Electrochemical conversion of chromium from tannery effluents for recycle in industrial applications

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Electrochemical treatment of tannery effluents is gaining interest nowadays, although various other methods (ozonation, activated carbon adsorption, chemical treatment) have also been used to remove or recycle chromium. Because of these methods facing operational problems or involving large amounts of chemicals (Kuppusamy, 2017), electrochemical treatment appears to be greener and more effective in comparison with most other commonly applied technologies (Kokkinos, 2021). Two different reactions are described in this study in order to reuse recovered chromium. The first one is the electrochemical reduction of hexavalent chromium to trivalent which can be recycled to tanning applications and the reverse reaction of oxidation of Cr(III) to Cr(VI), to be used in electroplating and chemical etching processes.

Cr(VI) wastewater leachates were electrochemically treated in a batch electrochemical reactor (350 mL). Ti-based anodes and a reticulated vitreous carbon (RVC) cathode were used in solutions of appropriate sulfuric acid concentrations (0.5 M H_2SO_4) to achieve Cr(VI) to Cr(III) conversion. A 97.5% Cr(VI) conversion was achieved in 8h of electrolysis and the obtained results gave a linear plot, pointing to zero-order kinetics. The value of current efficiency was 104% under the application of a constant current of 0.5 A, showing that chromium can be circulated in a tannery-based route, through its recovery with minimum losses.

On the other hand, an alternative electrolytic method of converting Cr(III) to Cr(VI) with the aim to be reused in other appropriate industrial applications, is that of electrochemical oxidation. This conversion does not need the use of chemical oxidizing agents and it preferably occurs in a near-neutral or alkaline environment (Carlos Alberto Martinez-Huitle, 2018). The produced hexavalent chromium solution can be recycled for reuse in Cr plating, as a strong oxidant in other plating applications or as an etchant of metals (Huma Lateef, 2009). The choice of suitable (anode/cathode) electrode material plays a vital role in electro-oxidation. PbO_2 was found as the optimum anode electrode and Pt/Ti as the cathode. A thin lead dioxide layer was formed on the surface a lead sheet (3.5cm x 6cm) using anodization for 1800 sec at a current of 3.15 A, applied through an Autolab (PGSTAT302N, Metrohm) potentiostat/galvanostat. Cr(III) electrooxidation was carried out in an 400 ml electrochemical batch reactor both with non-separated and separated cathode and anode compartments (separation helps avoid the conversion of Cr(IV) back to Cr(III) at the cathode). Electrodes were arranged to face each other at a distance of 5 cm and the effluent was continuously stirred under magnetic stirring to enhance mass transfer. In separated cells the cathode was inserted into a porous plastic envelope retrieved from a commercial lead acid battery. A DC-ELECTRONICS power supply was used to apply the desired current (at 0.5 A) at the electrodes. Using H_2SO_4 and NaOH the initial pH was adjusted to values in the 0-3 range. After 2 h of electrolysis of the effluent, a change in color from green to yellow was observed while the pH value dropped. This is the result of the following reactions occur during electrolysis:

a. at the anode: $2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-$

b. at the cathode: $6H^+ + 6e^- \rightarrow 3H_2\uparrow$

Overall reaction $2Cr^{3+} + 7H_2O \rightarrow CrO_7^{2-} + 3H_2\uparrow + 8H^+$

The removal reaction followed pseudo-first order kinetics (Zhuoyao, 2021). The change in color of tannery effluent was checked at 1h intervals. Sample Cr(III) concentration was estimated by the diphenylcarbazide method at 540 nm, using a UV-spectrophotometer (HACH DR6000 Benchtop). *Figure 1* represents the resulting Cr(VI) production from anodic oxidation of Cr(III) after 8h of electrolysis, with initial concentration of trivalent chromium equal to 5.82 g L^{-1}. Maximum conversion (68%) was obtained in cells with a separator, at pH=3 (current efficiency of 60%), while the current efficiency was 45% in case of non-seperated cathode and a 50% electrochemical conversion of trivalent chromium at the same optimum pH value. After 6h the conversion stopped, most likely due to the observed decrease of pH and its effect on reaction a. above.

The obtained results allows us to conclude that RVC cathodes and PbO_2/Pb anodes are promising electrodes for electrochemical recycling of Cr(III) and Cr(VI), originating from tannery waste waters.

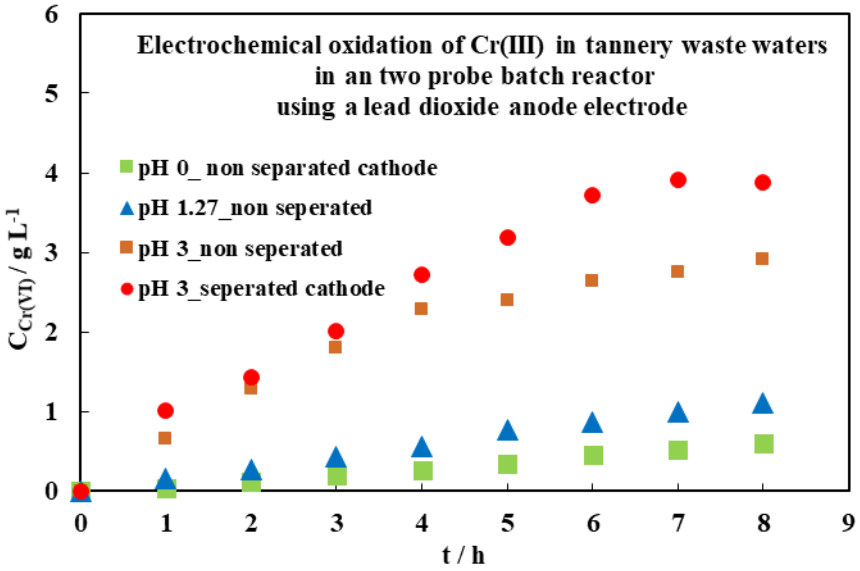

Figure 1. Concentration of produced hexavalent chromium vs time (h), during the electrolysis of 400 mL tannery effluents at a current of 0.5 A

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