Electroplating wastewater is considered one of the most hazardous liquid wastes due to the presence of high contraction of toxic metals. Consequently, treatment of such wastewater is essential to protect the environment and waterways. Heavy metal ions are frequently of high toxicity and require treatment to the allowable standards for wastewater discharge. Electrochemical methods are more suitable for heavy metals removal due to their ability to reduce metal concentration to less than the permissible limits as well as allowing recovery of valuable metals.

The aim of the present study is treating real electroplating wastewater. For this purpose, synthetic as well as real electroplating wastewaters were examined using soluble aluminum electrodes and insoluble carbon electrode along with ferric chloride and/or alum as coagulants. Factors affecting this treatment process were studied extensively, namely: current intensity, material of the electrode, pH and time. The obtained results proved that the best removal was achieved at 30 minutes and a potential difference 15 volt for aluminum electrode and 10 volts for carbon electrode. The later was combined with ferric chloride as coagulant. When the synthetic solution was examined using aluminum electrode, the removal rate reached 97.2%, 97% and 96% for Zn, Cu, and Ni, respectively. By using carbon electrode in combination with ferric chloride, the respective removal rate reached 97.5%, 97.2%, and 97.1%. By using the real electroplating wastewater and aluminum electrode, the removal rate reached 80%, 76.6% and 93.4% for Zn, Cu, and Ni respectively and by using carbon electrode and ferric chloride the achieved removal rate was 81.6%, 77.3% and 94.4% successively. It was concluded that the use of carbon electrode with FeCl$_3$ is more suitable than aluminum electrode due to the dissolution of aluminum ions from electrode into the solution.

**Keywords:** Electro-chemical treatment, electroplating wastewater, Electrocoagulation, heavy metals removal, potential difference, wastewater.

**Introduction**

One of the major challenges facing mankind today is environmental protection issue, particularly water resources as well as providing clean water for Mankind. Regrettably, rivers, canals, and other water bodies are being constantly polluted due to the indiscriminate discharge of wastewater both industrial and sewage [1,2]. Industrial activities are one of the major sources of contaminated wastewater to the environment. Electroplating wastewater, usually, contains relatively high concentration of heavy metals that should be given special care to eliminate such pollutants. Such industrial activities produce large volumes of wastewater that contain highly toxic substances including acids, cyanides, alkaline cleaning agents, degreasing solvents, oil and grease as well as various heavy metals [3, 4].
Heavy metals are not biodegradable, persistently toxic, and some are also carcinogenic [5]. About 30 to 40% of all metals in plating processes are effectively utilized in plated process. The rest are discharged with the rinsing water. Effluent containing 1000 mg/l of toxic heavy metals should be eliminated according to the permissible limits before discharge to the environment [8,9].

The treatment of wastewater has become an absolute necessity. Effective and feasible wastewater treatment systems are presented by different investigators including physical, chemical, biological, as well as a combination of these processes [10-13]. One of the most promising techniques is the electrochemical treatment which is based on the chemical additions and the recovery of metals [14]. The advantage of this promising technique can be summarized as follows: it is highly effective, low in maintenance cost, less labor demand, and fast achievement for metal elimination and recovery [15].

Electrocoagulation involves the generation of coagulant in situ by dissolving electrically either aluminum or iron ions from aluminum or iron electrodes, respectively. Metal ions generation takes place at the anode; hydrogen gas would also help to float the flocculated particles out of wastewater. This process is also given the method name "electro flocculation". Addition advantages of electrocoagulation (EC) include high particulate removal efficiency, compact treatment facility, relatively low cost, and possibility of complete automation [16].

Meanwhile, in this EC process, the electrode can be arranged in a mono-polar or bipolar mode. The materials, on the other hand, can be aluminum or iron in plate form or packed form of scraps such as steel turnings, millings, etc.

The chemical reactions that take place at the anode are given as follows:

For aluminum anode [17]

\[ \text{Al} \rightarrow \text{Al}^{3+} + 3\text{e} \] .................................(1)

at alkaline conditions: \(\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al}(	ext{OH})_3\) ..............(2)

at acidic conditions: \(\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}(	ext{OH})_3 + 3\text{H}^+\) ...(3)

The reaction at the cathode is: \(2\text{H}_2\text{O} + 2\text{e} \rightarrow \text{H}_2 + 2\text{OH}^- \) (4)

The chemistry behind the EC treatment process in water is such that the positively charged ions are attracted to the negatively charged hydroxides ions producing hydroxide ions with a strong tendency to attract suspended particles leading to coagulation [18].

For carbon electrode:

Ferric chloride or aluminium sulfate are the widely coagulants used in the EC system. Both ferric chloride and alum act as acids as they release hydrogen ions thus they decrease the pH of the water.

\[ \text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+ \] ...............................(5)

\[ \text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}(	ext{OH})_3 + 3\text{H}^+ \] ...............................(6)

The alkalinity of ferric chloride and aluminum sulfate can be calculated using the stoichiometric reactions as follows:

\[ \text{FeCl}_3 + 6\text{H}_2\text{O} + 3(\text{HCO}_3^-) \rightarrow \text{Fe(OH)}_3 + 3\text{Cl}^- + 6\text{H}_2\text{O} + 3\text{CO}_2 \] ...............................(7)

\[ \text{AlCl}_3 + 14\text{H}_2\text{O} + 6(\text{HCO}_3^-) \rightarrow 2\text{Al}(	ext{OH})_3 + 3\text{SO}_4^{2-} + 14\text{H}_2\text{O} + 6\text{CO}_2 \] ...............................(8)

[19, 20].

The aim of the present study is to investigate the efficiency of electrochemical system for the treatment of electroplating wastewater. Further aim is to determine the efficiency of electrocoagulation system in removing metallic pollutants including zinc, copper and nickel from both synthetic aqueous solutions and real industrial electroplating wastewater. Meanwhile, the aim is to demonstrate the efficiency of the electro-coagulation in the treatment of real electroplating wastewater.

Material and Methods

The industrial highly acidic electroplating wastewater effluent was obtained from candilars plant. The plant produces 30,000 m³ electroplating wastewater per year that is heavily loaded with variable amounts of heavy metals, namely: Ni, Cu, and Zn.

A synthetic electroplating wastewater solution was prepared from reagent grade chemicals without further purification in 20 litter stock solution consists at 1 g/l (NiCl₂, CuSO₄, and ZnCl₂). The pH of this synthetic solution was adjusted to pH=2 using H₂SO₄ and HCl.

The present study was carried out in a batch electrocoagulation (EC) of 500 ml capacity (Figure 1). The EC unit consists of a DC power supply and two electrodes namely: aluminum soluble electrodes and carbon insoluble...
electrode at the dimensions of (10 cm x 3 cm) each. Both ferric chloride \([\text{FeCl}_3]\) and alum \([\text{Al}_2(\text{SO}_4)_3\cdot14\text{H}_2\text{O}]\) were used with carbon electrode as a primary coagulant.

- The electrodes were cleaned by polishing, immersing in 10% hydrochloric acid and were rinsed with tap water prior every run followed by using the EC for the synthetic electroplating wastewater.

- The electroplating wastewater effluent concentration was maintained during each experiment.

- DC supply was used at (25 volt and 100 amp) power supply.

- The pH of the electroplating wastewater effluent was adjusted using calcium carbonate and sodium hydroxide to maintain the pH = 9.

Before and after each run 1ml of polyacrylamide was added to the electrolytic solution for flocculation. The effluent was then filtered and analyzed.

**Determination of optimum Voltage:**

The following study was conducted to evaluate the effect of voltage on the efficiency of heavy metals removal from the wastewater: a number of experiments were carried out at different voltage of 5, 10, 15 and 20V, at constant initial concentration of 1000 mg/l for each metal (namely: zinc, nickel and copper), 30 min.s, and pH= 9 using both aluminum electrode and carbon electrode and ferric chloride as coagulant.

**Determination of the optimum time:**

Extensive study was carried out at variable times namely: 15, 30, 45, and 60 minutes with the pre-determined optimum voltage using each electrode.

The obtained optimum voltage and optimum time were employed for both aluminum and carbon electrode along with the coagulant in electrocoagulation, where the percentage of removal was calculated as follow:

\[
\text{Percentage of Metal Removal (\%) = } \frac{C_0 - C_f}{C_0} \times 100 \%
\]

Where \(C_0\) and \(C_f\) are the initial and the final concentration (as mg/l) of a given metal respectively.

**Results and Discussions**

**Effect of applied voltage on aluminum electrodes:**

This study was carried out at a concentration of 1000mg/l for each metal namely Zn, Cu, and Ni, for a duration of 30 min. and pH=9. Voltage is the product of the current delivered to the electrode and its resistance to flow. It determines the rate of coagulant dose, the rate and size of the bubble production, as well as the flock growth that enhance a faster removal rate [21]

Results obtained (Fig. 2) indicated that as the voltage increased up to 15volts, the removal rate increased for all the studied metals. A removal efficiency reached 97.2%, 97%, and 96.8% for zinc, copper and nickel respectively. Such removal efficiency was achieved due to the formation of a passivation film on the aluminum anode at over potential values higher than approximately 5 V and to the oxidation and reduction reactions that took place in the reactor. It may, also, attributed to the fact that at high voltage, the extent of anodic dissolution increased and the amount of...
hydro-cationic complexes resulted in increase of the removal efficiency. By increasing the voltage over 15 volts, the removal efficiency declined (Fig. 2). This is mainly due to the presence of non-reactive ions such as Na⁺, SO₄²⁻ and Cl⁻ from the wastewater effluent that cause a diffusion current which is equal but opposite to the migration current at steady state [22].

**Effect of voltage on the decay of aluminum electrodes:**

It is well known that pH plays a significant role in electrocoagulation [23]. Results (Fig. 3) exhibited the effect of increasing the voltage and the decay as dissolution of aluminum from the Al electrode. This study was conducted at pH=9 and duration of 30 min. It was reported that at pH=8, the precipitation of Al(OH)₃ does not occur immediately in a substantial way [24]. It occurs only at the end of 30 minutes and at less than 15 volts. The dissolution rates of aluminum electrode was less than zinc, copper and nickel each, and it decreased with increasing the volt due to both dissolution of aluminum ions and to the precipitation of the aluminum hydroxide. Meanwhile, the concentration of Al³⁺ ions in solution increased with increasing both the potential and time to be stabilized at 15 volt.

**Effect of applied voltage using carbon electrodes:**

![Fig. 2. Effect of voltage on rate of metal removal using aluminum electrode. (Concentration of zinc, copper and nickel were 1g/l each at pH = 9 and duration 30 min.)](image)

![Fig. 3. Effect of voltage on the removal efficiency (as dissolution) of aluminum resulted from aluminum electrodes, pH = 9, and duration 30 min.](image)
This study was carried out at a concentration of 1000 mg/l for each metal namely Zn, Cu, and Ni, for a duration of 30 min. and pH=9 using 10 mg/l FeCl₃ as coagulant. Carbon has been previously used as an electrode material in electrochemical applications and in metal removal for a long time. The electrode at the cathode produces reducing conditions and H₂. At the anode, the electrode produces oxidizing conditions and O₂ [25]. The electrodes provide the opportunity for sequential reduction and oxidation for metal removal [25].

In the present investigation, ferric chloride (FeCl₃) and alum were used each separately with carbon electrode as primary coagulants. However, the results of our initial experimental proved that only ferric chloride induce successful results with carbon electrode. Therefore, it was decided to continue running our experimental study using only carbon electrode in combination with ferric chloride.

The effect of voltage on metals removal of was studied by using carbon electrodes in the presence of 10 mg/l FeCl₃ as coagulant, at concentration of 1000 mg/l of zinc, copper and nickel each, at pH = 9, and duration of 30 min. The results (Fig. 4) showed that by increasing the applied potential, more Fe³⁺ and OH⁻ were generated in the electrochemical cell. This enhanced the coagulant dosage at 10 volt and 30 minutes that accelerated the removal of zinc, copper and nickel up to the optimum values of 97.2%, 97.2%, and 97.1%, respectively. Above this optimum value; namely 10 volt and 30 minutes; the dissolution of Fe³⁺ increased greatly. This leads to excessive generation of oxygen accompanied with heat generation [26]. Consequently, no Fe³⁺ ions could be dissolve, as a result of slight decrease in the removal of zinc, copper and nickel down to about 96 %, at 20V.

Effect of voltage on the release of iron from using carbon electrode with FeCl₃ as coagulant:

Further investigation was carried out to study the effect of voltage on the removal efficiency of iron that was released from using ferric chloride as coagulant. The present study was carried out using carbon electrodes at pH=9, voltage from 5 to 20, and 30 min. Results (Fig. 5) indicate that increasing volts from 5 to 10 increased the removal rate up to the maximum, namely 97.8%. Further increase in the volts decreases the removal rate.

Effect of contact time using aluminum electrodes:

Time of electrocoagulation is the most important factor in this process. The present study was carried out to investigate the effect of variable contact time on metal removal using aluminum electrodes, pH=9 and 15 volt, concentration of Zn, Cu, and Ni were at 1g/l each. The studied variable time ranged from 15 min to 75 min. The results (Fig. 6) showed that the maximum removal efficiency was reached at 30 min. namely: 97.1%, 96.9% and 96% for of Zn, Cu, and Ni, respectively. The removal efficiency (decay) of aluminum was 95.2%. Over 30 min. contact time, the removal rate was declined gradually till 60 min due to the increased formation of hydroxide ions. Consequently, the pH of the liquid also increased to more than 10. The formed hydroxide is mainly Al(OH)_₄⁻ [27-29]. The removal efficiency for aluminum reached 95.2% Fig. (7).

Effect of contact time on carbon electrodes:

The present study was carried out at different
Fig. 5. Effect of voltage on the removal efficiency of iron resulted from ferric chloride as coagulant using carbon electrodes at pH=9 and 10 volt.

Fig. 6. Effect of time on metal removal using aluminum electrodes, concentration of zinc, copper and nickel at 1g/l each, pH – 9 and 15 volt.

Fig. 7. Effect of time on the removal of aluminum by using aluminum electrodes, pH – 9 and 15 volts.

contact times ranged from 15-60 min using 10 volts for carbon electrode, 10 mg/l FeCl₃ as coagulant, initial concentration of 1 g/l for zinc, copper and nickel each, and at pH=9. Results (Fig. 8) showed that the maximum removal efficiency was reached at 30 min. contact time, where the removal was 97.5%, 97.1%, and 97.2% for Zn, Cu, and Ni, respectively.

By comparing the use of aluminum electrode, the dissolution of aluminum ions was greater than using of carbon electrode (in combination with FeCl₃), where the removal efficiency by employing the former (i.e. aluminum electrode) was 95.2%, and for the later (i.e. carbon with FeCl₃) the removal was 97.8%.

Therefore, it can be concluded that the use of electrocoagulation process for removing heavy metals from wastewater is more efficient by using carbon electrodes (in combination with FeCl₃) in correlation with the use of aluminum electrode. This can be attributed to the fact that there is no release from the carbon electrode mass except of the consumption of ferric chloride as coagulant, due to the formation of excess flocks. The later can ultimately sweep away the metal from solution.

**Fig. 8.** Effect of time on rate of metal removal by using carbon electrodes in combination with 10 mg/l FeCl₃ as coagulant, at concentration of 1 g/l of zinc, copper and nickel each, at pH = 9 and 10 volt.

**Fig. 9.** Effect of time on the removal efficiency of iron resulted from FeCl₃ as coagulant using carbon electrodes, pH = 9, and 10 volts
Conclusions:

The electro-coagulation is an efficient process for the treatment of electroplating wastewater. Thus, the treated wastewater can be handled without any threatening to the environment with regards to heavy metals.

Effective removal rates were achieved by using either carbon electrode in combination with FeCl₂, as coagulant, and / or aluminum electrodes. However, the use of carbon electrodes in combination with FeCl₂ was slightly more efficient than using aluminum electrodes. This can be attributed to the high adsorption capacity of hydrous ferric oxides which gives highest removal efficiency values compared to aluminum electrode.

The best removal was achieved at 30 minutes contact time and a potential difference at 15 volts for aluminum electrode and 10 volts for carbon electrode with ferric chloride.

The removal efficiency for synthetic solution using carbon electrode with FeCl₂ was 97.5%, 97.2% and 97.1% for zinc, copper and nickel, respectively, versus using aluminum electrode the removal was 97.1%, 96.9%, and 96.7%, successively.

By treatment of real electroplating wastewater, slight decrease in the removal was achieved, namely 81.6%, 77.3%, and 94.4% for Zn, Cu, and Ni, respectively by using carbon electrode with ferric chloride, and 80%, 76.6%, and 93.4% successively by using aluminum electrode.

References


TREATMENT OF INDUSTRIAL ELECTROPLATING WASTEWATER BY ELECTROCHEMICAL...


المعالجة الكهروكيميائية للمخلفات السائلة الخاصة بالطلاء الكهربي باستخدام كلاً من أقطاب الألومنيوم أو الكربون

تعتبر أيونات الفلزات الثقيلة من المواد عالية السمية والتي يجب أن يتم معالجتها والتخلص منها للوصول إلى الحد المسموح به قبل صرفها في المصارف العادية، وكذلك أن تكون معالجة هذه المعادن خطوة أولى في إعادة استخدامها وتفعيل كمية المعادن إلى مستوى ملمع. لذا وُضِح أيضاً بأداء استرجاع هذه الفلزات من مخلفاتها. حيث أن هذا البحث هو معالجة مخلفات الطلاء الكهربي السائلة باستخدام أقطاب الألومنيوم القابلة للذوبان وأقطاب أخرى غير ذائبة مثل الكربون مع مواد تخثر مثل كبريتات الألومنيوم و كلوريد الحديد. وقد تم ذلك بإختبار متغيرات متعددة مثل فرق الجهد، نوع الأقطاب المستخدمة، والزمن. وقد أوضحت النتائج أن أفضل إزالة تم عند استخدام فرق جهد 96 فولت في زمن مقداره 15 دقيقة باستخدام أقطاب الألومنيوم بنسبة مئوية لكل من الخارصين، النحاس والنيكل 30٪، ونسبة من مخلفات الطلاء الكهربي السائلة و فرق جهد 93.4 فولت في زمن مقداره 15 دقيقة باستخدام أقطاب الكربون مع كلوريد الحديد بنسبة مئوية لكل من الخارصين، النحاس والنيكل 97.2٪، ونسبة مخلفات الطلاء الكهربي السائلة. وقد أوضحت النتائج أن استخدام أقطاب الكربون مع كلوريد الحديد كمادة تخثر أفضل في إزالة الفلزات من مخلفات الطلاء الكهربي السائلة من استخدام أقطاب الألومنيوم وذلك لأن قطب الألومنيوم المصعد يذوب بكمية كبيرة في المحلول مما يقل كفاءته في عملية الإزالة.