

Lecture Note

Comparing Chemical Coagulation and Electrocoagulation on removal efficiency of Chromium (VI) from Galvanic Effluents

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Abstract

Hexavalent chromium is a very toxic heavy metal moiety occurring in various industrial wastewaters, such as electroplating, anodizing, tanning dyeing effluents. Industrial effluents may contain hundreds mg/L of Cr(VI), whereas the upper allowed limit for effluent discharge to aquatic systems is 0.5 mg/L. In the present study, the removal of chromium from real electroplating effluents is presented using the chemical coagulation with addition of iron sulfate coagulant and the electrocoagulation process with iron electrodes. The optimal affecting parameters for the chemical coagulation process were found to be solution pH 11 and coagulant dose 500 mg/L, whereas for electrocoagulation pH 11 and applied current density 15 mA/cm². Both processes achieved a rapid and effective chromium removal of over 99.9 % with the electrochemical process being superior in terms of total operational costs.

Keywords: chemical coagulation; electrocoagulation; hexavalent chromium; ferrous sulfate; iron electrodes.

1. Introduction

Contamination of the environment with chromium originates from various industrial activities, such as metallurgical, anodizing, dyeing, tanning and dyeing plants. The oxidation state of the metal determines its toxicity. Hexavalent chromium is 100 times more toxic than trivalent. Industrial effluents usually contain 10 to 500 mg/L Cr (VI) that according to international environmental rules must be set at permissible levels before being discharged into the environment. The upper permitted levels of chromium are 0.5 mg/L for effluent discharge and 0.01 mg/L for drinking water respectively.

Various treatment methods for chromium removal have been proposed, such as chemical precipitation-coagulation-flocculation [1-3], adsorption [4], ion exchange [5] and electrochemical methods: electro dialysis-electrodeionization [6] and electrocoagulation [7-10]. Martin-Dominguez *et al.* [1] treated aquifer water with an initial total chromium concentration of 19.0 mg/L using iron as coagulation agent, followed by flocculation, sedimentation and sand-filtration steps and achieved more than 99% removal of Cr and a residual concentration of <0.05 mg/L. Qin *et al.* [2] tested for removal of Cr(VI) from contaminated groundwater in a flow-through pilot-scale system by reduction of Cr(VI) to Cr(III) with ferrous sulfate followed by coagulation and filtration leading to reduction of the influent Cr(VI) concentrations of 100 µg/L to very low concentrations < 5 µg/L. Complete reduction of Cr(VI) to Cr(III) was accomplished with Fe(II) doses of 10-50 times the Cr(VI) concentration. Stylianou *et al.* [3] investigated the reduction of Cr(VI) in pipe flocculation reactors using a molar ratio Fe(II)/Cr(VI) of around 3 leading to a reduction of Cr(VI) below 10 µg/L from an initial concentration of 300 µg/L.

Altun *et al.* [4] investigated the removal of Cr(VI) ions from aqueous solutions by adsorption on bio-chars produced by the pyrolysis of walnut shells at 450 °C (BC450) and the co-pyrolysis of walnut shells and 20 wt% tar sand (BCTS20) at the same temperature, where the Cr(VI) removal percentages under optimal conditions were 80.47 and 95.69% for BC450 and BCTS20, respectively. Meshram *et al.* [5] tested to removal of Cr(VI) from a model as well as from the untreated chromite mine effluent samples using the strong basic anion exchange resins, Amberlite IRA 400 and IRA 900. For an initial concentration of 50 ppm Cr(VI), IRA 400 was found to adsorb Cr(VI) completely in less than 6 min of contact time and was efficient in a larger range of pH (1–6), whereas IRA 900 was able to remediate 97% Cr(VI) in the pH range 4.5–5 in less than 10 min.

Dharnaik & Ghosh [6] used a laboratory-scale plate and frame-type electrochemical ion-exchange cell for removal of hexavalent chromium from synthetic wastewater containing 5 mg/l Cr(VI) under varying applied voltages. Up to 99% of chromium removal was noticed in the electrodeionization cell containing fresh resin at applied voltages of 10 V and higher. Akbal & Camci [7] tested the removal of heavy metals, Cu, Cr, Ni from metal plating wastewater by electrocoagulation and chemical coagulation. Chemical coagulation was performed using both, aluminum sulfate or ferric chloride, whereas electrocoagulation was done in an electrolytic cell using aluminum and iron electrodes. By chemical coagulation, Cu-, Cr-, and Ni-removal of 99.9% was achieved with aluminum sulfate and ferric chloride dosages of 500, 1000, and 2000 mg L⁻¹, respectively. Electrocoagulation with iron electrodes at a current density of 10 mA cm⁻², electroprocessing time of 20 min, and pH 3.0 resulted in 99.9% Cu-, 99.9% Cr-, and 98% Ni-removal.

In our previous work [8] we investigated the removal of hexavalent chromium from synthetic aqueous solutions and actual industrial electroplating wastewater with initial chromium concentrations of 200 – 800 mg/L by

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electrocoagulation with iron electrodes. Results revealed that best removal percentage was achieved at a current density 40 mA/cm in 50 minutes of electroprocessing time. In our other previous work [9] we proposed an electrocoagulation process powered by photovoltaic solar energy which was capable of reducing the initial Cr(VI) concentration from the initial value of 96 mg/L to less than the permissible limit and achieving a removal percentage of over 99%. El-Taweel *et al.* [10] experimented electrocoagulation with a new anode design consisting of hex nuts connected with a thin rode of iron and found as optimum conditions for hexavalent chromium removal, 100 mg of Cr(VI)/l, 0.55 A, 1.5 g of sodium chloride and pH 1.

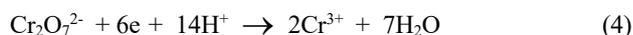
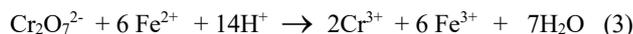
Chemical coagulation is a phenomenon where the dispersed charged colloidal particles of pollutants are neutralized by the highly and oppositely charged coagulant particles resulting in the formation of larger agglomerates and their final precipitation. Coagulation-flocculation is based on the reduction of the particles net surface charge and the elimination of their electric double-layer, which is caused by the addition of the well known coagulants, such as FeCl₃, Al₂(SO₄)₃ or organic polyelectrolytes.

A new alternative way to conventional chemical coagulation is the electrochemical coagulation or electrocoagulation, in which the coagulants Fe(OH)₃ and Al(OH)₃ are not added to the treated solution but are generated locally by electrodisolution of a corrodible anode made of iron or aluminum.

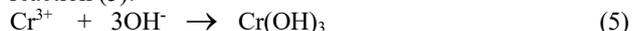
When iron anodes are used, the anodically produced Fe²⁺ and Fe³⁺ ions are combined with the cathodically produced OH⁻ ions forming the coagulants Fe(OH)₂ and Fe(OH)₃ according to reactions (1) and (2):



During the electrocoagulation process the hexavalent Cr(VI) ions are reduced to trivalent Cr(III) ions in two ways: a) chemically by reduction with the Fe²⁺ ions and b) electrochemically by reduction at the cathode according to reactions (3) and (4) respectively:



The generated Cr³⁺ ions react with the generated OH⁻ ions forming the insoluble precipitate Cr(OH)₃ according to reaction (5):



As far as we are aware, only few studies appear in literature combining the chemical and electrochemical coagulation and comparing their effectiveness in reducing the chromium concentration from wastewaters. In the present work, the removal of toxic Cr(VI) ions from real aqueous chromium wastes is studied by both, the conventional chemical coagulation and electrocoagulation. The parameters influencing the effectiveness of the two methods, such as pH, coagulant dose, chromium concentration, current density, and electrolysis time, are investigated and determined. The two methods are compared and evaluated.

2. Methodology

2.1 Reagents

All reagents, FeCl₃·6H₂O, NaOH, HCl, NaCl are of purity grade (Merck). The pH of the wastewater is adjusted by addition of appropriate amounts of 0.1 NaOH and 0.1M HCl solutions. The real wastewater sample was received from an electroplating unit located in Northern Greece. Its main characteristics are listed in Table 1.

Table 1. Main characteristics of treated real electroplating wastewater sample.

pH	4.1
Conductivity (μS/cm)	1524.0
Cr (VI) (mg/L)	300.0

2.2 Chemical coagulation process

Chemical coagulation experiments were carried out using the jar testing technique. The ferric chloride coagulant solution was prepared by dissolving a similar amount of FeCl₃·6H₂O in deionized water (30 g/L). The calculated volume of the coagulant solution is added to 200 ml of wastewater under rapid stirring at 200 rpm for 5 minutes. Then a slower stirring at 60 rpm was followed for another 25 minutes. Afterwards, the reaction mixture was allowed to stand for 60 minutes and finally was filtered out with polytrifluoroethylene filter paper (Whatman 0.45 μm) and the chromium concentration was determined in the filtrate.

2.3 Electrocoagulation procedure

The electrocoagulation experiments were carried out in a 500 mL cylindrical electrochemical cell with a volume of 200 mL of treated wastewater and stirring at 200 rpm. Three iron plates in parallel (one central cathode and two outer anodes) were used as electrodes, immersed to 5 cm in the treated solution with dimensions of 5 x 5 x 0.3 cm, a surface area of 25 cm and a distance of 1 cm between them. Every 10 minutes of electrolysis time, 2 ml samples are taken from the treated solution, filtered through filter paper (Whatman 0.45 μm) and carried for analysis.

2.4 Instruments

The DC power supply Agilent (E3612A, USA) served to provide constant measurements of current and voltage. Conductivity measurements were made with the conductometer (inoLab). The solution pH and temperature were measured with the pH-meter (Hana HI8314) comprising a temperature sensor. Atomic Absorption Spectroscopy (Perkin Elmer 5100) was used for determination of the chromium concentration.

3. Results and Discussion

3.1 Chromium removal by chemical coagulation

3.1.1 Influence of pH on chemical coagulation

The solution pH is one of the most important parameters that determine the effectiveness of the chemical coagulation process. To find the optimum pH value the chemical coagulation treatment was tested with initial pH values ranging from 3 to 11. Wastewater samples of same parameters of volume, initial chromium concentration, coagulant dose, operation time and different initial pH values were placed in the jar testing apparatus and after the coagulation performance the chromium concentration was analyzed. Figure 1 illustrates the effect of pH on chromium removal

during the chemical coagulation of the wastewater with the FeCl_3 coagulant.

Chromium removal is increased by increasing pH, giving optimum removal efficiency at alkaline $\text{pH} = 11$. For pH values 3 to 11 and 400 mg/L coagulant concentration, chromium removal efficiency ranges from 34.6 to 89.6%, respectively.

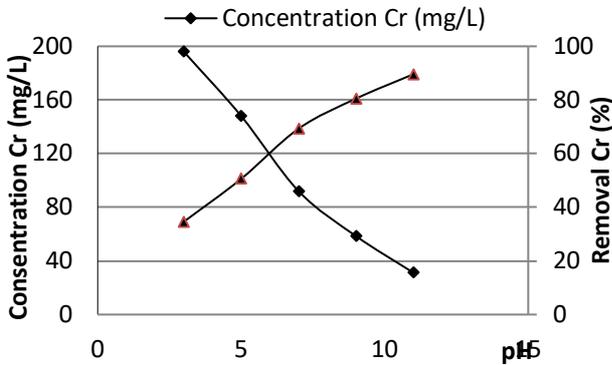


Fig. 1. Residual chromium concentration and removal percentage versus solution pH during chemical coagulation.

3.1.2 Effect of coagulant concentration on chemical coagulation

To find the optimum coagulant concentration, the wastewater samples were treated with various coagulant concentrations ranging from 100 to 600 mg/L, while keeping constant all other parameters, such as the investigated optimum initial pH 11, volume, initial chromium concentration and operation time. Figure 2 illustrates the effect of the concentration of the added ferric chloride coagulant on chemical coagulation to remove chromium from the treated electroplating wastewater.

The removal efficiency of chromium increases with increasing dose of coagulant. The percent removal efficiency of chromium is 34.9, 72.8 and 89.6 % for 100, 200 and 400 mg/L coagulant doses, respectively. Almost complete removal of chromium by 99.9% is achieved at coagulant doses of 500 mg/L or more. Our findings are in good agreement with the findings of Akbal & Camci [7].

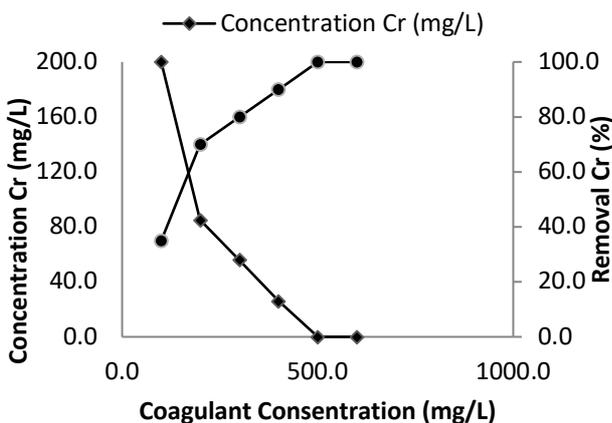


Fig. 2. Residual chromium concentration and removal percentage versus coagulant concentration during chemical coagulation.

3.2 Chromium removal by electrocoagulation

3.2.1 Influence of pH on electrocoagulation

As is known, the initial solution pH is crucial for the efficiency of electrocoagulation. For initial pH values < 7 , the observed increase in pH is due to the release of hydrogen and the formation of OH^- ions at the cathode. In an alkaline

environment ($\text{pH} > 8$) the final pH does not change markedly since the OH^- anions generated at the cathode combine with the generated Fe^{2+} and Fe^{3+} cations forming the corresponding necessary coagulant species $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ according to the reactions (3) and (4).

In addition, OH^- ions are coupled to the produced Cr^{3+} ions forming the insoluble $\text{Cr}(\text{OH})_3$ according to reaction (5). To demonstrate the influence of the initial pH on the electrocoagulation performance, experiments were carried out using a wastewater sample containing 300 mg/L Cr(VI) in the pH range 3-11. As shown in Figure 3, after a 20 min long electroprocessing time at the constant current density of 10 mA/cm^2 , the removal of Cr(VI) increased significantly with increasing pH throughout the pH range of 3-11. In our previous works [8, 9] we investigated that in the acidic environment ($\text{pH} < 3$) the removal of Cr(VI) is significantly reduced due to a decrease in the oxidation state of Fe^{3+} to Fe^{2+} . It is well known that Fe^{3+} ions favor the coagulation/flocculation process much more than Fe^{2+} ions. Sharma *et al.*, 2020 [11] reported that the slightly alkaline pH 9.5 was the best for removal of chromium (91.7%) and lead (91.3%) from electroplating effluents by electrocoagulation with iron electrodes.

Based on our experimental results, as illustrated in Figure 3, the electrochemical coagulation process showed at pH 11 a superior and almost complete removal of Cr(VI) ions ($> 99.9\%$) compared to conventional chemical coagulation (89.6%). This can be explained by the contribution of reactions (3), (4) and (5) to further significant reduction of Cr(VI) to Cr(III) ions and additional elimination of chromium by precipitation as insoluble $\text{Cr}(\text{OH})_3$.

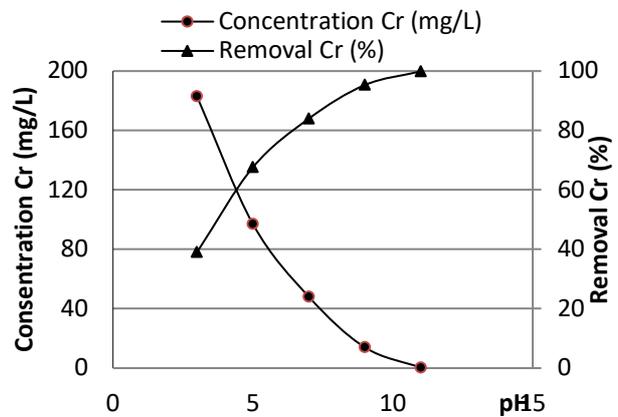


Fig. 3. Residual chromium concentration and removal percentage versus solution pH during electrocoagulation.

3.2.2 Influence of current density on electrocoagulation

As well known, the applied current density defines the dosage rate and particle size of the electrochemically generated coagulating agent and additionally also the rate of the hydrogen bubble production leading to a faster removal of pollutants. Koshla *et al.* [12] studied the large number of factors, such as electrode material, electrode surface/morphological properties, pH and current density affecting the size distribution of the gas bubble, which are generated by electrolysis and their importance on electroflotation and electrocoagulation processes.

Measurements were conducted at the current densities of 5, 10 and 15 mA/cm^2 , with the initial Cr(VI) concentration of 300 mg/L and the initial actual wastewater $\text{pH} = 4.1$.

According to Figure 4, the chromium removal efficiency increases, as anticipated, with increasing applied current density. The hexavalent chromium ions, Cr(VI), were first

reduced to trivalent Cr^{3+} ions according to reactions (3) and (4), which then were joined to the produced OH^- ions and precipitated as insoluble $\text{Cr}(\text{OH})_3$ as stated with reaction (5) or were adsorbed in the particles of the coagulating agents $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$.

For the applied current densities 5, 10 and 15 mA/cm^2 , the initial $\text{Cr}(\text{VI})$ concentration of 300 mg/L was reduced below the permissible limits (0.5 mg/L) in 35, 20, and 10 minutes, respectively. Similar findings of over 99 % chromium (VI) removal by electrocoagulation with iron electrodes have been reported by other researchers. Akbal & Camci [7] and Cheballah *et al.* [13] announced removal percentages of 99.9 and 100% respectively for hexavalent chromium with iron electrodes.

3.4 Comparison of chemical coagulation and electrocoagulation

The efficiencies of the two studied coagulation methods were compared on the basis of coagulant consumption, electricity consumption, electrode mass loss, the amount of sludge produced and the processing time required.

Sections 3.1.2 and 3.2.2 show that for the complete removal of chromium from the treated wastewater volume of 1 m^3 with the initial $\text{Cr}(\text{VI})$ concentration of 300 mg/L during the chemical coagulation process 0.9 kg of coagulant $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 30 minutes processing time are required, whereas 0.66 Kg of sludge is produced. The electrocoagulation process for the same wastewater volume of same chromium concentration requires 0.651 Kg of iron anode, 0.36 kWh of electricity whereas 1.23 Kg of sludge is produced.

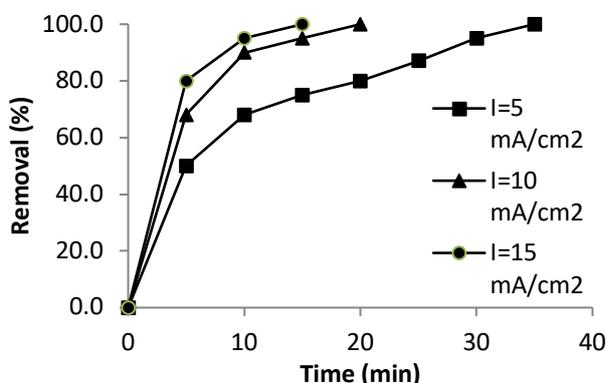


Fig. 4. Chromium removal percentage versus time at various current densities.

The total costs for chemical and electrochemical coagulation are estimated at 1.03 $\text{€}/\text{m}^3$ and 0.69 $\text{€}/\text{m}^3$ of treated wastewater respectively.

Both methods are therefore effective in removing hexavalent chromium from industrial electroplating effluents with the electrochemical process being advantageous over the chemical in terms of total costs.

Similar results of economic estimation have been reported also by other researchers. Akbal & Camci [7] investigated the total costs of 0.859 $\text{US}\$/\text{m}^3$ for chemical coagulation and 0.590 $\text{US}\$/\text{m}^3$ for electrocoagulation respectively when

treating electroplating effluents of 45 mg/L Cu, 44.5 mg/L Cr and 394 mg/L Ni. Aygun *et al.* [14] reported that the operating costs during the electrocoagulation treatment of dye house wastewater were approximately 2% for energy, 28% for electrode and 70% for chemical consumption.

Another aspect that should be taken into consideration is the fact that during the electrochemical treatment a considerable amount of electrolytic hydrogen gas is produced at the cathode due to electrochemical water splitting, which under suitable cell configuration could be collected and stored. The corresponding energy recovery through the produced hydrogen gas is given from next equation (1):

$$E_{H_2} = m_{H_2} \times 122 \text{ kJ/g}_{H_2} \quad (1)$$

where m is the mass of produced hydrogen and 122 kJ is the specific heat per g of hydrogen.

The amount of produced hydrogen and, therefore, the corresponding associated energy recovery can be calculated from Faraday's law of electrolysis and can amount to about 10-25 % of the needed electrical energy for conducting the electrochemical treatment. It depends mainly on the pollutant concentration of treated wastewater, the electrolysis time and the applied current density. In our previous work [15] we achieved, during the continuous electrocoagulation treatment of nickel phthalocyanine dye at the inlet flow rate 60 mL/min and current density 10 mA/cm^2 , about 175 L hydrogen gas per m^3 of treated wastewater, which corresponds to 12.5 % of energy recovery. Deghles & Kurt [16] reported energy harvesting of 15 and 16% during electrocoagulation of tannery wastewater using iron and aluminum electrodes respectively.

Thus, the electrochemical coagulation process offers a double useful objective, namely wastewater remediation and energy recovery.

4. Conclusion

The present study investigated the treatment of actual electroplating wastewater for removal of hexavalent chromium by chemical and electrochemical coagulation. The chemical treatment of a wastewater containing an initial concentration 300 mg/L Cr (VI) resulted in 99.9% effective removal of the metal at a coagulant dose of 500 mg/L $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 30 minutes.

The electrochemical treatment using iron electrodes achieved a rapid and effective 99.9% reduction of chromium with an applied current density of 10 mA/cm^2 and an electrolysis time of 20 minutes. Both methods of coagulation are effective for removing hexavalent chromium from industrial wastewaters, such as galvanic effluents. The electrochemical process has proved to be more advantageous over the chemical in terms of overall costs and effectiveness.

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