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Research paper

Study of the Mechanism of Chromium Removal in Tannary Effluent by Electrocoagulation Through Zeta Potential Measurements

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Abstract

The main objective of this paper is to discuss the behavior of the flocs formed during chromium (III) removal tests by electrocoagulation with iron electrode, through zeta potential measurements. The potential zeta is measured on chromium synthetic solutions and on the real tannery effluent previously treated by electrocoagulation. The effects of operating parameters such as time, potential electrolysis and pH on the zeta potential have been investigated. The obtained results show two different behaviors of the flocs in real tannery effluent and chromium synthetic solutions. Furthermore, the mechanism of electrocoagulation is elucidated.

Keywords: *Chromium; Electrocoagulation; Mechanism; Potential zeta, iron.*

1. Introduction

Chromium sulfate has been widely used as a tanning agent in the leather industry. In chrome tanning, only 70-80% of chromium applied is take up the leather, and the rest is discharged as waste, inducing an important source of chromium contamination. Some environment-friendly and sustainable methods have been reported to recover and remove the residual chromium (III). For example: precipitation [1-2], adsorption [3-5], ion exchange [6-7], membrane technologies [8]. Most of these methods suffer from some drawback such as high capital and operational cost. An alternative to physicochemical methods is the electrocoagulation. This latter is an electrolytic generation of coagulants due to anodic dissolution of sacrificial anode such as aluminum (Al) or iron (Fe). The generated coagulants destabilize the pollutants present in wastewater which could allow their subsequent aggregation and flocculation.
In the case of electrocoagulation process using iron anode, two mechanisms for the production of metal hydroxide have been proposed [9]:

• Mechanism I:
Anode: $2Fe \rightarrow 2Fe^{2+} + 4e-$
$2Fe^{2+} + 5H_2O + 1/2O_2 \rightarrow 2Fe(OH)_3(s) + 4H^+$
Cathode: $4H_2O + 2e- \rightarrow 4OH^- + 2H_2(g)$
Overall reaction: $2Fe + 5H_2O + 1/2O_2 \rightarrow 2Fe(OH)_3(s) + 4H_2(g)$

• Mechanism II:
Anode: $Fe \rightarrow Fe^{2+} + 2e-$
$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2(s)$
Cathode: $2H_2O + 2e- \rightarrow H_2 + 2OH^-$
Overall reaction: $Fe + 2H_2O \rightarrow Fe(OH)_2(s) + H_2(g)$
This technique has demonstrated his efficiency to treat the tannery effluent in previous studies carried out by the authors [10-11] and by other researchers [12-13].

There are several different mechanisms of aggregation that can occur during electrocoagulation and determining which mechanism governs the process is difficult. The most commonly used technique for characterizing the stability colloid suspensions is the measurement of particle zeta potential. The zeta potential is an important measure of the electrical potential at the floc surface, and the magnitude and sign of the zeta potential control the electrostatic interactions between the floc surface and polar species, other charged interfaces and particles in suspension [14].
To understand and know the mechanism governing the removal of the chromium form tannery wastewater by electrocoagulation, the zeta potential measurements are employed.
In the present study, the characteristics of the zeta potential of the flocs formed in electrocoagulation tests was evaluated under various conditions, such as potential and time electrolysis, pH , concentrations and type of solution.

2. Experimental

In our investigation, we use two types of sample:
- tannery wastewater, which is taken from a tanning operation from commercial tannery industry located in Casablanca, Morocco,
- and chromium synthetic solutions prepared from chrome alum $CrK(SO_4)_2$, 12 H_2O widely utilized in tanning process. Two concentrations are tested (200 mg/ l and 1.2 g/ l)

Experiments were carried out, at a laboratory scale, in cell equipped with two iron electrodes (anode and cathode with 6.4 cm^2 area) and satured Ag/AgCl as reference electrode. A potentiostat (VoltaLab, PGZ 100) is used to apply the desired potential (Fig. 1). In each run, 150 cm^3 of solution is placed into electrolytic cell. At the end of the experiment, the potential zeta is measured using a Malvern zeta potential analyzer (model zetasizer 3000 HS, Malvern Instrument).
The pH is measured after each test of electrocoagulation and noted pH_{end}.
The pH is adjusted to desirable value using NaOH or H_2SO_4 with high purity.
The chromium and iron concentration are determined in the solution by atomic absorption spectrophotometry (AAS, Varian model AA-20).

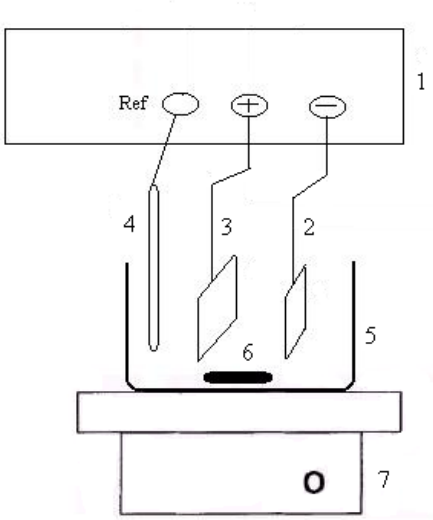

Fig. 1: Electrocoagulation set-up. 1: Potentiostat, 2: Anode, 3: Cathode, 4: Reference electrode, 5: Batch reactor, 6: Magnetic stir bar, 7: Magnetic stirrer.

3. Results and discussion

3.1 Zeta potential of chromium synthetic solutions

Figure 2 shows the evolution of the zeta potential, in the absence and the presence of chloride ions, as a function of the electrolysis time. This figure shows that for a concentration of 1.2 g / l of chromium III, the zeta potential is zero for all electrolysis time (the pH solution after electrocoagulation for all tests is between 4.5 and 5.5). The presence of chloride ions in the solution has no effect on the zeta potential and consequently on the charge of the flocs formed, even though the pH of the solution increases to 7. The figure also shows that when the concentration of chromium is low, the zeta potential is positive and increases with the electrolysis time ($4.5 \leq pH_{end} \leq 8$).
Figure 3 illustrates the evolution of the zeta potential, in the absence and the presence of chloride ions, versus the electrolysis potential. It is clear that with or without chloride ions in solution, the zeta potential is practically zero. Consequently the charge of the formed flocs is zero whatever the applied potential ($4 \leq pH_{end} \leq 4.5$). On the other hand, when the chromium concentration is low, the floc charges become positive. Thus, the zeta potential is positive and stable until the potential of 0.8 V. A potential greater than this value, it begins to increase ($6.5 \leq pH_{end} \leq 8$).
Those results demonstrate that only for diluting solution, value of the zeta-potential changed, and we refer to this as the “unstable region”. The shift in the zeta-potential values can be attributed to an unstable suspension, which subsequently results in the aggregation of particles [15]. In theory, it is the balance of the attractive vs. repulsive forces that determine the stability of the particle system; if the repulsive forces are greater than the attractive forces, and then the suspension remains stable. In our case, the repulsive forces take the

form of electrostatic repulsion that occurs between the particles. Further, dilution will only increase the separation distance between the particles, which should ultimately prevent the particles from interacting further and should thus reduce the magnitude of the attractive forces [15]. So, the concentration of Fe^{2+} and Fe^{3+} arises, in the medium, with potential and time electrolysis and leads to a more positive charge. Therefore, the zeta potential increases. The same trend is obtained by Yiquan and al [16] and Remero and al [17] when they studies the effect of metal cations on the zeta potential, respectively, of the fly ash and silica suspensions at various concentrations. The cations cause a compression of the diffuse parts of the double layer around the particles. As more cations are generated, the electrostatic repulsion between the particles decreases due to a more closely packed configuration in the boundary layer [16].

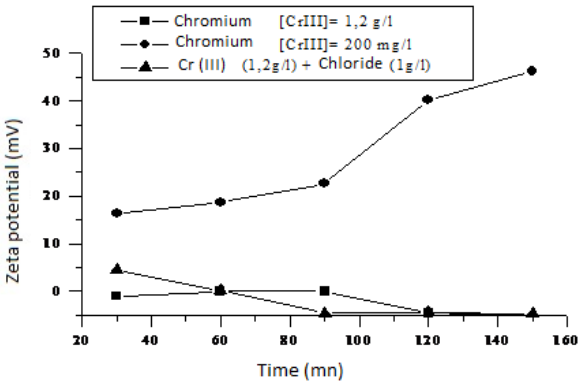

Fig.2: Evolution of the zeta potential with electrolysis time at E = 0.7 V, in the absence and the presence of chloride ions

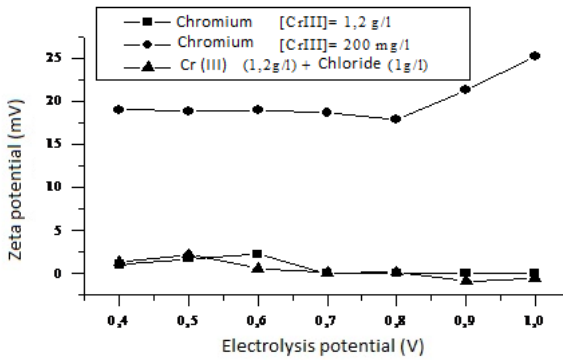

Fig.3: Evolution of the zeta potential according to the electrolysis potential, in the absence and the presence of chloride ions. Electrolysis time = 1H.

3. 2 Zeta potential of real tannery wastewater

Figure 4 shows the results of the zeta potential measurement of flocs formed during electrocoagulation tests, for the real tanning effluent at different times. We observe that the zero point of charge for tanning effluent is obtained at an electrolysis time of 60 minutes ($4.8 \leq pH_{end} \leq 5.8$). However, the 8-fold dilution of tanning effluent (representative of the global effluent of the tannery industry) has a zeta potential equal to zero for times less than 60 minutes. At a time greater than 60 minutes, the zeta potential becomes very negative ($5.8 \leq pH_{end} \leq 8$). In Figure 5, we represent the evolution of the zeta potential with electrolysis potential for the both types sample: real and the diluted effluents. We find that for tanning effluent, the zeta potential is negative at low potential, but from a potential of 0.6 V the zeta potential tends towards zero ($4.5 \leq pH_{end} \leq 5$). While, for the diluted form, it is zero whatever the applied potential ($5.8 \leq pH_{end} \leq 7.8$).

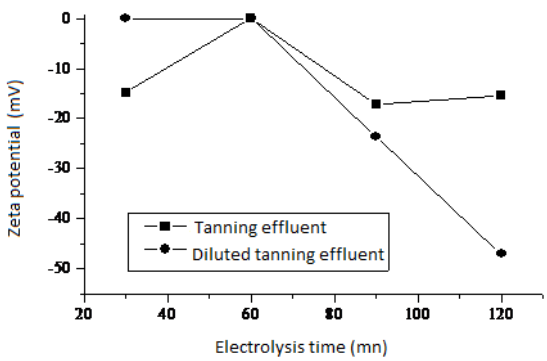

Fig. 4: Zeta potential for real tanning effluent as a function of the electrolysis time at E = 0.7V

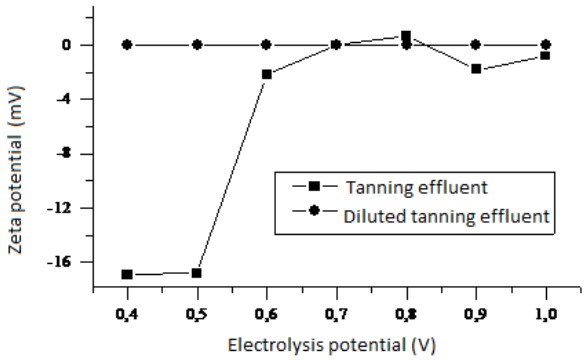

Fig.5: Evolution of the zeta potential as a function of the electrolysis potential at time of 1 h.

The results presented in these two paragraphs, allow us to conclude that the behavior of the flocs formed in the real tannery effluent is different from that of the synthetic solutions. This can be explained by the difference in the chemical composition of the two solutions. To better understand these behaviors, we performed zeta potential measurements on mixtures: [Cr (III), Fe (II)], [Cr (III), Fe (III)] and [Cr (III), Fe (III), Cl-], versus pH.

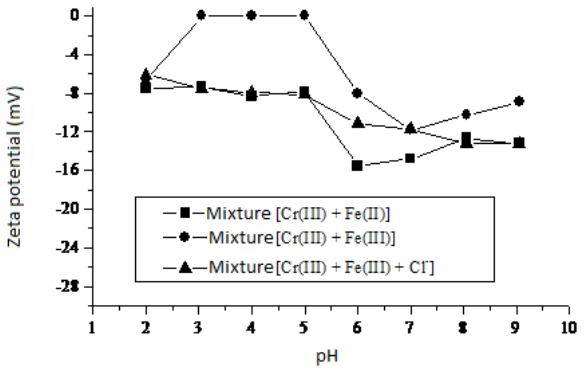

Fig. 6: Effect of the pH on zeta potential for three mixtures.

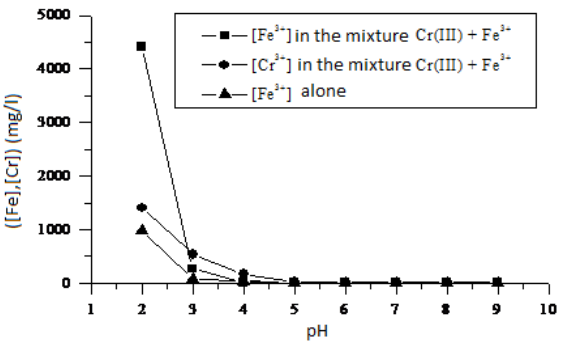

Fig.7: Evolution with the pH of the concentration of iron and chromium in the mixture of chromium and iron ($[Cr^{3+}]$ = 6 g / l and $[Fe^{3+}]$ = 7.1 g / l).

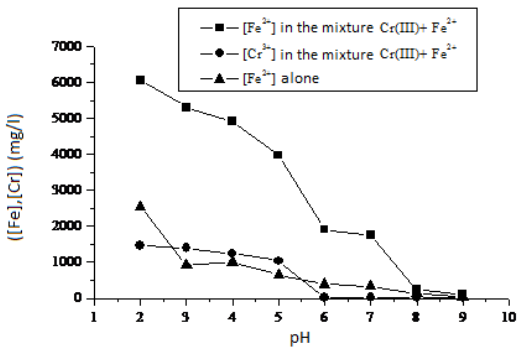

Fig.8: Evolution with the pH of the concentration of iron and chromium in the mixture of chromium and iron ($[Cr^{3+}]$ = 6 g / l and $[Fe^{2+}]$ = 7.1 g / l).

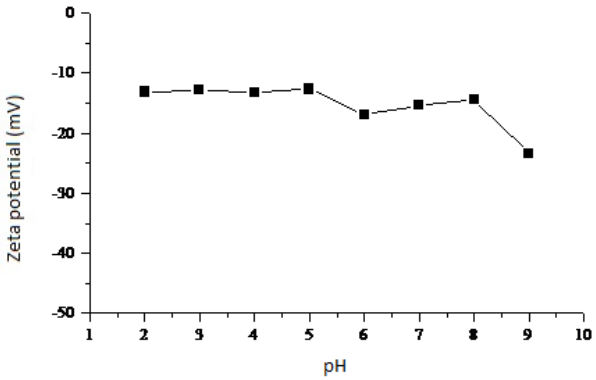

Fig. 9: Evolution of the zeta potential of tanning effluent with pH

Figure 6 shows the evolution of the zeta potential of these mixtures with pH solution. Comparing these results with those of the electro-coagulation for synthetic solution (1, 2 g / l of chromium (III)), we find that the zeta potentials of the mixture [Cr (III), Fe (III)] and [Cr (III)), Fe (III), Cl-] are most comparable with those of the electrocoagulation tests. Therefore, during the electrocoagulation experiments we have the formation of chromium hydroxide and iron (III) hydroxide. Indeed, during electrolysis, the iron anode oxidizes to Fe^{2+} ion. The presence of the chromium (III) in the solution will create a competition between the formation of ferrous hydroxide and chromium hydroxide. If we have the Fe^{3+} ions in the medium (Figure 6), we will have the formation of iron hydroxide III first (Ks $(Fe(OH)_3$ << Ks $(Cr(OH)_3)$). But, in the presence of Fe (II) in the medium (Figure 8), chromium (III) precipitates first. This results which is in agreement with the thermodynamic data (Ks $(Cr(OH)_3)$ << Ks $(Fe(OH)_2)$, leaves time for Fe^{2+} ions to oxidize to Fe^{3+} under the effect of the electrolysis potential or under the effect of the dissolved oxygen. As a result, we have the formation of the two hydroxides: the first is of iron (III) and the second is of chromium (III). The same reasoning can be formulated for the low chromium concentration, that is, the formation of chromium hydroxide followed by iron (III) hydroxide. The positive value of zeta potential can be explained by the excess of iron in the solution: the Fe^{3+} or Fe^{2+} ions generated during the electrolysis, which the quantity depends on the potential and the time of electrolysis, surround the flocs of hydroxide and hence the positive charge. The behavior of the flocs formed during the treatment of real effluent is different from that of the synthetic solutions. This may be due to the complex composition of tanning effluent. In figure 9 is shown the change of zeta potential versus pH of tanning effluent. As the pH is increased from 2 to 9, the zeta potential decreases from Zp = -15 mV to Zp = -24m, which is due primarily to the electrokinetic properties of colloidal particles that are influenced by the pH of the solution. As additional OH^- is added into the solution, the surface potential becomes more negative. The van der Waals force decreases, and repulsive electrostatic forces dominate [15]. The same trend is observed by Yiquan and al [15]. When comparing the values of the zeta potential of tanning effluent alone as a function of pH (Figure 8) with those of the electrocoagulation tests, we can conclude that at low time and low potential we have the formation of chromium (III) hydroxide. The zero point of the zeta potential can be explained by the fact that the Fe^{3+} ions surround the flocs of chromium hydroxide and neutralize his charge and hence the formation of iron (III) hydroxide. However, the negative charge encountered at high electrolysis times can be explained by the adsorption of the hydroxyl ions (OH^-) generated during the electrolysis which the quantity increase with time. In the case of diluted effluent, the zero charge of the flocs formed is due probably for the fact that the positive surface charge equals the negative surface charge or to the formation of chromium hydroxide and iron hydroxide (III) in the medium. In conclusion, during the treatment of tannery effluent by electrocoagulation, the chromium is precipitated as chromium (III) hydroxide by the hydroxyl ions (OH^-) generated during the electrolysis according the water reduction reaction at the cathode. On the other hand, the other pollutants can either be adsorbed on the surface of the Fe (III) hydroxide formed or they are trapped inside the pores present in this hydroxide.

4. Conclusion

In this study, the zeta potential of the flocs, formed during electrocoagulation tests using iron electrode, was measured under various conditions. The comparison of the zeta potential values of the flocs formed during the electrolysis in the real tannery effluent and in the synthetic solutions based on chromium (III) showed two different behaviors. However, the comparison with those of chromium solutions mixed with iron alone and with iron and chlorides at different pH, made to advance the hypothesis of elimination of chromium by precipitation in the form of chromium (III) hydroxide with the formation of Fe (III) hydroxide in tannery wastewater.

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