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ORIGINAL RESEARCH ARTICLE

Treatment and Characterization of Chromium from Tannery Industry Effluents by Electrocoagulation Process Using Aluminum Electrode

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Abstract

The performance of electrocoagulation using Aluminum electrodes for the treatment of chromium from tannery effluent using fixed bed electrochemical batch reactor was studied. The efficiency evaluation of electrocoagulation in removing chromium metal from Amhara region real industrial tannery wastewater, collected from Bahirdar, Debrebrihan, and Haik was investigated. The treated and untreated samples were determined by inductively coupled plasma-optical emission spectrometry. The effect of operational parameters such as applied current density, initial pH, initial metal concentration, temperature and Voltage was studied. The results indicated that Cr removed in all experiments with high removal percentages. The optimal results were obtained, regarding both cost and electrocoagulation efficiency with initial pH 3, concentration = 40 mg/L, electrolysis time = 30 min, current density = 40 mA/cm^2 and temperature of 25°C favored chromium metal removal. The maximum removal percentages of chromium were 84.42% for Haik, 92.64% for Bahirdar and 94.90% for Debrebrihan. Hence, after the electrocoagulation process, chromium may be used again as a tanning agent in leather processing.

Keywords: Chromium, Electrocoagulation, Aluminum, Tannery effluent

Introduction

Tannery industries are common sources of notorious odor. While local populations are daily aware of the air pollution including local authorities, if not concerned about tanneries' liquid effluents which tend to be higher in organic and inorganic suspended solids content accompanied by propensities for high oxygen demand and containing potentially toxic metal salt residues. Hence, the community had been exposed to different health hazards like asthma and water related diseases (Belay, 2010; Navid *et al.*, 2018).

Chromium (VI) is released into the environment from various industries, such as the electroplating, metal finishing, tannery and fertilizer industries; for those tannery industries have a potential of environmental impact by their chemicals used in operations (Ramesh *et al.*, 2007). Two adopted methods for tanning of raw hide/skin were; vegetable tanning and chrome tanning. The production processes in a tannery are categorized into four namely; beam house operations, tanyard operations, post tanning operations and finishing operations (Yussif *et al.*, 2016).

Effluent treatment methods were classified into three; physical, chemical and biological processes. However, a host of very promising techniques based on electrochemical technology which was developed and existing ones improved that do not require chemical additions. These include electrocoagulation, electroflotation, electro decantation, and others. Simple electrocoagulation reactor is made up of one anode and one cathode (Fig. 1). When a potential is applied from an external power source, the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals (Mohammad *et al.,* 2004, Nassef, 2012).

Following reactions are carried out at different Electrodes:

Anode: $Al - 3e \rightarrow Al^{3+}$

Cathode: $H_2O - 1e \rightarrow OH^-$

Alkaline condition: $Al^{3+} + 3OH^- \rightarrow Al(OH)_3$

Acidic condition: $Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$

$$2H_2O - 4e \rightarrow O_2 + 4H^+$$

Al^{3+}(aq) and OH^- ions generated by electrode reactions at the anode and cathode respectively react to form various monomeric species such as $Al(OH)^{2+}$, $Al(OH)^+_2$, $Al_2(OH)^{4+}_2$, $Al(OH)^{4-}$, and polymeric species such as $Al_6(OH)^{3+}_{15}$, $Al_7(OH)^{4+}_{17}$, $Al_8(OH)^{4+}_{20}$, $Al_{13}O_4(OH)^{7+}_{24}$, $Al_{13}(OH)^{5+}_{34}$, which transform finally into $Al(OH)_3$ according to complex precipitation kinetics (Bazrafshan *et al.*, 2015).

The variety of raw materials, chemicals, processes and technological variations were applied to the processes affect the type and quantity of wastewater and the applied purification technologies like EC process has been recommendable. Consequently, characterization of Tannery effluents is of great importance for the treatment of tannery effluents and their ecological impact on surrounding environment (Meri *et al*., 2003). However, most tannery industry effluents studies on the impact and characterizations as well as treatment of industrial effluents were not assessed. Therefore, Treatment and characterization of chromium from tannery industry effluents by electrocoagulation process using aluminum electrode.

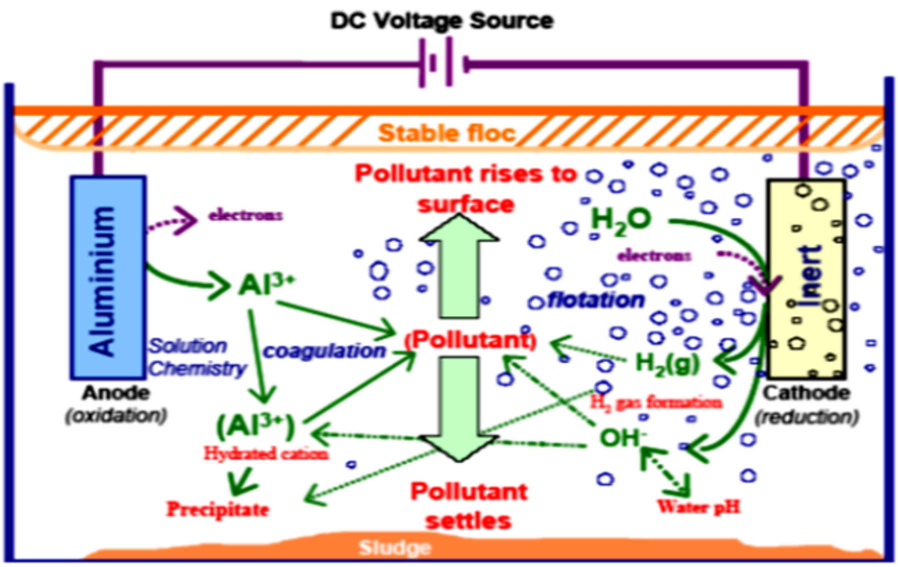

Figure 1. Eelectr chemical interactions occurring within an electrochemical reactor (Nassef, 2012).

Materials and methods

Sampling and Sample Collection

The study was conducted at the tannery industrial effluents of Bahir Dar, Haik and Debrebrihan Tannery industries in Amhara region. Representative effluent samples were collected from January to May, 2019, based on access, safety and potential sources of pollutions. The sample were transported by 1 L polyethylene bottles (APHA, 1999). The determination of chromium metal and characterization of aluminum electrode have been done. Samples for chromium metal analyses were fixed by adding 2–3 drops of nitric acid and stored at 4°C. The samples were characterized, analyzed and treated with the designed treatment technology in the University of Gondar and Addis Ababa Science and Technology University.

Electrocoagulation setup and characterization of sludge and electrodes

The experimental setup for the designed electrocoagulation (EC) process has done as shown Fig. 1. For each run a 0.6 L of wastewater effluent were mixed with 1 g of sodium chloride which is used as increasing electrical conductivities of the solution. The solutions were placed in to 1 L beaker. NaOH and HCl solutions were used to adjust pH. In separate two parallel plates with 2*30 cm dimension of aluminum electrodes were used and the plates are separated by a distance of 4 cm in EC technique. External power supply was applied through the different Al electrode systems using a DC power source equipped with digital ammeter and voltmeter is passed through the solution via the two electrodes during the different electrolysis running for optimization process. A 250 mL of the solution was taken at different time intervals in each run. During the EC process, the wastewater effluent in the beaker was mixed continuously with a 30 mm magnetic stirrer at the optimized 2000 rpm. Electrodes where rinsed with 5% hydrochloric acid followed by deionized water to avoid the electrode passivation. All runs were performed at room temperature.

Chemicals, reagents and standards

All chemicals used were analytical grade and used without further treatment. The chemicals used in this project work were sodium hydroxide (reagent grade, ≥ 98%, Blulux, India), concentrated hydrochloric acid (reagent grade, 35%, Blulux, India), and sodium chloride (AR grade, ≥ 99%). Standard solutions of heavy metal analyses were used for heavy metals analysis. Stock standard solutions of potassium dichromate ($K_2Cr_2O_7$) (Blulux, India) (1000 mg/mL) were used for the preparation of calibration curves for the determination of metals using ICP-OES. Morphology of electrodes was analyzed by Scanning Electron Microscope (SEM, SE DETECTOR R580) and X-Ray Diffraction (XRD). All the working solutions were prepared using distilled water except the cleaning of electrode with 0.1 M HCl solution.

Results and discussion

Optimization of pH on chromium removal

The removal efficiency of chromium was maximum at pH 3 (83.33%) (Fig. 2). When using aluminum electrodes, chromium removal increases during electrocoagulation while pH decreases. This is because, in acidic solution, Cr^{6+} ions are reduced to Cr^{3+} ions. Chromate has to be reduced before Cr is precipitated as hydroxide $Cr(OH)_3$ *(Calmano et al.*, 2008; Khairul *et al.*, 2016).

Optimization of electrolysis time on chromium removal

As electrolysis time increased from 10 to 30 min with a 10 min interval, the removal efficiency of hexavalent chromium was also increased.

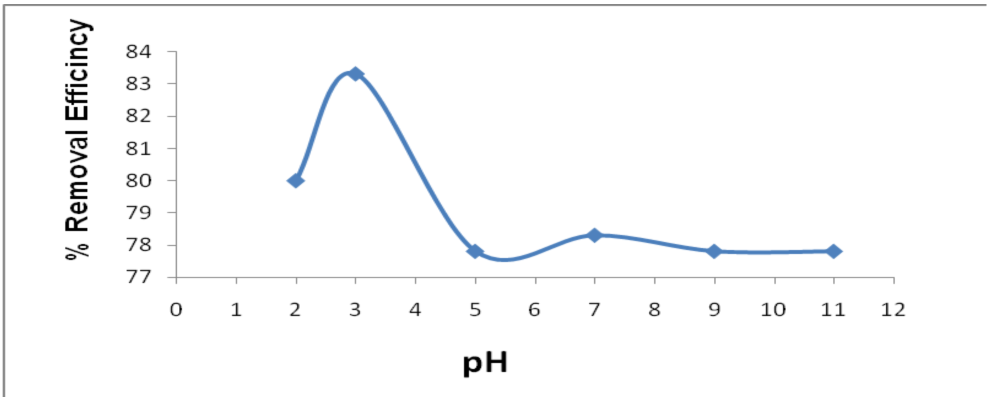

Figure 2. Effect of pH on the removal efficiency of 30 mg/L chromium through electro-coagulation for 30 min using voltage = 3V, current density = 20 mA/cm^2 and temperature = 25°C.

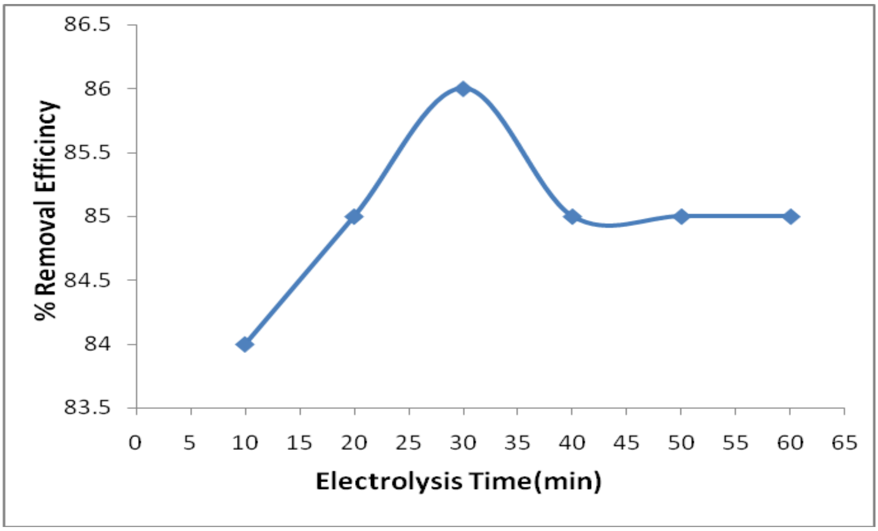

Figure 3. Effect of electrolysis time on the removal efficiency of 30 mg/L chromium at pH = 3, voltage = 3 V, current density = 20 mA/cm^2 and temperature = 25 °C.

with a percentage of 84 and 86%, respectively (Fig. 3). However, at additional time the removal efficiency scarcely decreased and it became constant at electrolysis time of above 40 min. Therefore, the optimum electrolysis time is 30 min which determines the rate of production of aluminum from aluminum electrode (Yehia *et al.*, 2015). The effluent removal efficiency is also a function of the electrolysis time. The pollutant removal efficiency increases with an increase in the electrolysis time. But, beyond the optimum electrolysis time, the effluent removal efficiency becomes constant (Yehia *et al.*, 2015). For an electrolysis time beyond the optimum electrolysis time, the effluent removal efficiency does not increase as sufficient numbers of flocs are available for the removal of the effluent (Yehia *et al.*, 2015). Cr^{6+} reduction from synthetic chromium solution could be under legal limits as long as treatment was between 20 and 60 min (Bazrafshan *et al.*,2015).

Optimization of current density on chromium removal

The current density is optimized at constant pH, electrolysis time and concentration using aluminum electrode. Regarding chromium removal using Al-Al electrode, this work demonstrated removal efficiency increased at 20mA/cm^2, 30mA/cm^{2}and 40 mA/cm^2 with 81.5%, 83.7% and 87.3%, respectively (Figure 4). However, increasing the current density above the optimum point (40 mA/cm^3) is not justified as most of the energy supplied would be dissipated into heating the reactor content and hence raising the temperature (Hamdan *et al.*, 2014). Current density is regarded as an important factor because it analyzes the coagulant dosage rate, bubble formation rate, size, and development of flocks, as they affect the efficiency of the EC process. The anode dissolution rate is directly proportional to the current density. However, an increase in current density beyond the optimal value has no effect on the contaminant removal efficiency (Samir *et al.*, 2016). According to Faraday's law, higher applied currents lead to greater production of ions, thereby enhancing the EC process (Gatsious *et al.*, 2015).

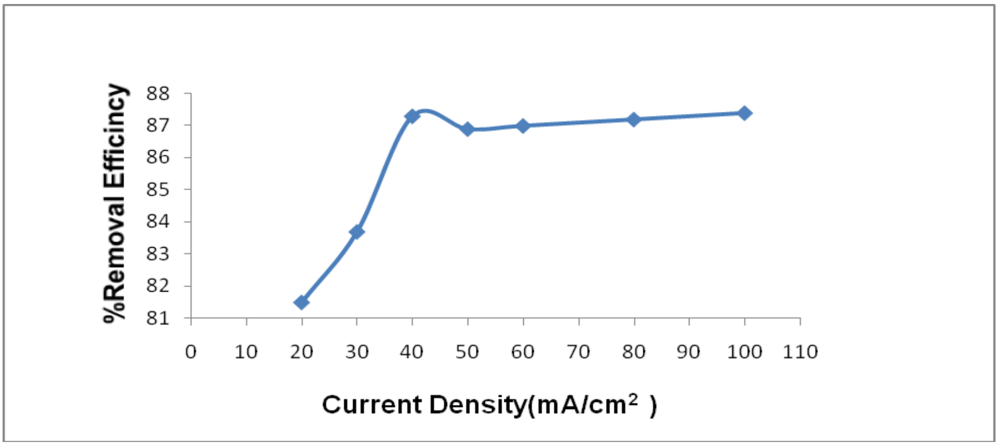

Figure 4. Effect of current density on the removal efficiency of 40 mg/L chromium through electrocoagulation for 30 min at pH 3 using voltage = 3 V and temperature = 25°C.

Optimization of voltage on chromium removal

As electrical consumption increased from 3 V and 5 V, the removal efficiency of hexavalent chromium also increased with a percentage of 84 and 85, respectively (Fig. 5). However, above 5 V electrical energy consumption the removal efficiency maintained constant. Therefore, theoptimum electrical energy consumption for this work is 5 V. It is clear that the major operating cost of the electrocoagulation process is associated with electrical energy during the process (Yehia *et al.*, 2015).

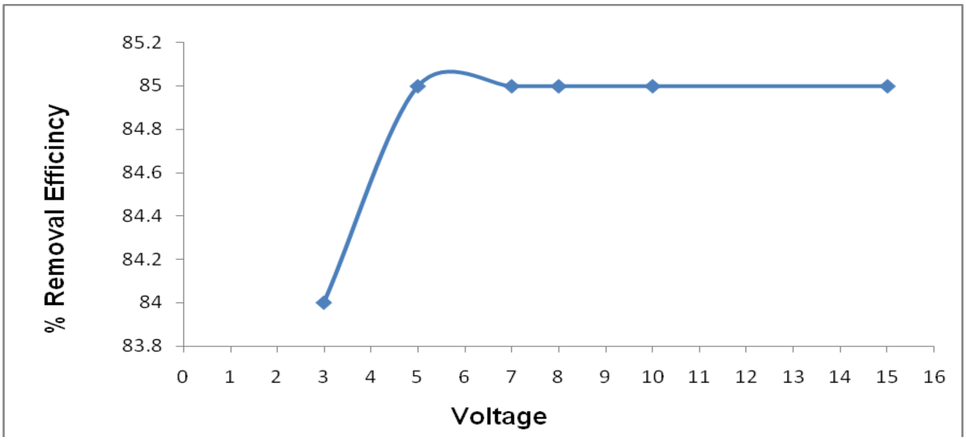

Figure 5. Effect of the applied voltage on the removal efficiency of 40 mg/L chromium

Optimization of temperature on chromium removal

The optimum temperature was 25 °C with removal efficiency of 84.58%. However, when the temperature increased from 25°C to 75°C, removal of chromium decreased from 84.58% to 83% (Fig. 5). This is due to the deposition of Cr (VI) on to metal hydroxides, generated during the electrocoagulation process (Parmar *et al*., 2011). This could be explain by Gibb's free energy (Parmar *et al*., 2011).

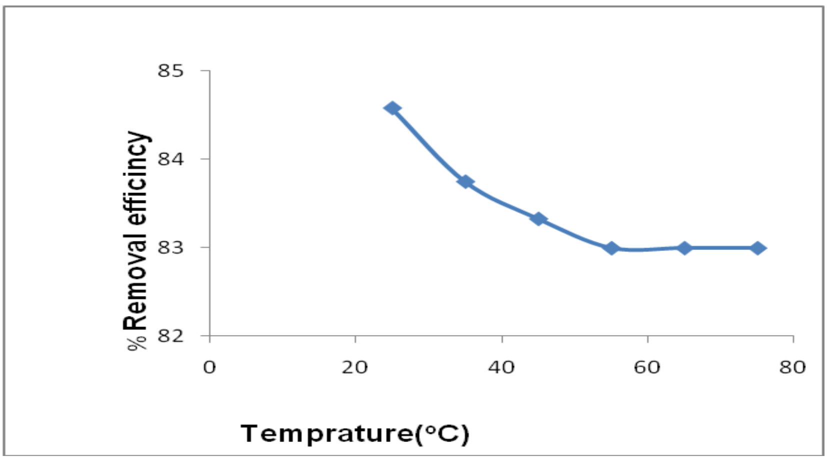

Figure 6. Effect of temperature on the removal efficiency of 40 mg/L chromium through electrocoagulation for 30 min at at applied voltage of 5 V, current density of 40 mA/ cm^2, pH 3 temperature of 25 °C.

Table 1 showed that determination of chromium before and after electrocoagulation using inductively coupled plasma optical emission spectrometry (ICP-OES) for different tannery treated and untreated effluents. Chromium (Cr) was found in these tannery effluents and removed with removal percentage of 92.64 for Bahir Dar tannery effluent and 94.93 for Debrebrihan tannery effluents respectively. Chromium (Cr) was removed from Hayk tannery effluent with removal efficiency of 84.42%. The concentration of chromium and manganese after electrocoagulation is below standard limit of WHO Guidelines (Table 1).

Table 1. Concentration of chromium determined in the different tannery effluents before (C_o) and after (C_o) the electrocoagulation process together with the percentage removal (%RE).

	Industrial Tannery Effluents								
	Bahir Dar			Debrebrihan			Haik		
	C_o	C_f	%RE	C_o	C_f	%RE	C_o	C_f	%RE
Cr	0.910	0.067	92.64	3.513	0.178	94.93	0.276	0.043	84.42

Characterization of tannery effluents using Scanning Electron Microscope (SEM)

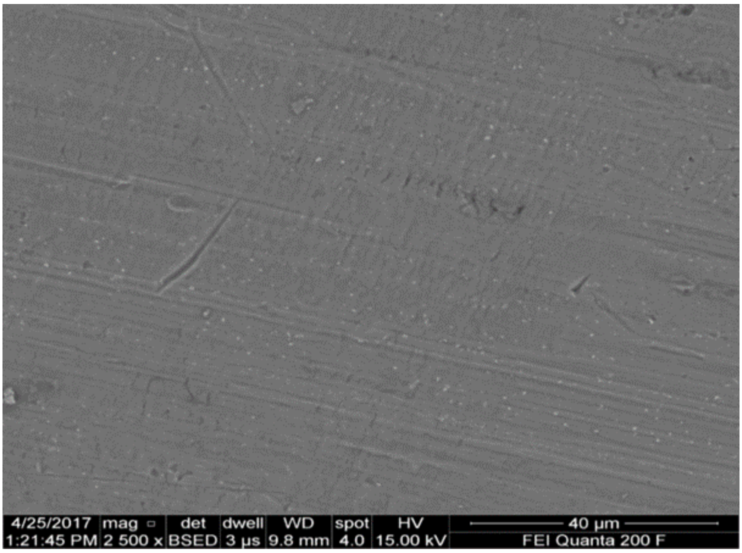

Figure 7. SEM micrography showing the surface morphology of aluminum plate electrode before EC treatment.

Figure 8 (a, b and c) shows the structural morphology of the anode electrode from EC treatment. That structure morphology of the electrode was analyzed using scanning electron microscope at an accelerating voltage of 500 KV under magnifications of 4031,14668 and 18763 shows the scanning electron microscope (SEM) image of the anode after treatment. The SEM image indicated the presence of fine coagulant particles on the surface (Vasudevan *et al.*,2009).

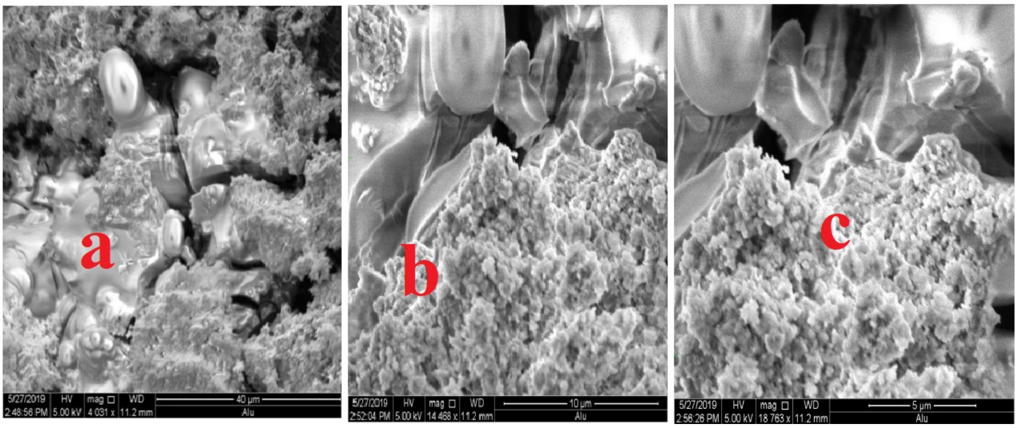

Figure 8. SEM morphology of anodic aluminum surface after EC treatment.

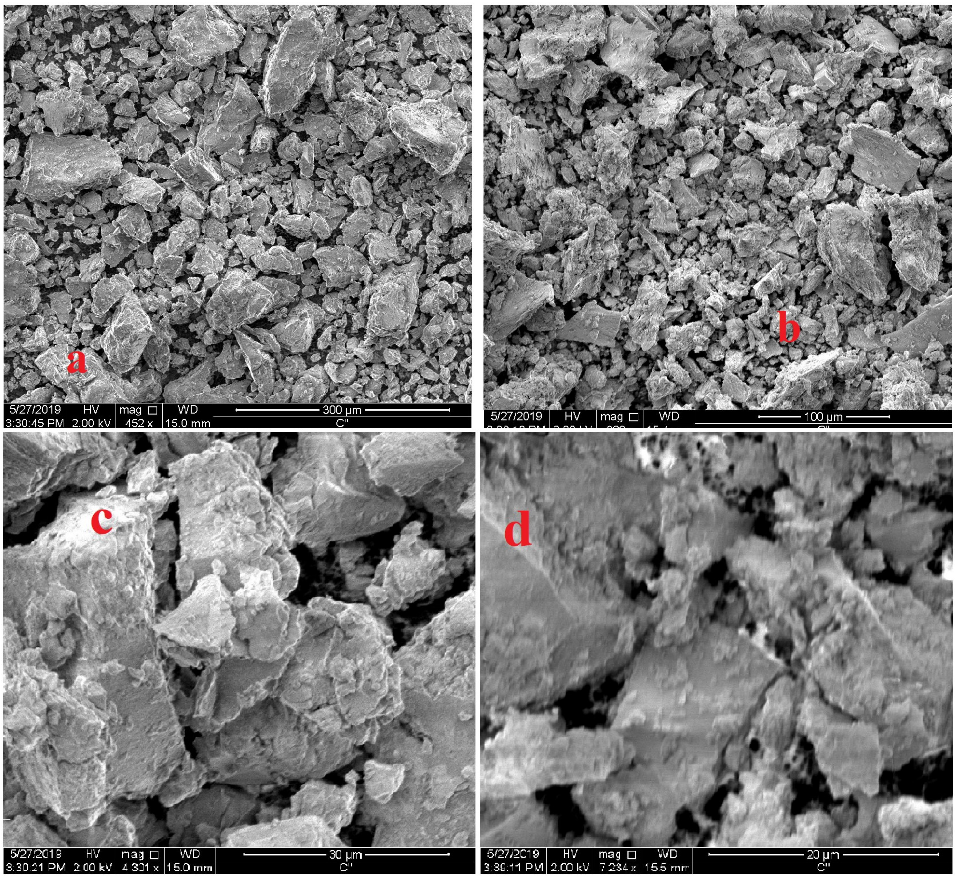

Figure 9. SEM micrography of typical surface morphology of sludge after EC treatment.

The structural morphology of the sludge formed from EC treatment was analyzed using scanning electron microscope at an accelerating voltage of 200 kV under magnifications of 452, 829, 4301 and 7234, respectively. From the SEM images of the sludge (Fig. 9 a, b, c and d), irregular and porous surfaces could be observed. The porous surface on the sludge gets filled by the oxidation ions.

At the anode, it can be seen that there was some aluminum oxide deposition on the surface of the electrode due to dissolution of the anode, generation of Al $(OH)_3$ for coagulation, with the pH of the solution around this area was acidic media. So, the morphological study of electrochemically treated sludge confirms that the oxidation takes place at the surface of the electrode (Tibebe *et al*., 2019 and Rajkumar *et al.*, 2016).

Characterization of tanneries effluents using X-Ray Diffraction (XRD)

XRD analysis was used to analyze the elemental constituents of chromium adsorbed aluminum hydroxide, and the results are shown in (Figure10). It shows the presence of chromium in the spectrum other than the principal elements Al and O. XRD analysis provided direct evidence the removal of chromium by using Aluminum hydroxide. Other elements detected in the adsorbed Aluminum hydroxide come from adsorption of the conducting electrolyte, chemicals used in the experiments, alloying and the scrap impurities of the anode and cathode [Vasudevan *et al.*, 2010].

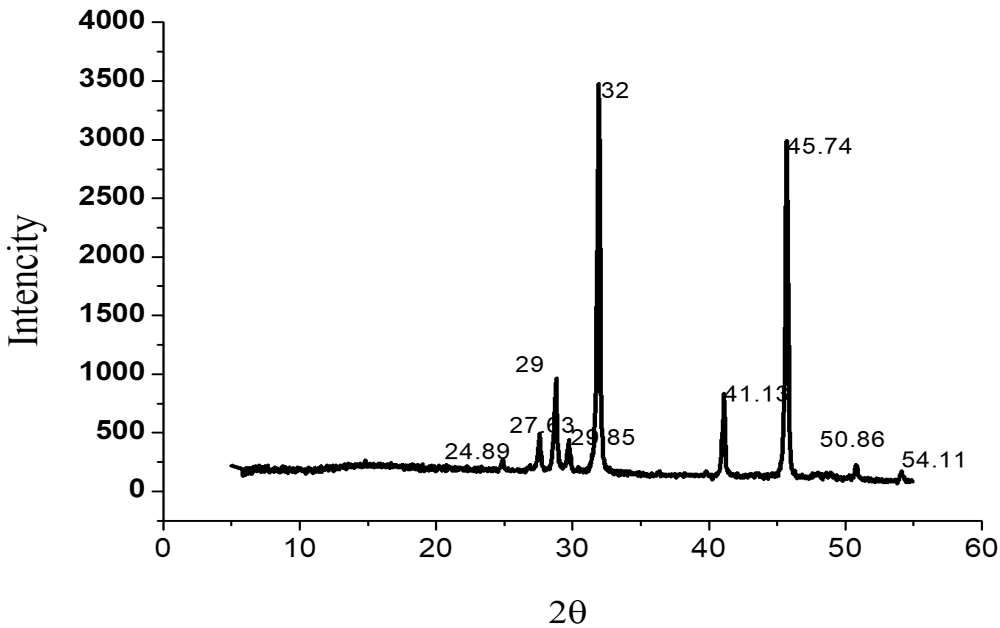

Figure 10 XRD spectrum of tannery effluent sludge after EC treatment.

Conclusion

The effect of chromium concentration, pH, electrolysis time, current density, applied voltage and temperature on the electrocoagulation of industrial tannery effluents using aluminum electrodes has been investigated. Accordingly, the best performance of chromium removal efficiency of 84.42–94.93% was achieved. The electrocoagulation method does not use any chemical reagent, which makes the process attractive for the treatment of chromium containing tannery effluents.

Acknowledgments

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Conflict of Interests

The authors declare that they have no conflict of interests.

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