Comparative performance evaluation of ozone oxidation and coagulation for the treatment of electroplating wastewater

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A B S T R A C T

Various attempts have been made to assess the wastewater characteristics (pH, biochemical oxygen demand, and chemical oxygen demand) and heavy metals (nickel (Ni), cadmium (Cd), chromium (Cr), and copper (Cu)) in electroplating wastewater being discharged from large scale industrial units. The results showed that the concentration of heavy metals was found to be in the following order: Ni was 27.57 mg/L, Cr was 60.10 mg/L, Cu was 0.80 mg/L, and Cd was below the detectable limit (BDL). Furthermore, the treatment efficiency for Ni containing electroplating wastewater was comparatively evaluated through ozone oxidation and physicochemical process (coagulation and flocculation). The wastewater treated with ozone showed effective results for up to 30–40 min and achieved 42% Ni and 26% Cr removal efficiencies. In coagulation and flocculation, six beaker jar tests were conducted to remove Ni and Cr by using three different coagulants and non-ionic polyacrylamide. Among all these coagulants, aluminum sulfate was found more effective in combination with polymer. The optimum removal efficiency was achieved at 90 mg/L doses of aluminum sulfate and 100 mg/L of polymer for 98% and 99% removal of Ni and Cr, respectively. Therefore, it can be concluded that the physiochemical processes (coagulation and flocculation) were the most efficient method as compared to ozone treatment.

Keywords: Coagulation; Electroplating wastewater treatment; Flocculation; Ozone oxidation

1. Introduction

Environmental issues, particularly chemical and biological water pollution, signify a key urgency for industries, civil society, and public authorities. Many developed countries are rapidly taking action to protect and conserve water sources by introducing strict legislations and policies. These regulatory frameworks impose appropriate treatment limits for the industrial effluents prior to their discharge into the environment [1,2]. A large volume of water is used in the electroplating industry for various processes and operations. Pollution problems arise because of the consumption of many types of metals and chemical salts [1]. Dumping of chemicals, leakages, and spray losses are the major causes of pollution. Different metals, chemicals, and cyanides used in a proportion of 2%–20% have vanished in wastewater. To lessen the problems of pollution, better remedial measures are needed [3]. Cyanides, metals, alkaline cleaning agents, degreasing solvents, and oils are included in the category of toxic substances which are part of the industrial wastewater such as acid mine wastewater and electroplating wastewater. Discharge of this industrial wastewater into the environment without any treatment accumulates various metals (like zinc,
copper, chromium, silver, and nickel) and pose threat to living organisms [4]. Nickel plating is the most common type of electroplating due to its corrosion resistance property and applications in decorative finishing. The most common process is the Watts bath in which \( \text{H}_3\text{BO}_3, \text{NiCl}_2, \text{and NiSO}_4 \) and organic additives are added to the bath for brightness coating [5]. Consequently, higher amounts of wastewater generated, containing nickel and organic compounds. Many health problems like asthma, skin irritation, conjunctivitis, and cancer are caused by short-term or long-term exposure to nickel exposure [4,5].

Different treatment processes such as flotation, adsorption, coagulation, and flocculation, ion exchange, micro/nano/ultra-filtration, electrolysis, electrocoagulation, and reverse osmosis can be employed for wastewater treatment. The removal efficiency of all these processes is greater than 99% but the rate varies with the type of the process and metal. Whereas removal of some molecules like organic additives is difficult and expensive as they are mostly resistant to conventional treatment methods [6]. Treatment of wastewater with ozone is regarded as one of the most effective treatment processes and is widely being used for few decades. The ozonation process decreases pollutants toxicity in electroplating wastewater [7]. Ozone is regarded as a highly selective oxidant and it is 3,125 times faster than chlorine in terms of its disinfection efficiency. Ozone is required in higher concentrations ranging from 10 to 15 mg/L for treatment because industrial wastewater has diverse properties. Heavy metals are oxidized into hydroxides and metallic oxides with ozonation, and all other types of organic and inorganic impurities are also oxidized [6,8].

The objectives of the present study included the determination of basic wastewater characteristics such as pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), nickel (Ni), cadmium (Cd), chromium (Cr), and copper (Cu) and to compare these values with regulatory standards. Moreover, the study also presented a comparative evaluation of ozone oxidation and physicochemical process (coagulation and flocculation) in terms of their treatment efficiency for nickel-containing electroplating wastewater. Ozone was selected based on its efficiency found in literature, mainly for its faster and effectiveness for treatment. Most of the studies were conducted to investigate the combined effect of ozonation and chemical coagulation. Ashraf et al. [9] investigated the individual coagulation process for wastewater and with 0.75 g/L alum dose, they found 78% removal and COD reduction method of ozonation is changed and is only 13.5% after 1 h ozonation. Masoomi et al. [10] also determined the efficiency of pre-ozonation and post-ozonation. They concluded that pre-ozonation without coagulation gave a maximum up to 32% removal efficiency of some parameters but with the combined effect of coagulation, it gave 76.9% removal efficiency. So, there are few studies present for its individual comparison.

### 2. Materials and methods

#### 2.1. Wastewater samples collection

Nickel-containing electroplating wastewater (EPWW) samples (\( n = 45 \)) were obtained from large-scale industries in clean plastic containers. Wastewater characteristics were measured. Different parameters pH, COD, 5 d BOD, copper (Cu\(^{2+}\)), nickel (Ni\(^{2+}\)), Cd, and Cr were measured by using standard methods [11]. After that wastewater was treated with ozone and, coagulation and flocculation to remove the concentration of nickel from wastewater.

#### 2.2. Analytical techniques

Wastewater characteristics were determined prior to treatment with ozone and physicochemical methods. The various effluent parameters such as pH, BOD, COD, and concentration of heavy metals (Ni, Cd, Cr, and Cu) were determined by using standard methods. Three concurrent readings of pH were taken by the pH meter. Biological oxygen demand (BOD) was determined by the incubation method. COD was determined by the photometric method, in which the COD value was measured using the photometer. For the determination of heavy metals, the sample was digested with aqua regia (3:1 H\(_2\)NO\(_3\) : HCl) in high-density polyethylene (HDPE) bottles to release its metal content. Atomic absorption spectrophotometer was used to carry out the analysis [11].

#### 2.3. Ozonation

Ozonation was performed to treat the nickel-containing electroplating wastewater (EPWW) in a bubble column reactor made of Plexi glass whose internal diameter was 3 cm (Model OZ-3G). Standard Ozone analyzer BMT 964 TECHNIK GMBH with temperature and pressure compensation was used for ozone calibration. First, ozone generator was switched on and left to heat up for 10 min. The wastewater was added into the reactor after determining the pH of the sample. Ozone was pumped into the water by operating the ozone generator having a capacity of 5 g/L for 60 min. The wastewater was sampled after every 10 min and the pH of the wastewater was determined with the help of a pH meter. Different temperatures 20°C, 30°C, and 40°C were maintained to evaluate the best performance at different time intervals. Samples were digested again for analysis in atomic absorption spectrophotometer.

#### 2.4. Coagulation and flocculation

Physicochemical treatment is deliberated as one of the best appropriate selections for heavy metal removal from wastewater. This treatment includes coagulation and flocculation while the pH of wastewater is also adjusted to increase the treatment efficiency. Different coagulants; such as aluminum sulfate, ferrous sulfate, and ferric chloride were used. Anionic polymers were used as flocculants. Different dosages of coagulants and flocculant at different pH were analyzed. The literature review showed that different metals dissolve at different pH values. Metals of our concern showed dissolved at pH 8.5 for Cr removal and 10.2 for nickel removal. Therefore, pH was adjusted at 9 by the general rule during the treatment of more than one metal [12].

#### 2.5. Dose optimization for coagulants

A conventional jar test was employed for coagulation, flocculation. 1 L wastewater was taken in every 6 jars
and the dose of aluminum sulfate was varied from 340 to 400 mg/L with an interval of 10 min and the concentration of flocculant was varied from 0 to 100 mg/L in each jar. After the addition of the coagulant or flocculant, all the samples were mixed rapidly at speed of 200 rpm for 2 min and then slowly mixed at the rate of 30 rpm for 3 min. Then the wastewater was allowed to settle for 55 min. The treated wastewater was withdrawn from the beaker by using a plastic syringe and digested using standard methods to release its trace metal contents and analysis was carried out by using atomic absorption spectrophotometer to analyze the concentration of Ni and Cr. The second coagulant used in this study was ferrous sulfate. The dose range of ferrous sulfate was 0–500 mg/L and the polymer dose was varied from 0 to 100 mg/L. Operating parameters were the same as described above for aluminum sulfate. The third coagulant was ferric chloride. The dose range of ferric chloride was 0–500 mg/L and the polymer dose was varied from 0 to 100 mg/L. Operating parameters were the same as described above for aluminum sulfate.

3. Results and discussion

3.1. Effluent characteristics

The characterization of the electroplating wastewater in terms of toxic metals along with different parameters is presented in Table 1. The pH of the wastewater was 6.7, which was in accordance with the permissible limits of the National Environmental Quality Standards (NEQS). A similar finding has been reported by Singh [13], where pH values ranged from 6.89 to 7.15. The COD and BOD were also in compliance with the NEQS. The concentration of toxic heavy metals such as nickel and chromium in the electroplating wastewater was very high as compared to other metals. The concentration of heavy metals was found as 27.6, 60.1, and 0.81 mg/L for Ni, Cr, and Cu, respectively. The concentration of nickel and chromium were exceeding the permissible limits of NEQS, that is, 1 mg/L for both metals. Ni used in metal-producing units in larger quantities and a high concentration of nickel is very toxic. Similar results were reported by other studies in which Ni concentration was 10.35 and 46 mg/L in electroplating effluent [14,15]. Whereas, the concentration of Cr (60.1002 mg/L) was also similar to other studies as Laxmi et al. [16] reported 60.78–62.82 mg/L of Cr in the metal producing units. Singh [17] reported 102 mg/L Cr in the plating effluent while Nagarajan et al. [18] reported 70.06 mg/L Cr. However, Cu was found within the permissible limits. The concentration of cadmium was below the detection limit (BDL). Almost similar results have been observed by Chhikara and Dhankhar [19] who reported a 0.63 mg/L concentration of Cu in electroplating wastewater. The higher concentration of Ni and Cr, as presented in this study, have the potential to cause mutagenic, genotoxic as well as cytotoxic effects on plant [20], human [21], and bacteria [22]. Therefore, it is mandatory to treat effluents before discharging them into the environment.

3.2. Effect of ozonation on the removal of heavy metals

The trend of Ni, Cr, Cu, and Cd concentrations during exposure of wastewater to ozone is presented in Table 2. Initially, the concentration of Ni was 27.6 mg/L and then there was a sudden decrease after 10 min of ozone treatment (17.39 mg/L). The concentration reduced further to 16 mg/L after 40 min of the ozone process. After that, it increased to 19.85 and 21.84 mg/L with 50 and 60 min of treatment. In Cr, after 10 min of ozone treatment, there was a significant decrease in Cr concentration, that is, 44.84 mg/L, then there was a slight increase after an additional 10 min of exposure to ozone. With the increase in time (30 and 40 min), the Cr concentration again reduced and slightly increased up to 43.99 and 44.5 mg/L, respectively. However, the concentration increased (60.08 mg/L) after 60 min of the experiment. The initial concentration of Cu was 0.8083 mg/L and after 10 min of ozone treatment, Cu concentration significantly decreased up to 0.3011 mg/L. Then there was no significant change for 40 min of the experiment. The concentration remained almost the same such as 0.20, 0.1911, and 0.18 mg/L after
20, 30, and 40 min of ozone oxidation, respectively. At the end of the experiment, the concentration again slightly increased and reached 0.24 mg/L after 50 min of treatment. The concentration of Cu was 0.28 mg/L at the end (60 min of the experiment). Ozone treatment has the ability to remove contaminants from wastewater by directly attracting them toward hydroxyl radicals which were produced in the decomposition process of ozone [23]. Heavy metals are oxidized to their higher oxidation states from transition metal and as oxides are less soluble in water, they get precipitated and can be easily removed through filtration. The solubility of the ozone and hydroxyl radical formation is directly affected by the pH [24].

Fig. 1 depicts the removal efficiencies increase gradually vs. time till 40 min for Ni, Cr, and Cu. However, after 40 min the removal rate declined with the increase in treatment duration. The removal efficiency of Ni reached 37%, 39%, 41%, and 42% after 10, 20, 30, and 40 min and then decreased to 28% and 21% after 50 and 60 min of treatment, respectively. An almost similar trend was observed in the case of Cr and Cu, their removal efficiencies showed an increase for an initial 40 min and declined. The reason for this trend is the decomposition reaction is faster at basic pH and hydroxyl radical potential is also higher. As a result, pollutants are degraded by the oxidation of ozone. At lower pH, the oxidation process of ozone dominates the reaction, whereas at higher pH the main reaction is *OH oxidation and this reaction is much faster than the previous one [25]. Another important reason is that ozone reacts with the degradation products that could be formed by oxidation through OH (usually carboxylic acids), which favors the decrease in pH of the sample [26]. In several studies, the same trend in the effect of change in pH on removal of contaminants from industrial effluents has been observed by other researchers [27,28].

The other important characteristic of the ozonation process is the change in pH. It is a very crucial factor because organisms living in aquatic habitats are directly affected by pH variation. It also affects the level of heavy metals toxicity ad other parameters [29,30]. Change in pH was monitored during the degradation of heavy metals through ozone oxidation. The pH of wastewater increased gradually with the increase of the removal reaction up to 40 min and then the decreased rate of observed as depicted in Fig. 2.

Hydrogen ions were produced continuously during the oxidation process of Ni, Cr, Cu, and the consumption of OH* by O₂ this may be the reason for the decrease in pH of the wastewater. However, the pH increased slowly when the initial pH was 6.7. The decrease in pH is associated with the decreased removal of heavy metals at 5.8. Similar results have been observed by Luo et al. [31], the effect of ozone flow rate, duration of treatment, and change in pH on the removal of ammonia by ozone oxidation. In the previous work, it has been concluded that the process of ozone produces the OH and spent the H⁺ ions or produce OH. In adding to this, enough ZVI can also lessen the reduction in pH value by reacting with H⁺. During decomposition, ozone generated more hydroxyl radicals at higher pH and the degradation rate of inorganic pollutants increased [32,33]. Fig. 3 shows the effect of temperature on metal removal efficiency. For Cu, Ni, and Cr the maximum removal was attained at 60 min on 40°C which was 83%, 80%, and 79%. Between all three metals, Cu has a high removal efficiency than Ni and Cr.

### 3.3. Effect of coagulation and flocculation on heavy metal removal

The removal efficiency of aluminum sulfate for nickel and chromium was determined at different doses, that is, 70, 80, 90, 100, and 110 mg/L (Fig. 4). Maximum treatment efficiency was observed at 90 mg/L coagulant dose. At this optimum dose, the concentration of Ni in the water sample was 4.87 mg/L and the concentration of Cr was 11.58 mg/L, which accounts for an efficiency of 82% and 81% for Ni and Cr, respectively. At the optimum dose, flocs of larger sizes were formed and settled down rapidly in the wastewater as compared to other samples. In other samples, flocs formed were comparatively smaller and so they mostly remain suspended and settled down very slowly. It was noted that, with the increase in coagulant concentration, the heavy metals removal rate increased but after 90 mg/L a reverse trend was observed with a further increase in coagulant concentration. According to a study conducted by Daud et al. [34], the removal efficiency was negatively impacted at low and high doses of coagulant. Initially, the removal rate of contaminants increased with the increase in the dose of aluminum sulfate from 120 to 200 mg/L. After the optimum dose of coagulant is reached, colloidal particles

![Fig. 1. Removal efficiency of ozone for nickel (Ni), chromium (Cr), and copper (Cu) containing wastewater.](image1)

![Fig. 2. Change in pH during ozone treatment.](image2)
are re-stabilized by the formation of positive charges and thus are difficult to remove, and consequently the removal efficiency declines [35]. Fig. 5 depicted the impact of polymer addition on Ni and Cr removal efficiency. It can be observed that the removal efficiency of the heavy metals after the addition of non-ionic polyacrylamide as polymer increased. The optimum dose of polymer is 100 mg/L for the removal of Ni and Cr. Removal efficiency of Ni and Cr reached 98% and 99% after the addition of 100 mg/L of polymer dose. The settling time was greatly reduced, and floc size was also increased in comparison to the treatment with the only coagulant. The treatment of wastewater is usually enhanced by adding polymers to coagulants. In some studies, polymers are also used as primary coagulants [36]. It is easy and safe to handle biodegrade polymers as compared to chemical coagulants [37,38]. The second coagulant was ferrous sulfate for heavy metal removal. The dose of the coagulant was varied from 100 to 600 mg/L and the removal efficiency at each dose was determined (Fig. 6). The optimum dose was evaluated to be 400 mg/L. At this dose, an 87% and 89% decrease in the concentration of Ni and Cr was achieved, respectively. There is a gradual decrease in the removal efficiency of both the metals with an increase in ferrous sulfate dose up to 600 mg/L. The settling of precipitates and agglomeration of flocs enhances with an increased dose of flocculent until the optimum

Fig. 3. Temperature effect on percentage removal efficiency (%) of Cu, Ni, and Cr.

Fig. 4. Percentage removal efficiency of aluminum sulfate for nickel (Ni) and chromium (Cr) at different doses.

Fig. 5. Percentage removal efficiency of aluminum sulfate (90 mg/L) with polymer (non-ion acrylamide) for nickel (Ni) and chromium (Cr).
Once the optimum dose of the coagulant is reached, further addition of ferrous sulfate in the wastewater interrupted, particles scattered and did not settle down easily. Non-ionic polyacrylamide was used as a polymer to aid the coagulation process. The dose of the polymer was varied from 0 to 100 mg/L in combination with the optimum dose of ferrous sulfate and the removal efficiency was calculated to evaluate the optimum dose of the polymer (Fig. 7). It can be comprehended from Fig. 8 that with the addition of 85 mg/L of polymer, the maximum removal efficiency was achieved, that is, 94% for Ni and 95% for Cr. In addition to aluminum sulfate and ferrous sulfate, ferric chloride was also used as a coagulant for heavy metal removal. The relative decrease in the concentration of Ni and Cr in wastewater at different doses of the coagulant is shown in Fig. 9. The dose of ferric chloride was varied from 50 to 300 mg/L and the optimum dose of ferric chloride was found at 200 mg/L. At the optimum dose, 76% and 83% decreased in Ni and Cr were achieved. The effect of polymer addition with an optimum dose of ferric chloride on metal removal is shown in Fig. 10. The removal efficiency was enhanced up to 94% for Ni with the use of 65 mg/L of polymer and for Cr, it reached up to 94% with the use of 45 mg/L of polymer. The removal efficiency showed a decline with the use of 100 mg/L of polymer with an optimum dose of ferric chloride. According to the present study, it was obvious that polymer addition to ferric chloride enhanced the coagulation process even at various polymer doses. The change in pH was observed during coagulation. The flocs strength was higher at pH 4 with re-growth.
capability in ferrous chloride polymer. Approximately the same results were also stated by Cao et al. [39].

It can be concluded from the comparison between ozonation and physicochemical treatment of electroplating wastewater that the latter is more effective in terms of heavy metal removal. For the ozone treatment, removal efficiencies of up to 42%, 27%, and 78% were achieved for Ni, Cr, and Cu, respectively. Whereas, in the case of coagulation, different coagulants used (like alum, ferrous sulfate, and ferric chloride) to achieve higher removal efficiencies individually as well as with non-ionic polyacrylamide. Aluminum sulfate was proved to be the best coagulant at the optimum dose of 90 mg/L with polymer addition of 100 mg/L to remove the Ni and Cr from electroplating wastewater. The removal efficiency was 98% and 99% for Ni and Cr, respectively. The inefficiency of ozone treatment can be attributed to the production of hydroxyl ions which bind with the effluent cationic ions and precipitate the metal as metal hydroxyls.

4. Conclusion

- It is concluded that the concentration of heavy metals from electroplating wastewater were found to be in the following order: Cr > Ni > Cu > Cd. To reduce the concentration of the following parameters, different processes were further evaluated and compared.
- Ozonation oxidizes the metals and its removal efficiency in Ni was up to 42 and in Cr 26%, respectively.
- In the coagulation process, the aluminum sulfate presented better performance. The removal efficiency of Cr was more than Ni (i.e., 99% and 98%, respectively), by the addition of 90 mg/L of aluminum sulfate and 100 mg/L of non-ionic polyacrylamide.
- Coagulation and flocculation proved to be more effective methods for the treatment of electroplating wastewater as compared to ozone oxidation. This study could pave the way toward enhancing the understandings of wastewater treatment systems.

References


