm^2, and electrode spacing of 2.5 cm while Song et al [44] reported 96% removal of the colour of dye concentration at an ideal pH of 10, 100 mg/L concentration, a CD of 10 mA/cm^2, and electrode distance of 3 cm.

2.5.4 Effect of Current Density

This is another important operational parameter in the electrocoagulation process. It provides information on the amount of energy been consumed. According to Khosla et al [45], the applied CD impacts the coagulant dose rate, the bubble generation rate and size, and the flocs growth, resulting in faster pollutant removal. As a result of the chemical dissolution of the cathode, the rate of OH^- ion production at the cathode during the electrocoagulation process is influenced by the current density [41]. For example, when the current density in the process increases the removal efficiency also increased, as demonstrated by Khosla et al [45] when Fe electrodes were used to remove chromium from wastewater. At an initial concentration of 800 mg/L and pH of 7.5, the removal rate of chromium increased (>99%) as expected with increasing CD from 10 - 40 mA/cm^2 during a 40 minute electrolysis time.

2.5.5 Effect of pH

The pH of the solution is another crucial factor influencing the performance of the EC process. It varies all through the process based on the type of electrode and starting pH. The conductivity of a solution, the dissolution of electrodes, and the production of hydroxides in EC are all determined by the pH of the solution. The nature of the pollutant determines the performance of the EC process; however, in general, pollutant removal was found to be most effective at pH near 7. The precipitation of $Fe(OH)_3$ is caused by the production of ferrous ions and their subsequent oxidation to ferric ions, and it is likely that this oxidation by oxygen increases as the pH rises. The production of $Fe(OH)_3$, which is responsible for the removal of the majority of contaminants in wastewater, explain the increased removal efficiency at neutral pH. Al electrode performs better at $pH \leq 7$.

Vansudervan et al [46] used stainless steel as a cathode and an Al alloy as an anode to remove arsenate at a CD of 0.2 mA/cm^2 and a pH of 7.0, the removal efficiency was 98.4%.

2.5.6 Effect of Temperature

Temperature can have a favourable or negative impact on the EC process; therefore, it must be carried out at room temperature. Pollutant removal effectiveness reduces with increasing temperature due to a decrease in metal hydroxide production, however, at low temperatures, pollutant removal efficiency is also poor due to a low anodic dissolution rate [47]. According to Chatzisyneon et al [48] using a TiO_2 anode at 80^oC and 5 mM NaCl can eliminate colour, phenols, and low 30% COD (chemical oxygen demand) with a CD of 50 mA/cm^2 of olive mill wastewater.

2.5.7 Effect of Initial Pollutant Concentration

One of the effective parameters in pollutant removal by EC is the initial pollutant concentration. The effectiveness of the pollutant removed using the EC process is reduced as the initial pollutant concentration is increased (keeping other parameters constant). This occurs because the metal OH floc formed in the solution is incapable of settling big pollution molecules [51,52]. Hansen et al [50] discovered that Fe electrodes could lower arsenic concentration by 96% (from 1000 to 40 mg/L). The oxidation of Fe^{2+} to Fe^{3+} determined arsenic removal efficiency for arsenic concentrations >5000 mg/L, and 98% arsenic removal was obtained for arsenic concentrations of 100 mg/L at pH 7, with an iron electrode placed approximately 3 cm from the bottom of the cell and an electrode surface of 16.7 m^2.

2.5.8 Effect of Stirring Speed

Another factor that affects the EC by increasing the movement of the ions generated is the stirring speed. Khaled [51] worked on cadmium removal using the EC process with the Al electrode, the speed at 300, 450 and 600 rpm. It was observed that at optimum high speed there is a higher removal efficiency of pollutant 95% within 30 minutes for 300 rpm and 99.5% within 60 minutes for 450 rpm but the removal efficiency begins to decrease at 600 rpm. This is because excessive stirring breaks down the flocs. This shows that below and beyond the optimum speed, the percentage of contaminants removed decreases.

2.6 Pollutant Removal Efficiency and Kinetics of EC Process

Using the Equation below, the percentage removal of pollutant (% removal) at time t can be calculated.

$$\%removal = \frac{C_{initial} - C_{final}}{C_{initial}} \times 100\% \qquad (1)$$

Where $C_{initial}$ = the initial pollutant concentration.

C_{final} = the final pollutant concentration at time *t*.

2.6.1 Operating Cost Analysis

The running cost of the EC process is mostly determined by the cost of the electrode, the cost of electrical energy, sludge disposal, and other fixed expenditures. The equation below can be used to calculate the operating cost.

$$Operating\ cost = a\ C_{energy} + b\ C_{electrode} \qquad (2)$$

Where C_{energy} is the energy consumption and $C_{electrode}$ is the electrode consumption per litre of effluent treated, which is achieved experimentally, “a” is the unit price of electrical energy and “b” is the cost of electrode.

The equation below can be used to calculate how much electrical energy is used per litre of wastewater treated.

$$C_{en} = \frac{U\ i\ t}{V} \qquad (3)$$

Where C_{en} = the electrical energy in kWh/L,

U = cell voltage in volt (V).

I = current in ampere (A).

V= volume (m^3).

and t = electrolysis time.

The number of electrodes consumed can be calculated by the given equation.

$$C_{el} = \frac{i\ t\ M}{F\ z} \qquad (4)$$

Where M= molar mass (g/mol)

F = faraday constant.

I = current in ampere (A).

Z = number of electrons.

and t = electrolysis time.

2.7 Applications of EC Technology

2.7.1 Textile Industry Effluents

These are one of the major polluting industries. Textile activities add to the effluent's complexity, making treatment a challenging one. Dyebath effluents hinder light penetration in water bodies because of their colour content, causing biological processes to be disrupted. Cerqueira et al [52] report the highest removal efficiency using Al and Fe electrodes, with colour removal of 93%, turbidity removal of 99%, and COD removal of 87% using Al electrodes, at pH 5 (initial pH), a reaction period of 30 minutes, and a CD of 1.5 mA/cm^2.

2.7.2 Leather Tanning Industry

The use of electrocoagulation to remediate wastewater from the leather industry has lately gained attention. This procedure has proven to be quite successful in eliminating organic waste and inorganic contaminants generated from effluent from the leather tanning industry using Al, Fe, and steel electrodes. At an initial pH value of 6.5–9.0 and duration of 15–45 minutes, Benhadji et al [53] observed complete removal of chromium using Al or Fe-based anodes. Other factors, such as current density and electrolysis time, were also found to influence the chromium removed from leather tanning industry effluents.

2.7.3 Pulp and Paper Industry

This industry consumes a lot of water, requiring enormous amounts of water during the manufacturing process. Papermaking operations are the most major sources of pollution in the pulp and paper sector. Organic matter, suspended particles, intense colour, and organic compounds are all present in high concentrations in wastewater from the pulp and paper sector. At a CD of 2.07 mA/cm^2 and a pH 7.9, Khansorthong and Hunsom [54] obtained removal efficiencies of 93.7% for colour and 73.6% for COD removal within 30 minutes.

2.7.4 Olive Mill Effluents

This is one of the most complex industrial effluents. Inorganics such KCl and NaCl etc., are found in olive mill effluent. Using an iron electrode at an ideal CD value of 25 mA/cm^2, Hanafi et al [55] observed polyphenols, COD and colour removal at 77%, 80%, and 88%, respectively.

2.7.5 Industrial Effluents Containing Metals

Cadmium, chromium, and other heavy metals pose a significant risk to humans and the environment. According to research, metals can be successfully removed using EC, particularly in the free form, if the operating parameters are optimal. Camci and Akbal [56] used Al and Fe electrodes to remove Nickel, Copper, and Chromium from a metal plating effluent. The removal of these metals was complete at a CD of 10 mA/cm^2 and pH 3 (initial pH) for a reaction period of 20 minutes.

Chapter 3

EXPERIMENTAL STUDY

This chapter discussed the analytical and research approaches used in this study, as well as the experiment methodology.

3.1 Reagents and Materials

This experiment's chemicals are all the analytical grades. Potassium dichromate ($K_2Cr_2O_7$) with a molar mass of 294.185 g/mol, NaOH (>99%), HCl (37%) were obtained from Merck KGaA, Darmstadt Germany. Both Fe and Al electrodes were purchased from a mechanical workshop in Famagusta, North Cyprus. The supporting electrolyte used was sodium chloride (NaCl).

3.1.1 Preparation of Chemicals

A stock solution of 500 mg/L of chromium was prepared by dissolving 0.5 g of potassium dichromate ($K_2Cr_2O_7$) in a 1000 mL volumetric flask with distilled water. The stock solution was further diluted to the desired concentration. Various concentrations were prepared for calibration curve by serial dilution of the chromium (Cr) solution. The pH of the chromium solution was adjusted to the desired level using 1 M hydrochloric acid (HCl) and 1 M sodium hydroxide (NaOH). The 1 M HCl was prepared by adding about 16.6 ml of concentrated HCl to 150 ml of distilled water in a clean and dry 200 ml volumetric flask, mixed and then made up to mark with distilled water and allowed to cool to room temperature. The 1 M NaOH was prepared by accurately weighing and dissolving 10 g of NaOH pellets in 250 ml distilled water, stirred and allowed to cool.

3.1.2 Analytical Methods

A pH meter was used to measure the pH and conductivity of the effluent (InoLab pH/Cond720, Germany). The current and voltage of the system were regulated using the DC power supply (MH03819, Frederiksen Denmark). The UV-Vis spectrophotometer (UV-1201V, Japan Shimadzu) was used to determine the absorbance measurement of chromium solution at 350 nm absorption peaks. The sludge produced from the iron and aluminium hydroxide coagulants was characterized by a Vertex 70 FTIR spectrophotometer.

3.2 Experimental Setup and Procedure

3.2.1 Electrocoagulation Reactor

In a 200 mL container with dimensions of 7 cm x 4 cm x 30 cm, the EC experiment was carried out and depicted in Figure 5. During this experiment, Al and Fe electrode pairs were used. The electrodes were mounted 2.5 cm above the reactor's base on support. The reactor was carved with an opening to maintain a constant electrode distance between the electrodes, which ranged from 1 cm to 7 cm. Throughout the experiment, the solution was constantly agitated at 100–400 rpm with a magnetic stirrer.

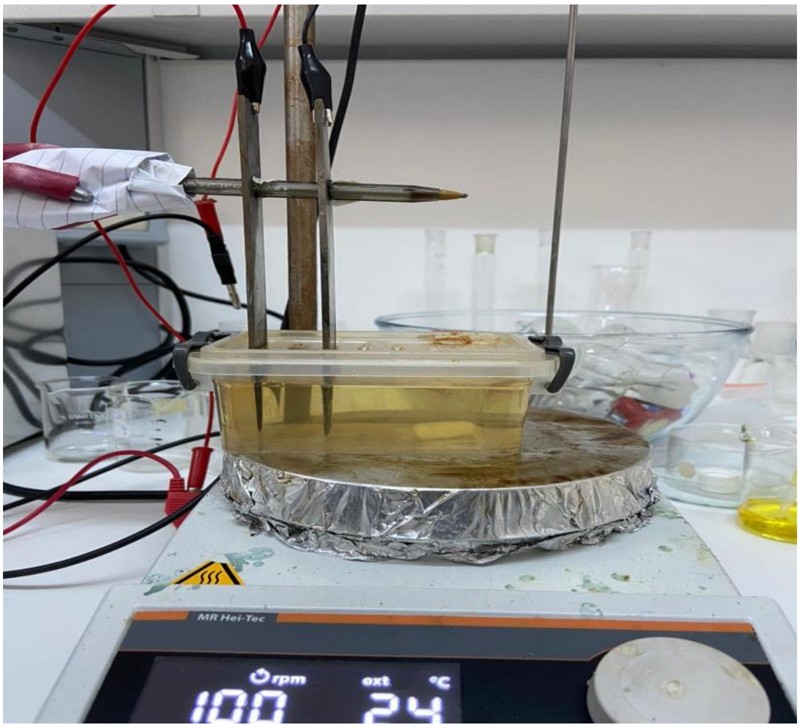

Figure 5: Schematic Setup of Electrocoagulation System

3.2.2 Electrocoagulation Process

Two Fe electrodes measuring 15.8 cm in length, 2.45 cm in breadth, and 0.35 cm in thickness and two Al electrodes measuring 16 cm in length, 2.7 cm in breadth, and 0.2 cm in thickness were used in this experiment. Both electrodes were pre-treated by cleaning the surface with a hard sponge to remove dust before immersing in 1 M HCl for 1 minute to limit electrode passivation likely caused by oxide deposit. After which, the electrodes are washed with distilled water and allowed to dry and then measured before proceeding with the experiment. It is worth noting that both electrodes were completely cleaned and measured before each experiment and at the end of the experiment in other to ascertain the electrode weight loss.

A container was used for the electrocoagulation experiment, as illustrated in Figure 5, with two pair of electrodes connected to a DC circuit, one as cathode while the other as an anode, under constant uniform magnetic stirring.

Both Fe and Al electrodes were subjected to this process. As a supporting electrolyte, sodium chloride (NaCl) was used, and it was added at the start of each experiment. At room temperature, the electrodes were dipped in the solution at 2.5 cm depth and then connected to the DC power supply. The power was switched on then the DC power source was controlled by fine-tuning the voltage and the voltage was set at the desired level. The average energy consumed was based on the amperage recorded at the start and end of the experiment, and the current in ampere was recorded from the digital panel meter. A digital timer regulates the treatment time. After each experiment, the treated wastewater was allowed to settle for a while, then filtered using a filter paper. The sludge was dried in the oven at 40^{o}C while the filtrate was analysed using the UV-Vis spectrophotometer at a specific wavelength. Effects of each parameter influencing the performance of the EC process were investigated according to the range of values of the parameters in Table 1.

Table 1: Parameters and values used in this study to investigate the performance of the electrodes.

Parameters	**Values**
Treatment time	5 minutes – 60 minutes
pH	3, 5, 8, 10
Concentration of pollutant (chromium)	10 mg/L, 15 mg/L, 25 mg/L
Voltage	3 v, 6 v, 9 v
Electrolyte (NaCl)	0.5 g, 1 g, 1.5 g
Stirring speed	100 rpm, 200 rpm, 400 rpm
Electrode distance	1 cm, 2 cm, 4 cm

3.3 Experimental Analysis

The concentration of chromium ion that remained in the solution was analysed by the UV-Vis spectrophotometer and the percentage removal of chromium ion was calculated using the following equation:

$$\%\, removal = \frac{C_i - C_f}{C_i} \times 100\%$$

where C_i = initial concentration.

C_f = final concentration.

The weight loss of both electrodes was determined by measuring the mass before and after every experiment and the experimental mass of metal that dissolved during the electrocoagulation process was calculated as follows:

$$M_{experimental} = M_{initial} - M_{final} \tag{5}$$

Where $M_{initial}$ = mass before the experiment.

M_{final} = mass after the experiment.

The electrode efficiency was determined using the equation below:

$$E_{efficiency} = \frac{M_{experimental}}{M_{theoretical}} \times 100\% \tag{6}$$

The $M_{theoretical}$ can be calculated using the equation:

$$M_{theoritical} = \frac{M\, i\, t}{n\, F} \tag{7}$$

Where M = electrodes molar mass; Al= 29.98 g/mol, Fe= 55.85 g/mol

i = current

t = time

n = number of electrons transferred; Al= 3, Fe= 2

F = Faraday constant (96486 C/mol).

3.3.1 Preparation of Calibration Curve

The calibration curve was plotted by first preparing a stock solution of chromium then serial dilution was done to get different concentrations.

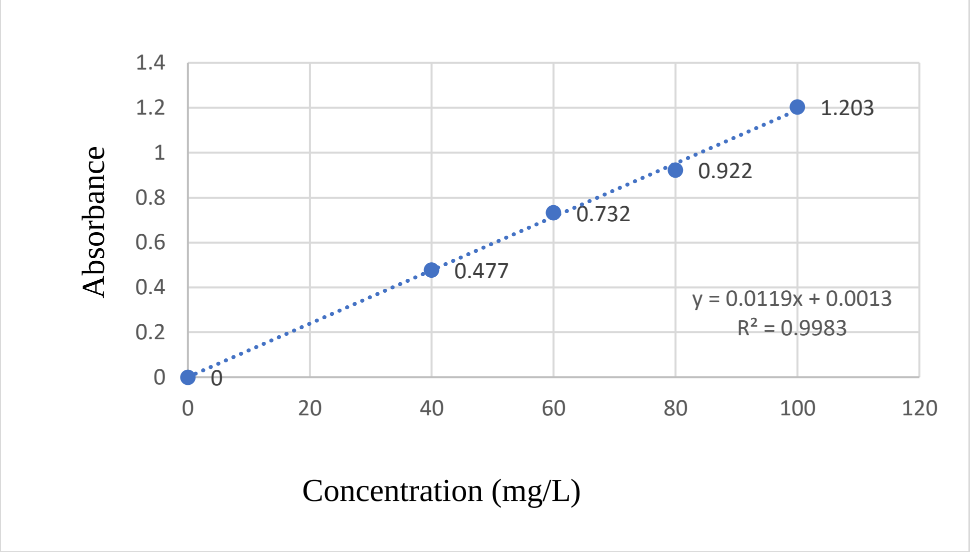

Figure 6: Calibration curve for chromium solution at 350nm

3.3.2 Sludge Characterization

After each experiment, the treated water is allowed to cool then filtered using a filter paper**.** The sludge collected was then dried in the oven at about 40^{o}C. After drying, the sludge was further ground into powder form before it is being analyzed by the Fourier Transform Infrared spectrophotometer (FTIR). The characterization of the sludge aids in understanding the EC technique's removal mechanism.

Chapter 4

RESULTS AND DISCUSSION

4.1 Effects of Operating Parameters

Several operating parameters, including the effect of pH, pollutants concentration, voltage, electrolyte, distance, and speed, influence the electrocoagulation process. To optimize the treatment procedure for removing chromium ions from an aqueous solution, all these parameters were studied. For each parameter, the results achieved, and trends noticed are discussed below.

4.1.1 Effect of Variation in The Solution pH

The efficiency of the EC is influenced by the solution pH. Throughout the procedure, the medium pH varies (3-10) depending on the type of electrode material used and the initial pH. Herein, the experimental conditions are defined in the figure legend. Figure 7 shows that the removal percentage of Cr using Fe electrode is low at pH 3 (35%), increases significantly at pH 5, peaks at 83% at pH 8, and then drops to 70% at pH 10. At both strongly acidic and strong alkaline pH, other researchers have reported lower removal [27,34]. They attributed it to the formation of amphoteric $Fe(OH)_3$, which results in soluble cations Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)^{2+}$ (at acidic pH) and monomeric anions $Fe(OH)^{4-}$, $Fe(OH)_6^{3-}$ at strongly alkaline medium.

However, using Al electrode removes 95% of chromium at pH 3, drops to 88% at pH 5, and finally to 24% at pH 10.

Mahmad et al [57], who utilized Al electrode to treat total chromium and turbidity, found a similar decreasing tendency as the pH of the solution was raised. It is worth noting that for both Al and Fe electrodes, the final pH of the solution increased when the initial pH was less than 7. This is due to the hydrogen evolution at the cathode [17]. However, because the produced OH^- ions at the cathodes were consumed by the generated Fe^{3+} ions at the anode resulting in the needed $Fe(OH)_3$, the final pH in the alkaline medium (pH>8) does not vary greatly. Also, OH^- ions can also partially react with Cr^{3+} ions to produce $Cr(OH)_3$, an insoluble hydroxide precipitate.

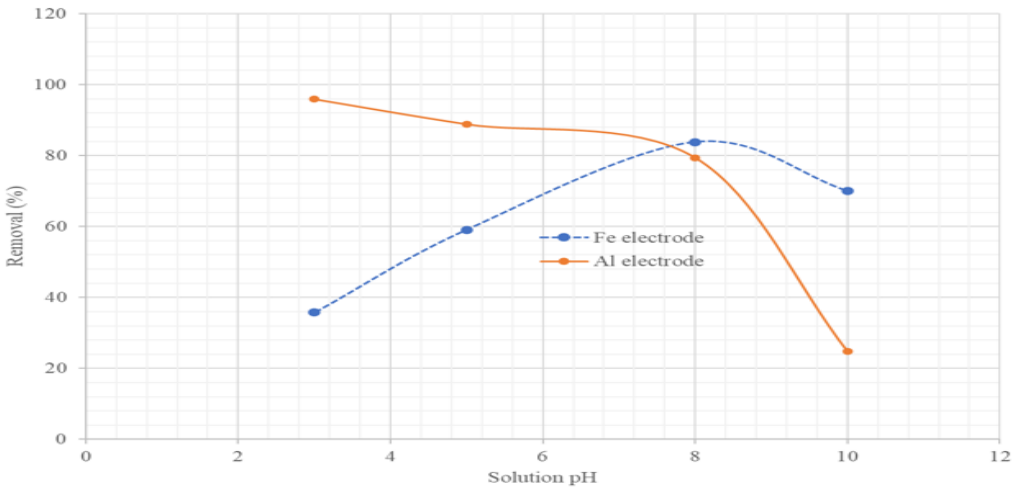

Figure 7: Effect of solution pH on the removal of Cr ion using Fe and Al electrodes. (Experimental conditions: solution pH adjusted to 3, 5, 8, and 10; 0.5 g NaCl, chromium concentration of 25 mg/L, 6.0 V, a distance of 2 cm, stirring speed of 100 rpm and treatment time of 60 minutes).

4.1.2 Effect of Initial Concentration

To explore the effect of increasing the initial concentration of the pollutant from 10 mg/L, 15 mg/L, and 25 mg/L on the removal efficiency of chromium ions, a series of tests were carried out. The experimental conditions are defined in the figure legend.

Figure 8 showed that as the concentration increases the percentage removal also increases from 71% (10 mg/L) to 78% (15 mg/L) then finally to 81% (25 mg/L) using Fe electrode. For Al electrode, similarly, the removal percent showed an increasing trend. When 10 mg/L Cr was applied, the percentage removal rose from 75% to 95% when 25 mg/L was used. This is due to the fact that the metal hydroxide flocs formed are sufficient to coagulate the large number of contaminating molecules as the initial concentration increases [41]. The trend seen in this study contrasts with many other findings in the literature, which claim that as the initial pollutant concentration rises, the removal effectiveness decreases.

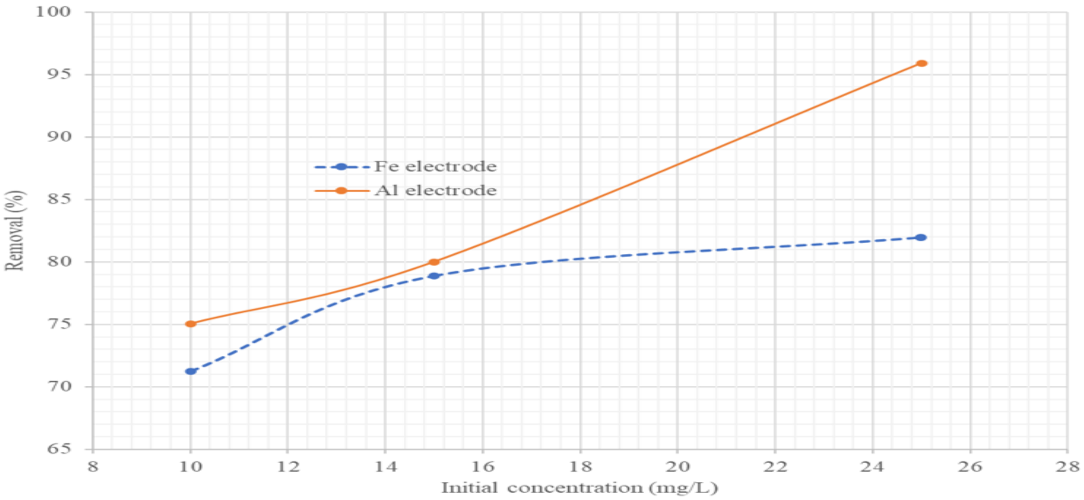

Figure 8: Effect of initial concentration on the removal of Cr ion using Fe and Al electrodes. (Experimental conditions: initial concentrations; 10 mg/L, 15 mg/L, and 25 mg/L, pH 8 and 3 for Fe and Al electrodes respectively, 0.5 g NaCl, 6.0 V, a distance of 2 cm, stirring speed of 100 rpm and treatment time of 60 minutes).

4.1.3 Effect of Voltage Applied

This has a direct impact on the EC process performance. Generally, when the applied voltage is increased, the time required to reach the study state condition is reduced. The experimental conditions are defined in the figure legend.

The result shows that as the voltage increases the percentage removal increases from 75% for 3 V to 81% for 6 V and 90% for 9 V for Fe electrode as shown in Figure 9 While for Al electrode, as the voltage increases the percentage removal increases from 61% for 3 V to 95% for 6 V and 100% for 9 V. this could be because of the difference in $E_{potential}$ of Fe and Al which is +0.77 V and -1.66 V respectively. The reason for this is that the amount of Al^{3+} and Fe^{3+} dissolved in the reaction system during the EC process is determined by the voltage. More Al^{3+} and Fe^{3+} are dissolved as the voltage is increased. As a result, the number of $CrFe_2O_3$, $Fe(OH)_3$, and $Al(OH)_3$ particles in the solutions increases, resulting in increased surface area for contaminants to adsorb. Moreover, when the applied voltage is increased, the rate of H_2 gas generation increases and the size of the bubbles reduces, leading to a greater upward flux and faster pollutants removal and flotation of sludge [50]. A similar observation was reported by Bazrafshan et al [58]. The same voltage was applied for both Fe and Al and

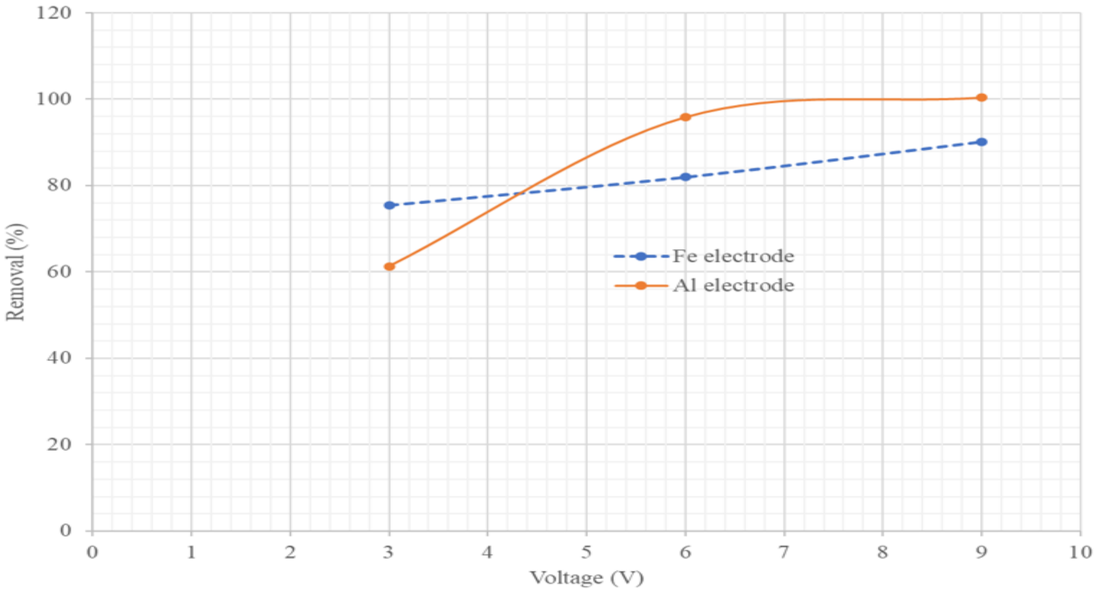

Figure 9: Effect of voltage on the removal of Cr ion using Fe and Al electrodes. (Experimental conditions: voltage; 3 V, 6 V, 9V, pH 8 and 3 for Fe and Al electrodes respectively, 0.5 g NaCl, chromium concentration of 25 mg/L, a distance of 2 cm, stirring speed of 100 rpm and treatment time of 60 minutes).

4.1.4 Effect of Electrolyte Type

In the EC, an electrolyte is commonly used to increase the conductivity of the solution. In this study, the dosage of the electrolyte (NaCl) was varied from 0.5 g, 1 g and 1.5 g while other parameters remained constant. The presence of Cl^- reduces electrode passivation, hence, the removal efficiency increases. Using Fe electrode, there was an increase in the percentage removal from 88% to 95% when the dosage of NaCl was increased from 0.5 g to 1.5 g as demonstrated in Figure 10, this is due to an increase in the conductivity of the solution [59]. Similarly, when Al electrode was used and the amount of NaCl increased from 0.5 g to 1.5 g the percentage removal remained at 100%.

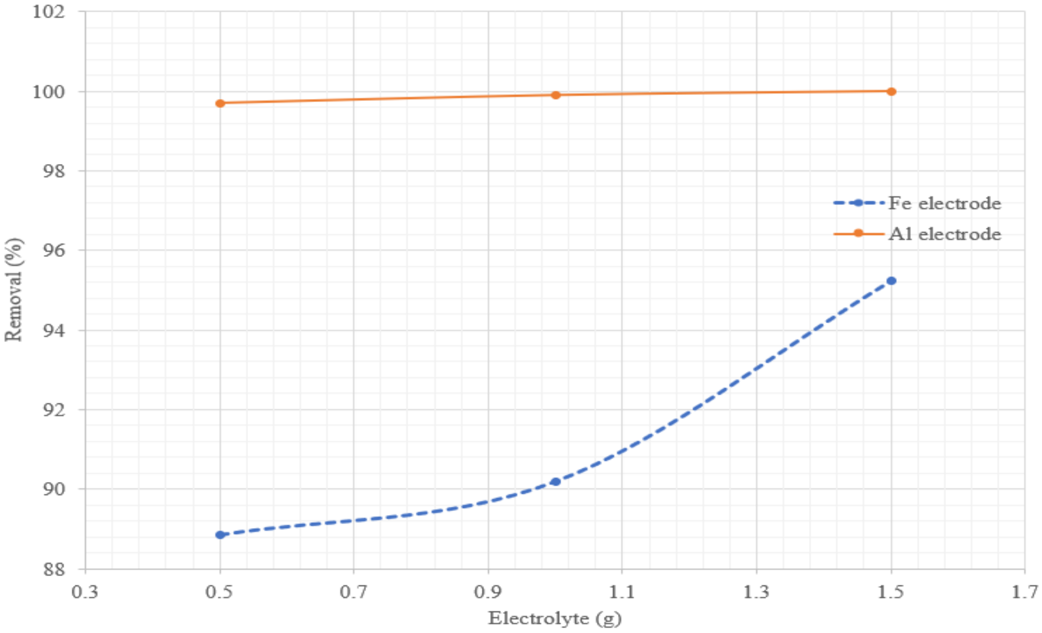

Figure 10: Effect of electrolyte on the removal of Cr ion using Fe and Al electrodes. (Experimental conditions: electrolyte (NaCl); 0.5 g, 1 g, 1.5 g, pH 8 and 3 for Fe and Al electrodes respectively, chromium concentration of 25 mg/L, 9.0 V, a distance of 2 cm, stirring speed of 100 rpm and treatment time of 60 minutes).

4.1.5 Effect of Electrode Distance

This is important because the electrostatic field depends on the distance between the anode and the cathode. The experimental conditions are defined in the figure legend. The result shows that there was an increase in the percentage removal from 93% to 95% when the distance is increased from 1 cm to 2 cm then begin to decrease as the distance is increased to 4 cm from 95% to 90% for Fe electrode as shown in Figure 11. For Al electrode, the result shows that there was an increase in the percentage removal from 98% to 100% when the distance is increased from 1 cm to 2 cm then begin to decrease as the distance is increased to 4 cm to 59%. This is due to the low interaction of chromium ions with metal hydroxides flocs, the accrued solid particles, and bubbles. Similarly, Thirugnanasambandham observed that from 1 cm to 2 cm the removal efficiency of Cr increased from 92% to 97% then decreased to 94% when the distance of the stainless-steel electrode used was increased from 2 to 4 cm during the experiment [60].

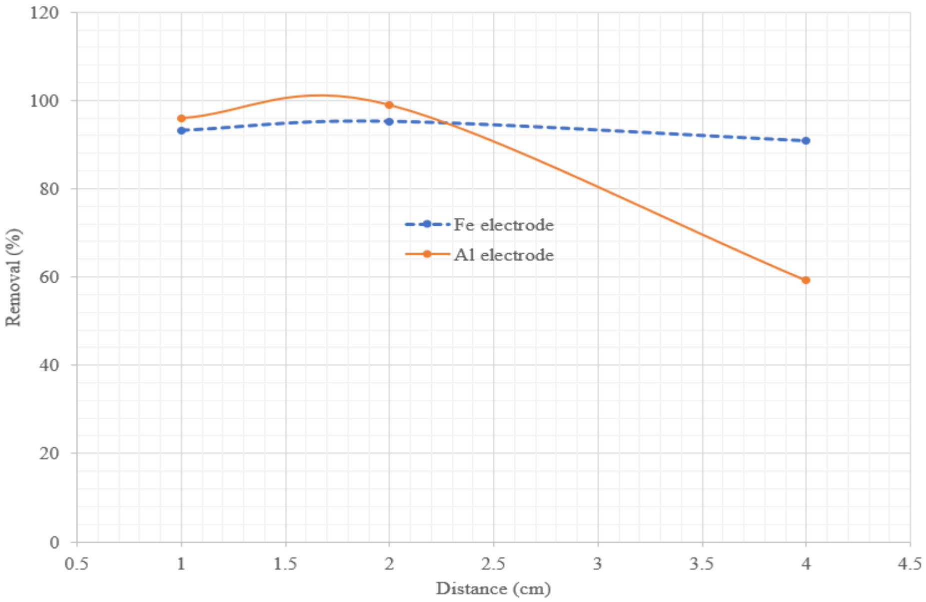

Figure 11: Effect of distance on the removal of Cr ion using Fe and Al electrodes. (Experimental conditions: distance; 1 cm, 2 cm, 4 cm, pH 8 and 3 for Fe and Al electrodes respectively, chromium concentration of 25 mg/L, 9.0 V, 1.5 g NaCl, stirring speed of 100 rpm and treatment time of 60 minutes).

4.1.6 Effect of Stirring Speed

The influence of agitation speed was investigated when the reaction cell was stirred at 100 rpm, 200 rpm and 400 rpm to find the optimum speed for the removal of chromium by the EC process. The experimental conditions are stated in the figure legend. As shown in Figure 12, the result shows that the percentage removal of chromium solution reached 95% at 100 rpm using Fe electrode. Then the percentage removal decreased to 58% at 200 rpm then attained 96.5% at 400 rpm. On the other hand, using Al electrode the percentage removal of chromium solution reached 100% at 100 rpm then decreased slightly to 98% at 200 rpm then 100% at 400 rpm. Although an irregular trend was noted, it is worth noting that increasing the stirring speed results in a higher percentage of contaminants removal. This is due to the rapid hydrolysis of water, which results in the creation of $Fe(OH)_3$ and $Al(OH)_3$, which act as adsorbents that adsorb chromium ions. Khaled et al [51] similarly observed that the elimination of Cd from phosphate synthetic effluent increased to 99.5% as the stirring speed was increased from 300 rpm to 450 rpm.

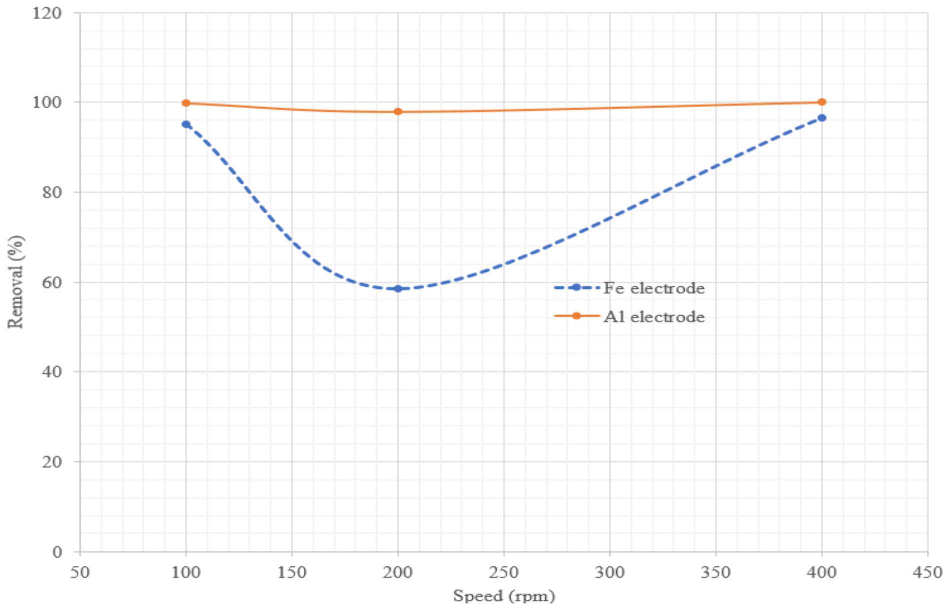

Figure 12: Effect of stirring speed on the removal of Cr ion using Fe and Al electrodes. (Experimental conditions: stirring speed; 100 rpm, 200 rpm, 400 rpm, pH 8 and 3 for Fe and Al electrodes respectively, chromium concentration of 25 mg/L, 9.0 V, 1.5 g NaCl, a distance of 2 cm and treatment time of 60 minutes).

4.2 FTIR Analysis

After the electrocoagulation process, the sludge collected from the treated wastewater at different pH was analysed using the FTIR as shown in Figure 13.

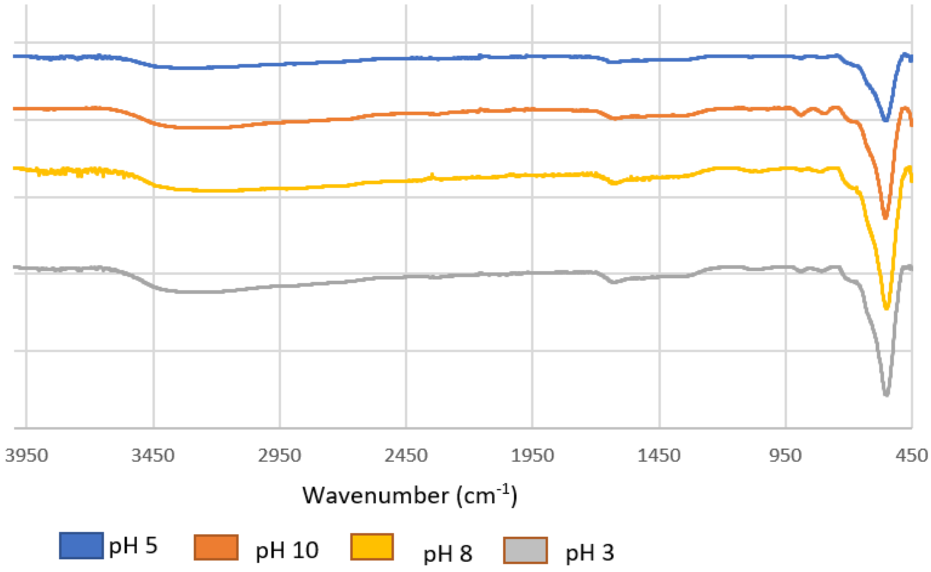

Figure 13: FTIR spectra of sludge from the EC process formed at different pH using Fe electrode.

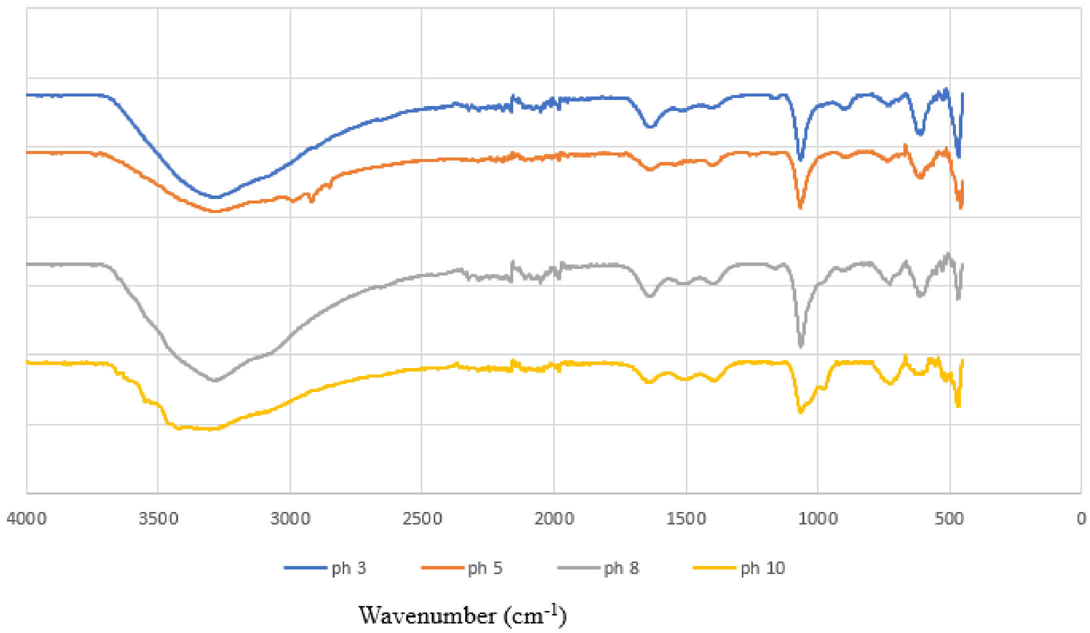

Figure 14: FTIR spectra of sludge from the EC process formed at different pH using Al electrode.

At different pH (3, 5, 8 and 10), two major peaks appeared around 680 and 450 cm^{-1} which are attributed to Fe-O (octahedral) and Cr-O (tetrahedral) respectively using Fe electrode [61]. Patil et al [61]studied the IR spectra of ferrites and has attributed the peak around 680 cm^{-1} to the intrinsic vibrations of the octahedral complexes and the peak around 450 cm^{-1} to intrinsic vibrations of tetrahedral complexes, which are bond-bending vibrations. The very small peaks around 799 cm^{-1} shows that $K_2Cr_2O_7$ adsorbed on the nanoparticle $Cr_2Fe_2O_4$. Same observation was reported in an article by Cao et al [62] where he used α-Fe_2O_3 to adsorb chromate around 790 cm^{-1}.

On the other hand, using Al electrode, at different pH. Figure 14 shows peaks around 3300 cm^{-1} which refers to O-H stretching and this band becomes wider and this might be as a result of the formation of some complexes at low pH such as $Al(OH)_2^+$ and $Al(OH)_3$ and $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ and $Al_{30}O_8(OH)_{56}(H_2O)_{24}^{18+}$ [63].

However, peaks around 1400 cm^{-1} to 1650 cm^{-1} refer to C=O stretching and C=C. In the sludge, the bands appeared with different intensities and similar observation was noticed by Vicente et al [64]. And also, peaks around 1066 and 480 cm^{-1} indicate the presence of Al-O bonds and AlO(OH) in the sludge [65].

4.3 Treatment Cost for Chromium Removal by Electrocoagulation Method

The operating cost (C_{op}) can be calculated using the formular in equation 2.

From equation 3, the energy consumption can be calculated as:

For Fe electrode: $C_{en} = \frac{9\times0.16\times1}{0.0002}$ = 7.2 KWh m^{-3}.

For Al electrode: $C_{en} = \frac{9\times0.3\times1}{0.0002}$ = 13.5 KWh m^{-3}.

The cost of 1 kg of iron is US$ 1.5 and an aluminium electrode is US$ 1.1 but the mass estimated cost of a 0.061274 kg of Fe and 0.015403 kg of Al used in this research are US$ 0.0919 and US$ 0.0169, respectively.

The amounts of Fe and Al electrodes consumed can be calculated using the formular in equation 4 as:

For Fe electrode: $C_{el} = \frac{0.16\times3600\times55.845}{96485\times2} = 0.1667$.

For Al electrode: $C_{el} = \frac{0.3\times3600\times26.982}{96485\times3} = 0.1007$.

From equation 2, the operation cost can be calculated as:

Fe electrode: $C_{(op)=}$ (0.093×7.2) + (0.0919×0.1667) = $ 0.68 per m^3.

Al electrode: $C_{(op)=}$ (0.093×13.5) + (0.0169×0.1007) = $ 1.26 per m^3.

Electrode consumption of Fe is higher than that of Al. this was expected due to theoretical calculation of E_{cell} as follow: $E_{cell} = E_{reduction} - E_{oxidation}$

In both cases, water is reduced to OH^- and H_2 gas. $E_{reduction}$ = -0.83 V, $E_{oxidation}$ of Al is +1.66 V however, for Fe +2 and +3 are +0.44 V and +0.036 V respectively. Therefore, E_{cell} for Al is -2.49 V on the other hand, for Fe +2 and +3 are +1.27 V and -0.866 V respectively. If E_{cell} is positive means the reaction is spontaneous and vice versa. Herein, at all cases E_{cell} is negative however, the negativity of E_{cell} Al is higher than E_{cell} Fe which leads to difficulty in oxidation and lower electrode consumption [66]. The electrode efficiency can be calculated using the formular in equation 6.

From equation 5, $M_{experimental}$ can be calculated as (mass obtained from optimum conditions):

Fe electrode: $M_{experimental} = 60.553\text{ g} - 60.417\text{ g} = 0.136\text{ g}$

Al electrode: $M_{experimental} = 15.056\text{ g} - 14.963\text{ g} = 0.093\text{ g}$

$M_{theoritical}$ = C_{el} which is the amount of electrode consumed.

Fe electrode: $E_{efficiency} = \frac{0.136}{0.1667} \times 100\%$ = 81.5%.

Al electrode: $E_{efficiency} = \frac{0.093}{0.1007} \times 100\%$ = 92.4%.

Chapter 5

CONCLUSION

The EC was used to remove chromium ions from synthetic wastewater solution using both Fe and Al electrodes. The UV-vis was used to analyse the treated wastewater and the FTIR was used to characterize the sludge produced during the process. The treatment process was subjected to various conditions, resulting in substantial outcomes and observable trends which are.

- In this work I was able to achieve 96.5% removal efficiency for chromium ion using Fe electrode at pH 8 for 60 minutes using 1.5 g of NaCl electrolyte, a voltage of 9, electrode distance of 2 cm, chromium concentration of 25 mg/L and stirring speed of 400 rpm.
- For Al electrode, maximum removal of 100% was obtained at pH 3, in the presence of 1.5 g of NaCl (electrolyte), a voltage of 9, electrode distance of 2 cm, chromium concentration of 25 mg/L and stirring speed of 400 rpm at a treatment time of 60 minutes.
- Two significant peaks were observed near 600 and 488 cm^{-1} which are attributed to Fe-O (octahedral) and Cr-O (tetrahedral) respectively at pH 3, 5, 8 and 10 also. This confirms that the sludge contained mainly the metal hydroxides as expected.
- The optimum pH in this study for chromium is pH 8 using Fe electrode and pH 3 using Al electrode.
- Fe and Al electrodes demonstrated 81.5% and 92.4% electrode efficiencies in this study based on the actual and theoretical amounts consumed.

When Al and Fe electrodes are employed, it will cost roughly 1.26 $ and 0.68 $ to remove 100% and 96.5% of 0.0002 m^3 of chromium, respectively, under ideal conditions. In terms of removal efficiency, treatment duration, and cost, the results show that EC can be used to treat heavy metal polluted water and wastewater. More research is needed, however, to confirm its true capability in real wastewater, as well as in the presence of numerous interfering pollutants.

Future Work

Further study with actual real wastewater containing chromium and other interfering pollutants will be done to expand the practical application of EC technology. The reactor tank will also be built up to at least 10 L, and the effect of numerous electrode arrangements will be studied in both batch and continuous treatment modes.

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