Electrocoagulation/electroflotation of real printing wastewater using copper electrodes: A comparative study with aluminum electrodes

Safwat M. Safwat, Ahmed Hamed, and Ehab Rozaik

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ABSTRACT
Most studies investigated electrocoagulation/electroflotation process (EC/EF) using either aluminum or iron electrodes. The main aim of this study is to investigate the performance of EC/EF to treat printing wastewater under various experimental conditions using copper electrodes. The effects of several variables, including different electrode materials (copper and aluminum), different current densities, electrolysis time, and spacing between electrodes on the removal efficiency of various parameters were investigated. The results showed that the maximum removal efficiencies for COD, TDS, and oil and grease were obtained when using a copper electrode. The maximum removal efficiencies were obtained at a gap distance of 4 cm.

1. Introduction
Printing processes are used for several applications such as printing books and newspapers, clothing, circuit boards, and electrical appliances. Wastewater from printing can cause environmental risks due to the high chemical oxygen demand (COD). Chemical coagulation and biodegradation are among the conventional processes used for treatment of printing wastewater. For chemical coagulation, large amounts of sludge will be generated. Treatment of the sludge is expensive, and secondary pollution may occur if it is not handled properly. Regarding the biodegradation treatment, microbial activity may be inhibited due to the presence of toxic pollutants in the printing wastewater. Consequently, it is essential to treat printing wastewater through an innovative and efficient treatment technology.

Electrochemical wastewater treatment technologies such as electrocoagulation, electro-oxidation, and electroflotation are found to be promising technologies for wastewater treatment. These technologies are environmentally friendly options that produce low amounts of sludge, do not require chemical additives, and have a minimal footprint. Electrocoagulation and electroflotation can be a substitute for conventional coagulation and flotation, respectively, in wastewater treatment plants. In electrocoagulation/electroflotation process, sacrificial anodes, such as aluminum, dissolve due to an applied current, thus producing active coagulant compounds. This technology combines the benefits of coagulation, flotation, and electrochemistry. Electrocoagulation/electroflotation (EC/EF) offers many advantages over traditional coagulation/flocculation, such as higher efficiency, shorter retention time, prevention of secondary pollution caused by added chemicals, and simple operation. Coagulation/flocculation uses chemical coagulants/flocculants such as metal salts or polyelectrolytes, while EC/EF generates coagulants in situ through electrolytic oxidation of a sacrificial anode material which results in much less sludge production. The theories behind coagulation/flocculation and EC/EF are basically the same. Both methods remove particles from wastewater by destabilizing repulsive forces that keep the particles suspended in water. When the repulsive forces are destabilized, the suspended particles will form larger particles called flocs that can settle. In EC/EF, a direct current (DC) voltage is applied to an electrochemical cell with anode and cathode metal electrodes, immersed in wastewater as the electrolyte. There are three main processes that happen during the electrocoagulation/electroflotation process: (i) oxidation of the anode, (ii) generation of gas bubbles at the cathode, and (iii) flotation and sedimentation of the flocs formed. When a current is applied to the process, oxidation reactions take place on the sacrificial anode producing cations, and reduction reactions that occur on the cathode. Those
Metal hydroxide species provide effective destabilization of suspended solids. At the cathode, hydrogen gas is continuously generated. Flocculated particles are formed and pollutants are removed with the aid of scavenging and floating. The removal mechanism could be via adsorption, charge neutralization, or sweep coagulation. In the EC/EF process, the electrochemical reactions with metal M as electrodes are as follows:

\[ \text{At the anode: } M \rightarrow M^{n+} + ne^- , \text{ for coagulation} \]
\[ \rightarrow 2H_2O + 2e^- \text{, for flotation} \]

Various types of wastewater have been successfully treated using EC/EF. Previous studies have shown that EC/EF is a successful treatment process for treatment of industrial wastewater, especially those of high strength and toxic materials. One study showed that over 97% of heavy metal ions from metal plating wastewater were removed using electrocoagulation. Another study showed that the maximum efficiencies of phenol removal from aqueous solutions with aluminum and iron electrodes were 94.72% and 98.0%, respectively. Removal of phenol from oil refinery wastewater was also investigated using electrocoagulation with an aluminum screen anode, and the removal efficiency of phenol reached 97%. In a study investigating the treatment of paper mill effluents using electrocoagulation, the removal efficiencies using an aluminum electrode were 70% of biochemical oxygen demand, 98% of phenol, and 75% of the COD after 7.5 min. While using an iron electrode, the removal efficiencies were 80%, 93%, and 55%, respectively. During treatment of poultry slaughterhouse wastewater by electrocoagulation, the removal of the COD reached 93% with aluminum electrodes, while the maximum removal of oil and grease obtained was 98% with iron electrodes. Treatment of olive oil mill wastewater was also studied using electrocoagulation. Under a 30-min retention time, the removal efficiency of the COD was 52% and 42% when using aluminum anode and iron anode, respectively. Electrocoagulation was used to investigate the removal of polycyclic aromatic hydrocarbons in a paper-making wastewater, and the results showed that the process effectively removed a total of 86% of polycyclic aromatic hydrocarbons by mass in the effluent. Moreover, the electrocoagulation process was able to treat fluoride by reducing its concentration from the initial 6.0 mg/L to lower than 0.5 mg/L. A group of researchers used electrocoagulation to treat baker’s yeast production wastewater. The results showed that the maximum removal efficiencies of the COD, total organic carbon, and turbidity under optimal operating conditions were 71%, 53%, and 90% for the aluminum electrode and 69%, 52%, and 56% for the iron electrode, respectively. The EC/EF can be used as a pre-treatment step to reduce the contaminant loads of high strength industrial wastewater, such as printing wastewater, prior to the following treatment steps. It is worth noting that most studies investigated EC/EF using either aluminum electrodes or iron electrodes as the sacrificial anode. Since other types of electrodes, such as copper electrodes, showed promising results when used in EC/EF, it is essential to investigate these types with real wastewater to show their performance compared to the most widely used electrodes (aluminum or iron). To the best of authors’ knowledge, EC/EF using a copper electrode has not been investigated yet in the treatment of printing wastewater. Hence using EC/EF process with copper electrodes can be regarded as a new and potential method for treatment of printing wastewater. The main aim of this study is to investigate the performance of the EC/EF process using copper electrodes in batch operating mode to treat real printing wastewater under various experimental conditions using copper electrodes. The configuration of EC/EF process used in this study is the simplest type mentioned in literature. The effects of the operating variables, including different electrode materials (copper and aluminum), different current densities (CDs), electrolysis time, and spacing between electrodes, on the removal efficiency of several parameters were examined. These parameters were COD, total dissolved solids (TDS), and oil and grease. The energy consumption for the electrocoagulation cell was also calculated in this work.

### 2. Materials and methods

#### 2.1. Characteristics of real printing wastewater

The wastewater used in this study was collected from the printing industry in Egypt. The characteristics of wastewater are shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>6.8</td>
</tr>
<tr>
<td>COD</td>
<td>mg/l</td>
<td>7150</td>
</tr>
<tr>
<td>TDS</td>
<td>mg/l</td>
<td>6800</td>
</tr>
<tr>
<td>Total suspended solids (TSS)</td>
<td>mg/l</td>
<td>72.5</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>mg/l</td>
<td>385</td>
</tr>
<tr>
<td>Color</td>
<td>-</td>
<td>Yellowish</td>
</tr>
</tbody>
</table>

Table 1. Characteristics of wastewater.
2.2. Electrocoagulation system setup

The EC/EF unit is shown in Figure 1. Batch experiments were performed under a constant temperature of 20°C ± 2°C for 90 min. The EC/EF unit consists of an electrochemical reactor which was a one-liter glass beaker with magnetic stirring. The unit contained two parallel electrodes connected externally to a DC power supply. The cathode electrode was stainless steel, and the anode electrode was either copper (Cu) or aluminum (Al). The submerged surface area of each electrode was 28 cm$^2$. The gap between the electrodes was 4 cm, but some experiments have been performed with 2 and 6 cm gaps. The stirring speed was kept low (100 rpm) to avoid shearing of the flocs. The electrolysis time was maintained in the range of 5–90 min. Four CDs; 7, 14, 21 and 28 mA/cm$^2$, were examined. An ammeter and voltmeter were used to check the current intensity and the voltage during the EC/EF process. Samples were periodically withdrawn then filtered to eliminate sludge formed during electrolysis for further analysis.

2.3. Analysis

Influent and effluent samples were collected for analysis. In addition, COD, TSS, and oil and grease were measured according to the standard methods. The TDS and pH were measured using a multi-meter. The pollutant removal efficiency (%) after treatment was calculated using the following formula:

$$\text{Removal efficiency(%) = } \frac{(C_0 - C_e)}{C_0} \times 100$$

where $C_0$ and $C_e$ are the influent and effluent concentrations of pollutants, respectively. The sludge generated during the EC/EF process was analyzed using a Fourier transform infrared (FTIR) spectrometer. The morphologies of the anode electrodes were investigated using scanning electron microscopy (SEM). Chemical coagulation tests were conducted using the jar test. Copper sulfate and aluminum sulfate (Loba Chemie, India) were used as coagulants to simulate copper and aluminum electrodes. Experiments of conventional coagulation included flash mixing for 1.5 min at 100 rpm and slow mixing for 20 min at 30 rpm, followed by a 20 min settling period, after which the samples were collected for further analysis. All chemicals were of analytical grade. All experiments were run in duplicate, and the results were reported as the average of the measurements.

3. Results and discussion

3.1. Effect of current density on EC/EF

In the EC/EF process, a CD that determines the rate of hydrogen bubble formation and the growth of flocs was applied between the two electrodes to promote the dissolution of the electrodes to form coagulant species. The effect of the CD was analyzed for copper and aluminum electrodes between 7 and 28 mA/cm$^2$. Figures 2 and 3 show the removal efficiencies of the COD and TDS, respectively. As can be observed, the rate of removal of the COD for all CDs increased rapidly during the first 10 min. Then, the rate of removal efficiency of the COD decreased due to the desorption phenomenon. Furthermore, oxidation reactions that promoted the corrosion phenomena might lead to the formation of stable oxide layers on the surface of anode electrodes. These layers caused passivation effects, so decreased the efficiency of EC/EF cell. The maximum values of the COD removal efficiencies after 10 min were 60% and 49% for copper and aluminum electrode, respectively. The maximum values of the COD removal efficiency after 90 min were 67% and obtained at a CD of 28 mA/cm$^2$. For the aluminum electrode, the maximum value of the COD removal efficiency after 90 min was 55% and obtained at CD of 21 mA/cm$^2$. At a CD of 28 mA/cm$^2$, the removal efficiency of the COD was higher during the entire period when using the copper electrode, while the removal efficiencies of the COD for CDs of 14 mA/cm$^2$ and 21 mA/cm$^2$ were very close.

For the TDS removal efficiency, the performance of the copper electrode was better than that of the aluminum electrode for all CDs. The maximum removal efficiencies of the TDS after 90 min were 24% and 7% for copper and aluminum electrodes,
respectively. During the EC/EF process, the wastewater remains yellowish in color when using the aluminum electrode, while the color changed from yellowish to blue when using the copper electrode. The blue color was due to the dissociation of copper into the wastewater. The number of ions released as Cu$^{2+}$ or Al$^{3+}$ depends on the applied CD and determines the amount of the resulting coagulant. Consequently, the rate of formation of metal hydroxide increased as the amount of metal ions that dissolved into the wastewater increased. This increased the removal efficiencies of both the COD and TDS. Moreover, adsorption of pollutants occurred on the surface of metal oxides, hydroxides, and oxyhydroxides.\textsuperscript{[3,37]} The reduction of pollutants could also be due to the destabilization mechanism that comprises three main steps: compression of the double layer, followed by charge neutralization, then floc formation.\textsuperscript{[37]} Moreover, the increase of CD led to an increase in the generation of hydrogen bubbles and a decrease in their sizes. This results in the removal of pollutants through flotation. In the case of the aluminum electrode, the maximum removal efficiency of the COD was not obtained at the maximum CD used. This might be because higher CDs increase the turbulence in the system. Increasing the turbulence can affect the coagulation process because the particles will not have enough time to agglomerate and remove the pollutants.

**Figure 2.** COD removal efficiencies over time at various current densities: a) Cu electrode, b) Al electrode.

**Figure 3.** TDS removal efficiencies over time at various current densities: a) Cu electrode, b) Al electrode.

The pH increased for all values of CDs over time. This might be due to the reactions occurring at the cathode. During the EC/EF process, water molecules receive electrons and dissociate into hydrogen bubbles and hydroxyl ions, causing an increase in pH values. The increase of pH values in the case of the copper...
electrode was more than those for the aluminum electrode for all CDs. This indicates that the amount of dissociation of water molecules in the case of copper electrode was more than that for the aluminum electrode. The higher pH values were obtained for both types of anodes at the higher CDs (21 and 28 mA/cm²), and this is because at high CDs, corrosion of the cathode occurs due to the intensive production of hydroxide anions. Copper is dissolved to produce divalent ions Cu²⁺ ions, forming copper hydroxide, which thermodynamically forms at 7.7. For pH values between 4 and 9.5, Al(OH)₃ (s) predominates. The increase in pH values during EC/EF process favors the formation of these hydroxides. These hydroxides trap the colloids/pollutants in a sweep coagulation manner as they precipitate leading to a higher COD removal.

Figures 5 and 6 show the effluent TSS and oil and grease when using copper and aluminum electrodes at different CDs. The copper electrode provides the best removal efficiency for oil and grease. For oil and grease, intensive fine hydrogen bubbles were formed at a CD of 21 mA/cm², which adhered to the oil droplets and raised them to the surface the of solution in a sweeping action called sweep flocculation, as shown in Figure 7. The number of flocs formed with the copper electrode was more than that of the aluminum electrode at all CDs, leading to more TSS in the effluent for the copper electrode. Since a high removal of pollutants occurred at a CD of 21 mA/cm², the next experiments for both types of electrodes were performed at this value of CD.

3.2. Effect of spacing between electrodes

It is known that the gap distance between electrodes affects the ohmic potential of the EC/EF cell and the energy consumption. The effects of spacing between electrodes were investigated at a CD of 21 mA/cm². Figures 8 and 9 show the removal
The maximum removal efficiencies were obtained at a spacing of 4 cm. Although decreasing the gap distance leads to decreasing the resistance between the electrodes and increasing the efficiency of the pollutant removal, this was not the case in this study. When increasing the spacing to 6 cm or decreasing it to 2 cm, the pollutant removal efficiencies decreased compared to those at spacing of 4 cm. This phenomenon might be due to the configuration of the system. The cross-section of the reactor was circular, and the spacing of 4 cm between electrodes was approximately equidistant between the two electrodes and between each electrode and the edge. This equidistance might lead to two results: i) uniform distribution of flocs inside the reactor and ii) minimization of the disturbance that could occur to the flocs during mixing compared to the disturbance when the electrodes are very close to each other or when they are very close to the edges. Moreover, the small gap distance between the electrodes led to a high electrostatic effect that hinders the particle collision. More electrochemically generated gas bubbles caused turbulence, while the big gap distance significantly decreased the formation of flocs.

The behavior during the removal of pollutants was almost the same for all gap distances. The rate of removal of the pollutants was high during the first 10 min, then decreased until the end of the experiments. The maximum efficiencies of the COD removal when using the copper electrode for the gap distances of 2, 4, and 6 cm were 19%, 65%, and 15%, respectively. The maximum efficiencies of COD removal when using the aluminum electrode for the gap distances 2, 4, and 6 cm were 24%, 55%, and 15%, respectively. The maximum efficiencies of TDS removal when using the copper electrode for gap distances 2, 4, and 6 cm were 8%, 24%, and 5%, respectively. The maximum efficiencies of TDS removal when using aluminum electrode for the gap distances 2, 4, and 6 cm were 7%, 3%, and 5%, respectively. Removal of the COD and TDS using the copper electrode were higher than those when using the aluminum electrode for all gap distances. The effluent values of oil and grease in the case of the copper electrode were less than those for the aluminum electrode as shown in Figure 10. The values of TSS in effluent increased in the case of the copper electrode when compared to those values obtained from the aluminum electrode. This is because the number of flocs formed in the case of the copper was more than that formed in the case of the aluminum. This confirms that the EC/EF unit...
Figure 8. COD removal efficiencies over time at various gap distances a) Cu electrode, b) Al electrode.

Figure 9. TDS removal efficiencies over time at various gap distances a) Cu electrode, b) Al electrode.

Figure 10. Effluent Oil and grease, and TSS at various gap distances.
with the copper electrode performs better than the EC/EF unit with the aluminum electrode.

### 3.3. Characterization of the by-products obtained from the EC/EF by FTIR

To characterize the by-products, FTIR analyses were carried out. Figure 11 shows the characterizations of the sludge samples produced at 21 mA/cm² using copper and aluminum electrodes. It can be observed that FTIR spectra for sludge samples showed some spectroscopic changes. The finger-prints of the two sludge samples between 400 cm⁻¹ and 1500 cm⁻¹ were not identical, confirming the presence of different components. These different components were due to the dissociation of either copper or aluminum electrodes during the electrocoagulation process. The FTIR spectra of the two sludge samples showed a broad and intense band between 3000 cm⁻¹ and 3700 cm⁻¹, indicating the presence of an OH group. The presence of this group enhanced the adsorption of the counter ions during settling. This confirms that adsorption is one of the removal mechanisms of the EC/EF process.

### 3.4. Morphologies of electrodes

The morphologies of copper and aluminum electrodes were investigated before and after electrocoagulation at a CD of 21 mA/cm². Figure 12 shows the SEM images of the electrodes before and after the treatment. For both the copper and aluminum electrodes, corrosion happened to the anodes after the EC/EF experiment, confirming the occurrence of the treatment process. The surface of the copper electrode contained cracks, while that of the aluminum electrode was rough and contained dents. The formation of a large number of cracks and dents in anodes is attributed to the consumption of metal at active sites of electrodes due to the generation of oxygen at the surfaces. The corrosion in the copper electrode was a uniform corrosion, while that for the aluminum electrode was a pitting corrosion. Uniform corrosion is better than pitting corrosion, since it is easier to predict.

### 3.5. Electrical energy consumption

Key factors, such as energy cost, must be taken into consideration in the process optimization. The energy consumptions required for the treatment of the printing wastewater versus the operating time at different CDs is shown in Figure 13. The electrical energy...
consumption (EEC) was calculated in terms of kwh/m$^3$ of treated effluent using the following equation:

$$ EEC(kwh/m^3) = \frac{UIt}{V} $$

where $U$ is the average cell voltage (V), $I$ is the current intensity (A), $t$ is the time of electrocoagulation treatment (h), and $V$ is the volume of effluent to be treated (l). The results show that energy consumption increased with the CD. The values of energy consumption for the copper electrode were more than those for the aluminum electrode. The maximum values for energy consumption were 14 kwh/m$^3$ and 13 kwh/m$^3$ for the copper electrode and aluminum electrode, respectively. The values of the COD removal efficiencies after 10 min with a CD of 21 mA/cm$^2$ represented more than 90% of the total COD removal efficiencies obtained after 90 min, as observed in Section 3.1. As a result, 10 min can be considered the optimum condition. The maximum values for energy consumption at a CD of 21 mA/cm$^2$ were 0.86 kwh/m$^3$ and 0.8 kwh/m$^3$ for the copper electrode and aluminum electrode, respectively. These values are within the range of values mentioned in the literature for energy consumption with the electrocoagulation processes, lying between 0.002 and 58 kwh/m$^3$.[43] These observations show that the copper anode is more energy demanding than the aluminum.

### 3.6. Performances of chemical coagulation

Copper sulfate and aluminum sulfate were used at different dosages (10 g/l-160 g/l) to investigate the difference in performance between chemical coagulation and electrocoagulation, as shown in Figure 14. Figure 15 shows the removal efficiencies of the COD using chemical coagulants. The values of the COD removal efficiencies increased with increasing coagulant doses. Aluminum sulfate gives better results when compared to copper sulfate. The maximum removal efficiencies of the COD were 14% and 28% for copper sulfate and aluminum sulfate, respectively. These values are much lower than those obtained using electrocoagulation, although the amount of coagulant used is practically very high (160 g/l). These results confirm that the performance of electrocoagulation is better than that of chemical coagulation in treating printing wastewater.

### 3.7. Limitations of the study

The lack of information about concentrations of copper and aluminum ions in the effluent is one of the limitations. These ions can cause environmental problems. The concentrations of these ions in effluent were not...
included in the present study, as the study focused on the ability of EC/EF process in reducing influent pollutants of real printing wastewater. Another limitation is the time period after which the anode electrodes will need to be replaced due to dissociation in the solution during treatment process.

4. Conclusion

This work studied the treatment of printing wastewater using the EC/EF process. Two different electrodes (copper and aluminum) were examined. The results showed that the pollutant removal efficiencies when using the copper electrode were better than those found when using the aluminum electrode. The maximum value of the COD removal efficiency was around 67%, obtained at a CD of 28 mA/cm$^2$. For the aluminum electrode, the maximum value of the COD removal efficiency was 55%, obtained at a CD of 21 mA/cm$^2$. The values of pH increased for all values of CD over time. The maximum removal efficiencies of the TDS after 90 min were 24% and 7% for the copper and aluminum electrodes, respectively. EC/EF process was not sufficient in removal of color, so further treatment is needed to remove color from effluent. The maximum removal efficiencies were obtained at a gap distance of 4 cm. Characterizations of the sludge samples produced at 21 mA/cm$^2$ were carried out by FTIR. The finger-prints of the samples were not identical, confirming the presence of different components. The morphologies of the copper and aluminum electrodes were analyzed before and after electrocoagulation. For both copper and aluminum electrodes, corrosion happened to the anodes after the EC/EF process confirming the occurrence of metal dissociation. The corrosion in the copper electrode was a uniform corrosion, while that for the aluminum electrode was a pitting corrosion. The results showed that energy consumption increased with the CD. The performance of electrocoagulation was better than that of the chemical coagulation in treating real printing wastewater.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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