

CHROMIUM REMOVAL FROM TANNERY WASTEWATER THROUGH ELECTROCOAGULATION

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ABSTRACT

The paper has focused on the chromium removal from tannery wastewater through electrocoagulation. The zinc (13.20 cm x 5.30 cm) and copper (13.20 cm x 5.30 cm) plates were used as electrodes for the electrocoagulation process. The effectiveness of the electrocoagulation for chromium removal efficiency was examined investigating various parameters: applied voltage, time, and current density. In the batch experiment, 500 mL chromium-containing wastewater was used for electrocoagulation. Chromium content in the raw wastewater was 340.1 mg/L and after treatment at optimized conditions, chromium content was 6.9 mg/L. The chromium removal efficiency was obtained 98.0%. The reduction of biochemical oxygen demand (BOD) was 64.6%. Although total dissolved solids (TDS) was slightly increased. The increment of current density causes forming Zinc hydroxide causes damage to electrodes. The electrocoagulation is an effective technique to remove chromium from the wastewater especially tannery wastewater.

Keywords: Tannery effluent, Chromium, Electrocoagulation, Electrodes, Current density.

1. INTRODUCTION

Water pollution by heavy metals, especially chromium has sparked much concern to societies and regulatory authorities around the world. Due to wide usage of chromium by different industries such as metal plating, paints and pigments, leather tanning, textile dyeing, printing inks and wood preservation, huge amounts of wastewater containing chromium are discharged into the environment.

Tannery effluents are ranked as the highest pollutants among all industrial wastes. They are especially large contributors to chromium pollution (Belay, 2010). In tannery, basic chromium sulfate is used widely as tanning agent (Fahim, Barsoumb, Eid & Khalil, 2006). On average, 60-70% of total chromium salts react with the hide protein and the rest of 30-40% of the chromium remains in the solid and liquid phases (Ismailia, Mesdaghinia & Vazirinejad, 2005). Tannery wastewater decreases the quality of water bodies into which they are discharged. Disposition of tanning effluents e.g., chromium into the environment creates inauspicious outcomes by modifying the normal physiochemical properties of soil and water (Sarker, Basak, & Islam, 2013). Chromium contamination of soil, surface water, groundwater, and air under specific conditions is demonstrated e.g., trivalent chromium is harmful to aquatic life and fish at excess level (>5.0 mg/L) (Overah, 2011). Chromium is not biodegradable that tends to accumulate in living organisms, causing serious diseases and disorders (Mohan, Kunwar, & Vinod, 2006). It has the toxic effect on humans at high doses. Trivalent chromium form is an essential trace element when present in micro level (Dahbi, Azzi, Saib, Guardia, Faure, & Durand, 2002). Chromium is discharged into the environment into two forms: trivalent and hexavalent. In contrast, the toxicity of tetravalent chromium is relatively low and in its trace amounts, it is not a problem for the environment (El-Taweel, Nassef, Elkheriany, & Sayed, 2015). On the other hand, hexavalent chromium form is 500 times more toxic than the trivalent chromium (Kowalski, 1994).

Various techniques have been employed for the treatment of heavy metals, including precipitation, adsorption, ion exchange and reverse osmosis. Among this precipitation is most commonly used in industries (Pachimatla, Pushkara, & Maheshwaria, 2014). To get more effective treatment electrocoagulation is considered to be used (Khalaf, Mubarak, & Nosier, 2016). In spite of having electrocoagulation not to be a new technology which had been known from 19th centuries, it hasn't been widely applied because of relatively large capital investment, expensive electricity requirement. However, electrochemical technologies have turned back since it is eco-friendly technology (Rajkumar & Palanivelu, 2004).

Electrocoagulation (EC) is one of the methods, which employs the direct current to remove pollutants (Akbal & Camcı, 2011). In recent decades, this method has been developed to be used for the treatment of industrial wastewater comprising metals. In this method, an electric current passes through two electrode plates and induces metal oxidation in its cation. At the same time, water is reduced to hydrogen gas and hydroxide ion. In this way, EC process produces metal cation through the electrochemical method and by using consumable anodes (Arroyo, Pérez-Herranz, Montanés, García-Antón, & Guinón, 2009). The Hydrolysis of cation within water forms a hydroxide with dominant species suited to pH solution. In General, mutual reactions between the species occur in a different manner within the solution and consequently lead to the removal of the pollutants.

In this study, an investigation was made to remove chromium from the tannery wastewater through electrocoagulation. The performance of electrocoagulation process was determined to investigate different parameters: applied voltage, current, and time using zinc (Zn) and copper (Cu) electrodes.

2. MATERIALS AND METHODOLOGY

2.1 Sample Collection

Chrome tanning wastewater was collected from the tannery at Jessore, Bangladesh. The wastewater containing chromium sample was collected in a plastic container, pre-washed with diluted nitric acid, and immediately transported to the laboratory for experimentation.

2.2 Reagents

Reagents: nitric acid (Merck KGaA, Germany), sulphuric acid (Merck KGaA, Germany), perchloric acid (Merck, India), N-phenyl anthranilic acid (Merck, India), ferrous ammonium sulphate (Merck, India) and glass beads (Loba Chemie, India) were purchased from a local scientific store, Khulna, Bangladesh.

2.3 Characterization of chrome tanning wastewater

Physicochemical parameters of the untreated and treated spent chrome liquors: chromium content, total dissolved solids (TDS), total suspended solids (TSS), pH, electrical conductivity (EC), turbidity, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) in the chrome tanning wastewater was measured. All measurement was maintained in triplicate.

2.3.1 Determination of Chromium

Chromium content in the untreated spent chrome liquor and after treatment in the filtrate was performed by the titrimetric method by following the official methods of analysis of Society of Leather Technologist and Chemists (SLTC, 1996) official method of analysis (SLC 208). A 50 mL of sample was taken in 500 mL conical flask. Heating was started after mixing of 20 mL nitric acid and 20 mL of concentrated sulphuric acid & perchloric acid mixture. The funnel was placed in the mouth of the conical flask for refluxed and after complete digestion, with the acid mixture, the solution turned into red brick color. Extra 1 minute continued heating

and quickly brought down from the heating and cooled in a water bath. 100 mL distilled water and few glass beads were mixed with the solutions and boiled 10 minutes for chlorine removal. 10 mL of 30% concentrated sulphuric acid was added after cooling and took for titration with ferrous ammonium sulfate. 5-6 drops of N-Phynylanthralinic acid used as anindicator and end point detected by green color.

2.3.2 Determination of pH

pH was measured by the digital pH meter (UPH-314, UNILAB, USA). Before measuring pH, the meter was calibrated in the two points with standard solutions of pH 4.01 and pH 7.00, respectively.

2.3.3 Determination of TSS, TDS, EC, and turbidity

TSS and TDS of the chromium-containing wastewater and treated liquor were determined following APHA-2540D method. A well-mixed sample was filtered through a weighed standard filter paper and the residue retained on the filter was dried to a constant weight at 103-105°C. The increase in weight of the filter represents the total suspended solids. To obtain an estimate of total suspended solids, the difference between total dissolved solids and total solids was calculated. Electrical conductivity (EC) was measured by using the conductivity meter (CT-676, BOECO, Germany) and the turbidity was measured with a portable turbidity meter (Hach 2100Q, 2100Q, Germany).

2.3.4 Determination of BOD

Biochemical oxygen demand (BOD) was measured by APHA standard method 5210B (APHA, 2012). Dilution water was prepared by placing the desired volume of water in a bottle and phosphate buffer, magnesium sulfate, calcium chloride and ferric chloride solutions. pH was adjusted at 6.5 to 7.5 with sulphuric acid or sodium hydroxide solution. Sample volume 300 mL was filled in BOD bottle with enough dilution water thus insertion of stopper will remove air, leaving no bubbles. A blank sample (only diluted water) was also incubated as a rough check on the quality of diluted water and cleanliness of incubation bottle. Initial DO was measured with DO meter (DO-580, BOECO, Germany). BOD bottle was incubated at 20±1°C for 5 days. After 5 day incubation, final DO was determined and calculated as BOD.

2.4 Batch-wise electrocoagulation test

The schematic diagram of the electrocoagulation process is shown in Fig. 1. A zinc plate (13.20 cm × 5.30 cm) and copper plate (13.20 cm × 5.30 cm) were used as anode and cathode. In the batch experiment, 500 mL chromium-containing wastewater was used for electrocoagulation process where electrodes were immersed in the wastewater. Direct current (DC) was supplied and at different time interval 50 mL supernatant was taken for chromium measurement.

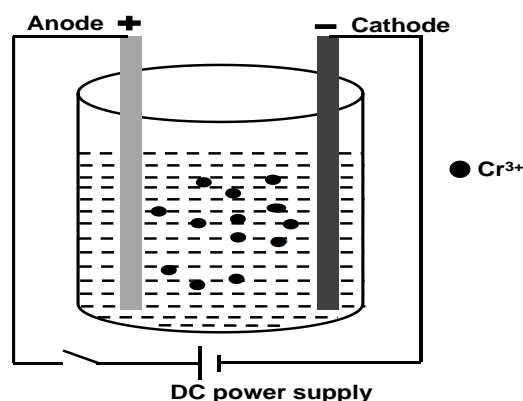
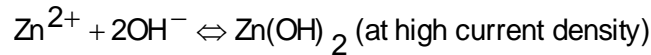
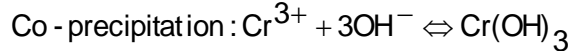
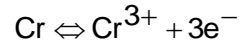
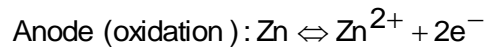
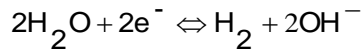


Figure 1: Schematic diagram for electrocoagulation process

Electrocoagulation process involves the generation of coagulants and form co-precipitation. Water is ionized by DC supply and produce hydroxyl radical and hydrogen gas. In the cell, the following reactions occur.



2.5 Process optimization

The electrocoagulation process was optimized to obtain maximum chromium removal efficiency. Tests were carried out to optimize the chromium removal parameters: applied voltage, time and the current density. The optimized conditions were established by investigating the chromium removal efficiency.

3. RESULTS AND DISCUSSION

3.1 Optimal Voltage

In the batch experiment, chromium removal efficiency was observed at different voltages: 6V, 9V, 12V, 15V and 18V by electrocoagulation. It is clear from the Fig. 1 that with increasing the applied voltage chromium removal efficiency was increased. At applied voltage 6 V, 9 V, and 12 V chromium removal efficiency was 57.2%, 58.7%, and 64.8%, respectively. It seems that with increasing the applied voltage upto 12 V, chromium removal efficiency was increased very slightly. But, at applied voltage 15 V, chromium removal efficiency was maximum (80.1%). Unfortunately, above applied voltage (>15 V), chromium removal efficiency was decreased (72.5%). Therefore, the applied voltage was selected 15V for chromium removal through electrocoagulation.

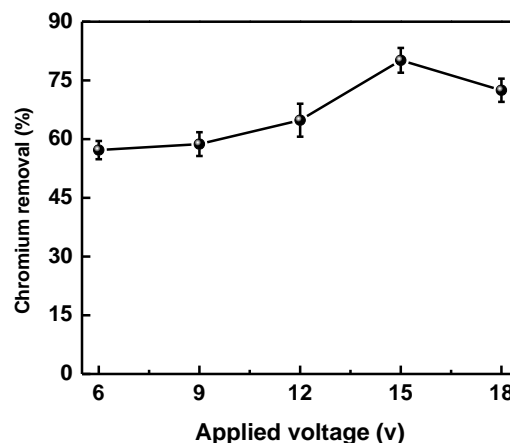


Figure 2: Effect of applied voltage on chromium removal efficiency

3.2 Optimal Current Density

In electrocoagulation, current density is one of the most important parameters. With applied several current density in the cell e. g., 0.07 mA/cm², 0.10 mA/cm², 0.17 mA/cm², 0.24 mA/cm², 0.36 mA/cm² and 0.46 mA/cm²; chromium removal efficiency was found 51.1%, 60.3%, 71.4%, 92.4%, 95.4%, and 93.9%, respectively. It is obvious from Fig. 2 that there was a good liner relationship between current density (0.07, 0.10, 0.17, 0.24 mA/cm²;

correlation coefficient $R^2=0.983$) and chromium removal efficiency. The chromium removal efficiency for the current densities 0.24 mA/cm², 0.36 mA/cm² and 0.46 mA/cm² was almost same (92.4%, 95.4%, and 93.9%).

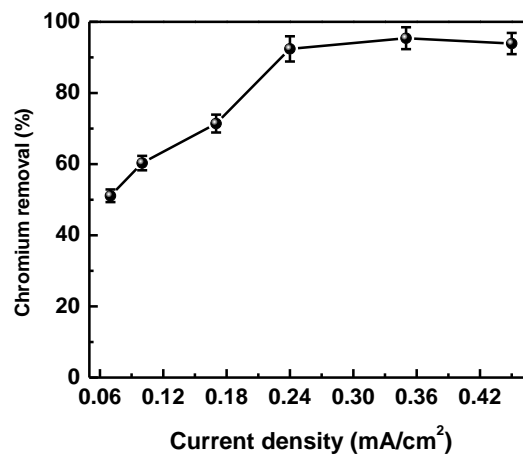


Figure 3: Effect of current density on chromium removal efficiency

At higher the current density e. g., 0.42 mA/cm² amount of co-precipitation forming of Zn(OH)₂ was so much. It is observed that with increasing the current density, the turbidity of wastewater was also increased. Thus, 0.36 mA/cm² considered the favorable current density for electrocoagulation technique.

3.3 Optimal Time

Time is one of the essential parameters for the removal of chromium from the tannery wastewater. In Fig. 3 represents the effect of time on chromium removal at different time interval as 6h, 12h, 18h, 24h, and 30h was observed at constant voltage and current density. Fig. 3 also indicates that chromium removal efficiency was gradually increased with increasing the process time. The removal efficiency for 6 h, 12 and 18 h was 27.77%, 63.37%, and 97.96%, respectively. After 18 h, chromium removal efficiency was decreased as the time was increased.

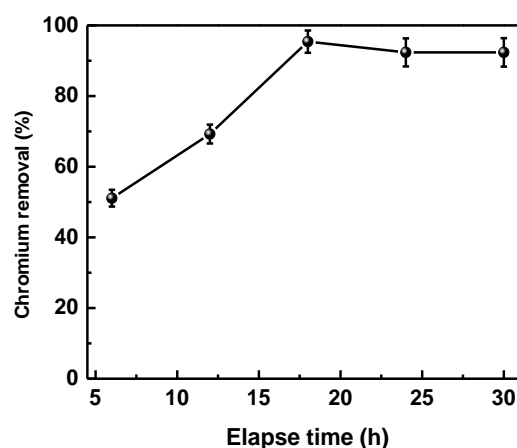


Figure 4: Effect of time on chromium removal efficiency

It may be the reason is that after 18 h, chromium removal efficiency was decreased because the coprecipitated Cr(OH)₃ dissolved and return to the aqueous phase. The chromium removal efficiency by this electrocoagulation was declined and simultaneously the

TDS was increased. Therefore, 18h was decided as the optimum time for chromium removal in this electrocoagulation process.

3.4 Removal Efficiency at Optimal Conditions

Considering all the parameters for electrocoagulation obtained data is presented in Table 1. The physicochemical parameters were obtained at optimized conditions: pH, TDS, BOD, chromium, turbidity, and EC were 7.0, 2756 g/L, 780 mg/L, 6.9 mg/L, 57 NTU and 8.7 mS, respectively.

Table 1: Data comparison between raw sample and treated sample

Parameters	Raw sample	Treated sample	ECR,1997
pH	4.8	7.0	6-9
TDS (g/L)	2248	2756	2100
BOD(mg/L)	2200	780	250
Cr (mg/L)	340.1	6.9	2.0
Turbidity (NTU)	233	57	-
Conductivity (mS)	7.5	8.7	-

The Table 1 shows that the TDS of the treated liquor was slightly increased and rest of the parameters were decreased as near to the discharged level. The reduction of BOD, chromium, and turbidity was 64.6%, 98.0%, and 75.5%, respectively.

4. CONCLUSION

In batch wise electrocoagulation process was effective to remove chromium from the tannery wastewater. Although total dissolved solids were slightly increased. The removal efficiency of chromium at optimized condition was 98.0%. The reduction of BOD and turbidity was 64.5% and 75.5%. The investigation indicates that it was an effective technique to remove chromium from the tannery wastewater.

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