

Trivalent chromium wastewater treatment

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Abstract. This scientific paper deals with the study results for treatment of the wastewaters generated in the leather industry from trivalent chromium. Wastewater purification is realized by its treatment in a diaphragm electrolyzer. It is shown that during the electrolysis the increase in pH in the electrolyzer cathode chamber occurred. This leads to the precipitation of chromium hydroxide. The ratio of chromium extraction from the drain is determined by the amount of passed electricity and does not depend on the current load on the cell. The maximum ratio of chromium extraction from the effluent is achieved with a pass of 0.113 A·h/g and made 99.97%. A further increase in the amount of electricity passed through the cell leads to the increase in the chromium content in the waste water. The minimum energy consumption for the chromium extraction from the drain is observed at a current of 0.5 A and is equal to 4.38 kW·h/m³.

1. Introduction

The wastewater containing trivalent chromium is generated in galvanic industries, and is also the main inorganic component of tannery effluents. Consequently it is generated wastewater containing the chromium (III) up to 4 g/l and pH \approx 3.25. Influencing the composition and properties of natural waters, chromium (III) compounds cause allergies, local irritation of the skin and mucous membranes after long-term contact, affect the kidneys, inhibit tissue respiration and cause cancer [1-3].

The losses of chromium from spent solutions cannot be neglected due to the relatively high cost of 800 to 1000 dollars per ton. Only the leather industry consumes annually about 65 thousand tons of chromium compounds. From this amount 20 thousands of tons goes into products, and the rest is lost with waste. Moreover, 25 thousands of tons drain with spent solutions [4]. In connection with the above mentioned, it is of interest to study the process of wastewater purification from chromium (III) by its treatment in the cathode chamber of a diaphragm electrolyzer. After simple processing, the resulting chromium (III) hydroxide can be reused in the process of tanning leather or sent to metallurgical enterprises to produce chromium [5-9].

2. Materials and methods

The study of the chromium extracting from wastewater was carried out in a laboratory electrolyzer, consisting of two chambers separated by a belting membrane. The volume of each chamber was of 250 ml. Titanium plates coated with ruthenium oxide were used as electrodes. The distance between the electrodes in all experiments remained constant and was 4 cm. The experiments were carried out with model wastewater solutions, the initial concentration of chromium in which was 4 g/l, and the pH was 3.25. The sample volume in all experiments remained constant.



The experimental technique was as follows. In the cathode chamber of the electrolyzer was placed 200 ml of a model solution of the drain. 200 ml of a 1% sodium chloride solution were poured into the anode chamber of the electrolyzer. After the required amount of electricity was passed, the solution from the cathode chamber was moved into a cylinder and kept there until the complete precipitation of chromium hydroxide. The clarified portion was analyzed for chromium content.

3. Results and discussions

The presence of a diaphragm dividing the cathode space of the electrolyzer leads to the fact that the recombination process of hydrogen and hydroxide ions is determined by its diffusion through the diaphragm. The intensity of mass transfer of hydrogen and hydroxide ions through the diaphragm increases with increasing difference in the concentration of these ions in the cathode and anode chambers of the electrolyzer. When the formation rate of hydrogen hydroxyl and hydrogen ions on the electrodes and the speed of its mass transfer through the diaphragm become the same, the change in the pH of the medium in the cathode and anode chambers of the electrolyzer will stop. The dependence of the effluent pH in the cathode chamber on its treatment time in the electrolyzer at various current loads, presented in Figure 1, is quite complex. At the initial time, the increase in the catholyte pH is restrained by the formation of chromium hydroxide, and the influence of this process on the growth rate of the pH value is especially noticeable at low current loads. So, with an increase of the cathode chamber pH due to the formation of OH^- ions on the cathode as a result of electrolysis at a current load of 0.5 A for 60 minutes, as provided by the Faraday laws, it should be 4.12 units. The real increase in pH (Figure 1) was only 1.26 units. After completion of the chromium (III) hydroxide precipitation, a fairly intense increase in pH occurs, this is clearly noticeable at high current loads. This process continues until the catholyte pH reaches about 11. Next, a decrease in the rate of pH growth occurs, which is due to the increasing influence of the recombination of H^+ and OH^- ions on the diaphragm. Upon reaching a catholyte pH approximately 12.5 units, a further increase in the hydrogen index of the medium in the cathode chamber practically ceases. It should be noted that the increase rate of the pH value in the electrolyzer cathode chamber is determined by the current load.

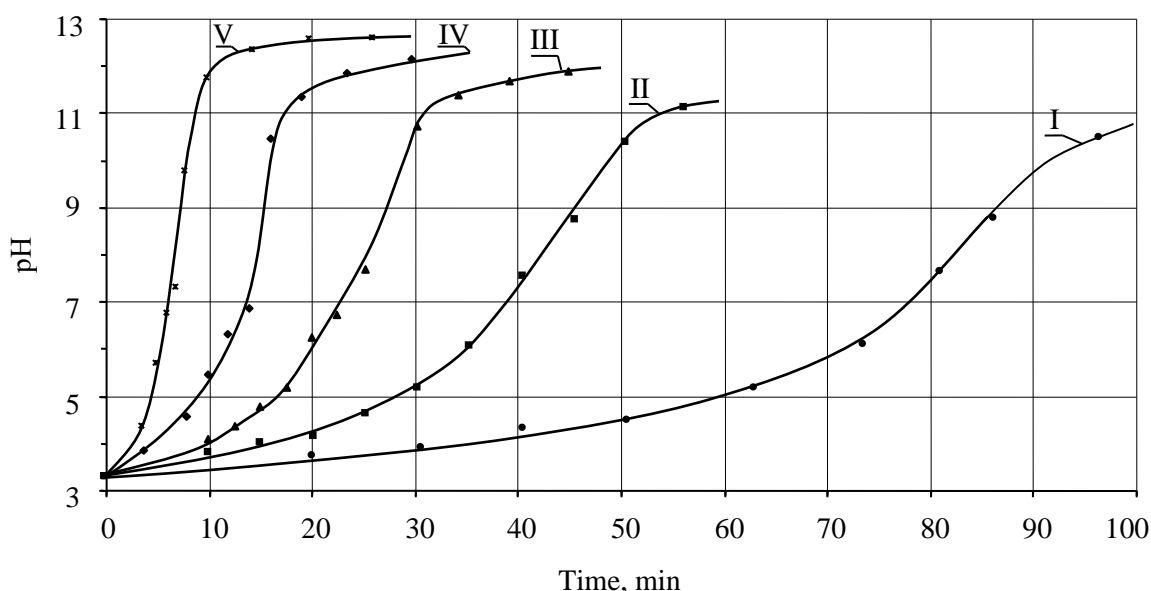


Figure 1. Dependence of the effluent pH on the waste treatment time.
Current intensity: I – 0.5 A, II – 1.0 A, III – 1.5 A, IV – 2.5 A, V – 5.0 A.

The influence of processing time on the chromium extraction from wastewater was studied at current loads from 0.5 A to 5.0 A in increments of 0.5 A. The results of the dependence of the concentration of chromium in the effluent on the time it was processed in the electrolyzer are shown in Figure 2. As the data shows the dependence of the residual chromium concentration in the effluent on time can be divided into three periods. This is peculiar to the current load of 1.0 A. At the initial time from 0 to 10 minutes, the rate of chromium extraction from the effluent makes 0.035 g/l · min. In the period from 10 to 25 minutes, the rate of chromium extraction from the effluent makes 0.205 g/l · min. At the final stage, when the process time is more than 25 min, the rate of chromium extraction from the effluent decreases again, and becomes equal to 0.038 g/l · min. It can be seen that with an increase in the current load on the electrolyzer, the chromium deposition also increases.

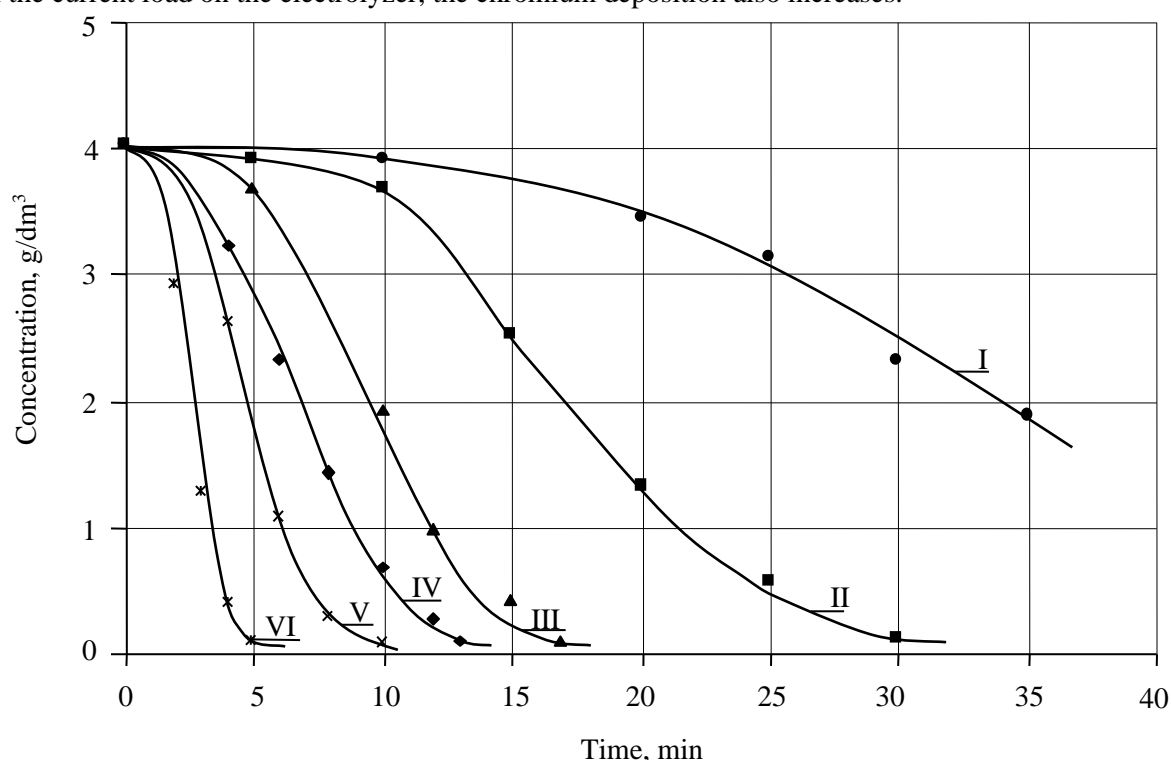


Figure 2. Dependence of the chromium (III) concentration in the effluent on the waste treatment time. Current intensity: I – 0.5 A, II – 1.0 A, III – 1.5 A, IV – 2.0 A, V – 3.0 A, VI – 5.0 A.

After certain time of electrolysis (for a current load of 1.0A for about 40 minutes), the precipitation of chromium (III) hydroxide begins, which leads to an increase in its concentration in the effluent. This is due to the presence of amphoteric properties in chromium. Until the pH of the medium in the cathode chamber does not exceed a value of 8, a precipitate of chromium (III) hydroxide is formed:



After the medium pH in the cathode chamber exceeds 8–8.5, the formation of soluble metachromic acid begins:



The minimum concentration of chromium (III) in wastewater for different values of the current strength in the electrolyzer is shown in table 1.

The minimum chromium (III) concentration in the wastewater is reached at a current strength of 0.5 A and is 0.85 mg/l. The maximum permissible concentration of chromium (III) in the water bodies of drinking, cultural and domestic water use is 0.5 mg/l [10].

Therefore, before discharging such wastewater into a reservoir, it is necessary to dilute it for 1.5–2 times. This is possible when this effluent enters the factory collector.

Table 1. Minimum concentration of chromium (III) in the wastewater

Current, A	Concentration of chromium (III), mg/l
0.5	0.85
1.0	0.98
1.5	1.35
2.0	1.35

It should be noted that the depth of chromium deposition from the effluent does not depend on the current load at which the electrolyzer operates, but is uniquely determined by the amount of electricity passed through (Figure 3).

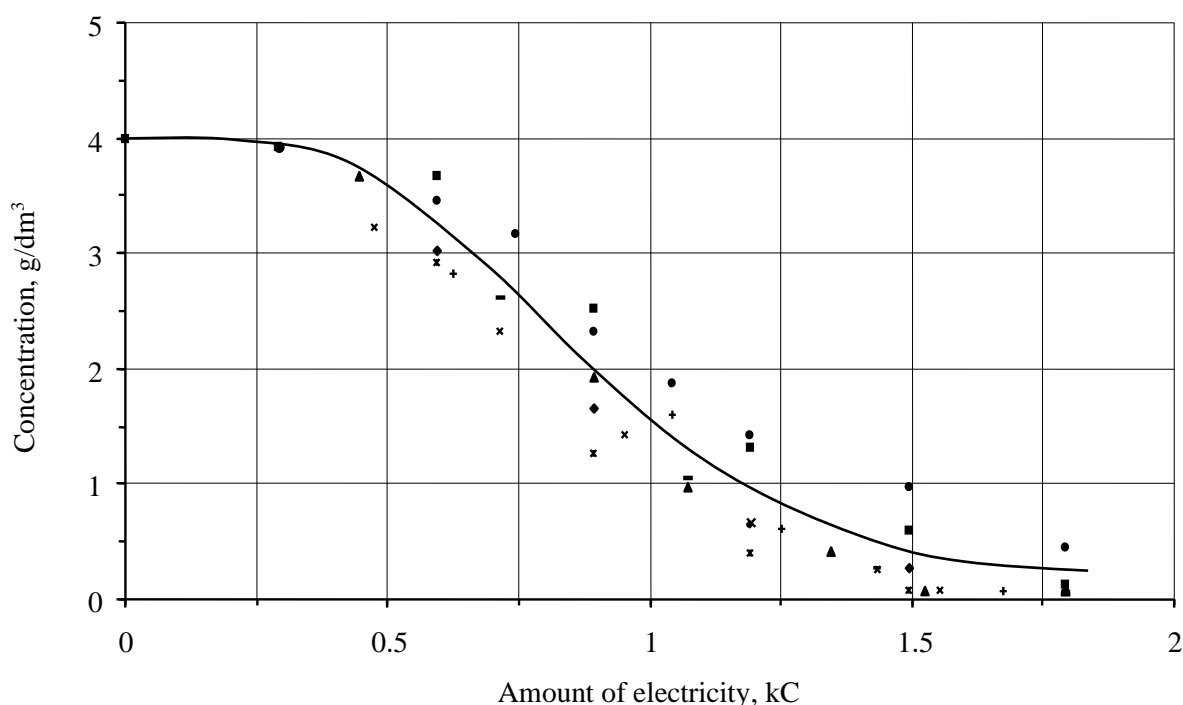


Figure 3. Dependence of the chromium (III) concentration in wastewater on the amount of passed electricity. Current intensity: • - 0.5 A, ■ - 1.0 A, ▲ - 1.5 A, ◆ - 2.0 A, × - 3.0 A, * - 5.0 A.

The dependence of the cost of electricity for the chromium extraction from the effluent on the extraction ratio at various current loads on the electrolyzer is shown in Figure 4. An analysis of the results shows that the energy consumption depends on the ratio of chromium extraction from the effluent and on the current load. With a change in the extraction ratio from 20 to 80%, energy consumption increases from 2.86 to 6.14 kW·h/m³ at the current load of 1.0 A, and from 5.85 to 10.71 kW·h/m³ at the current load of 5.0 A, i.e. almost doubled. At the ratio of chromium extraction from the effluent from 80 to 100%, energy consumption increases from 6.14 to 8.8671 kW·h/m³ at the current load of 1.0 A, and from 10.71 to 21.14 kW·h/m³ at a current load of 5.0 A, that is, almost twice.

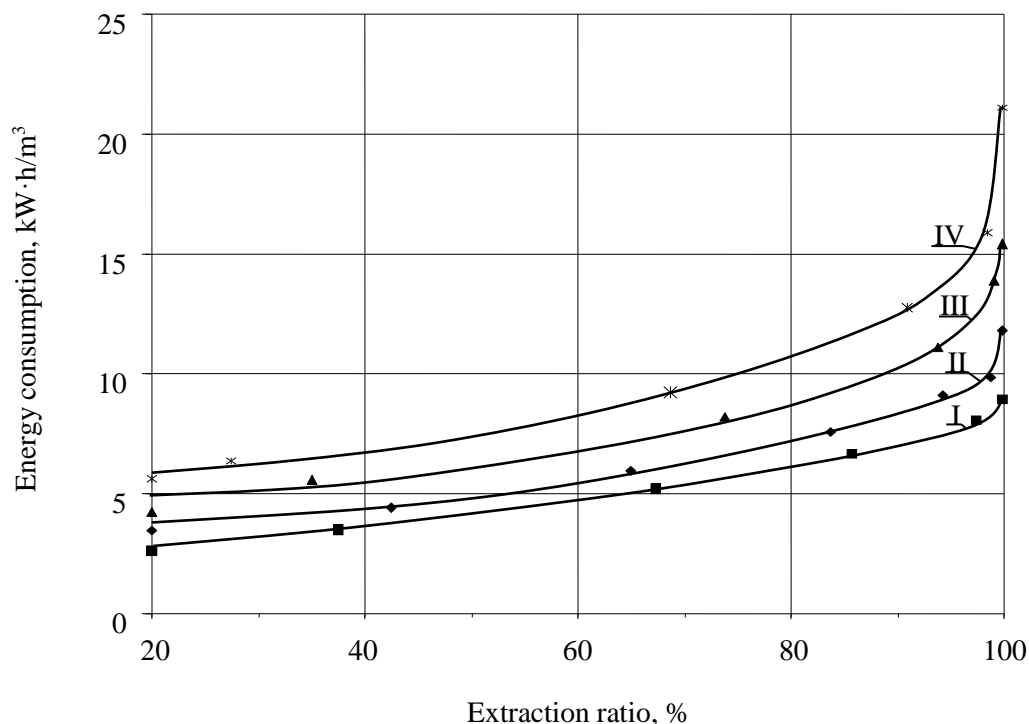


Figure 4. The dependence of energy consumption on the extraction ratio Current intensity: I – 1.0 A, II – 2.0 A, III – 3.0 A, IV – 5.0 A.

4. Conclusion

The experimental results obtained in the study of the chromium precipitation process by wastewater treatment in a diaphragm electrolyzer show that in this way chromium can be extracted from the effluent by almost 100%. As it follows from the data shown in Figures 1 and 2, the pH change in the cathode chamber of the electrolyzer is consistent with the change in the chromium concentration in the effluent during its processing.

It may be seen that a significant increase in pH begins after almost complete chromium precipitation. So for a current load of 1.0 A, the chromium precipitation from the effluent ends after 30 minutes of electrolysis (Figure 2). The pH value in the cathode chamber of the electrolyzer at this load (Figure 1) changes during the first 3 minutes of the process from 3.25 to 5.3, that is, by 2.05 units, and over the next 20 minutes from 5.3 to 11.2, that is, already at 5.9 units. For a time period of more than 50 min, the change in pH becomes almost insignificant. This behavior of the pH value from the time of the process is due to the fact that at the initial stage, the hydroxyl ions formed at the cathode bind to chromium, forming a hydroxide precipitates. When the precipitation of chromium from the effluent ends, a significant increase in pH is observed, the speed of which is higher, the greater the current load. The tendency of the pH index to a limit for a sufficiently long process time is associated with the recombination of OH^- ions formed at the cathode and H^+ ions formed at the anode.

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