



Chromium(III) recovery from tanning wastewater by adsorption on activated carbon and elution with sulfuric acid

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ABSTRACT

Chromium(III) recovery from tanning wastewater by means of adsorption on activated carbon and elution with sulfuric acid was studied. Tests were carried out at laboratory scale on an effluent of industrial origin. Initially, proteinaceous materials and fats were separated via sieving followed by ultrafiltration. The chemical composition of the sample thus precleansed was (in g/L): 1.09 chromium(III); 10.36 sulfate; 11.10 sodium; 9.57 chloride; 0.40 proteinaceous materials; and 0.20 fats. Adsorptions were made at 20, 30, and 40°C, establishing what temperature favored chromium(III) uptake. At 40°C, the maximum cation fixation was 40.2 mg/g, and the lowest content in an equilibrium solution was 3.9 mg/L. As regards sodium, chloride, and sulfate, the concentrations before and after the treatment were similar. Likewise, it was found that protons were also retained, modifying the pH of the liquid medium. Adsorption isotherms were analyzed using the Langmuir, Temkin, and Freundlich models. Finally, the extraction of the adsorbed tanning agent with sulfuric acid was evaluated. A recovery of 96.5% was achieved with 0.9 N at 70°C (13.23 g/L Cr³⁺; 42.98 g/L sulfate; and 0.40 g/L NaCl).

Keywords: Activated carbon, Adsorption-elution, Chromium, Langmuir-Temkin-Freundlich models, Tanning wastewater

1. Introduction

The cost of effluent remediation is high, and no marketable goods can be produced from this process. The possibility of implementing a technique to remove hazardous substances and enable their recycling offers a clear economic and environmental benefit. This would be the case of the leather industry when chromium(III) (32-34% basic chromium(III) sulfate) is one of the reagents used.

For each kilogram of processed skin, between 3.0 and 5.0 L of tanning wastewater is released. Its composition varies with the kind of leather produced and the type of manufacturing process employed. The major components and most frequent contents are: 0.6-2.5 g/L chromium(III); 10-20 g/L sulfate; 12-21 g/L sodium; 9-26 g/L chloride; 1-4 g/L proteinaceous materials; and 1-3 g/L fats [1-5]. It should be noted that during this activity the transformation $\text{Cr}^{3+} \rightarrow \text{Cr}^{6+} + 3\text{e}^-$ does not occur. Such reaction only takes place naturally under very specific conditions.

Chromium is a transition element that has different oxidation states, although the most common ones are the trivalent

([Cr(H₂O)₆]³⁺) and hexavalent (CrO₄²⁻ or Cr₂O₇²⁻) states. The first species is very stable, and small quantities are required for the satisfactory performance of certain biological functions in human beings. Chromium(VI) can be found in various products and, even at low concentrations, it has adverse effects on health [6-9]. In the Province of Buenos Aires, a district in Argentina where a large number of tanneries are located, the maximum values allowed in a liquid effluent that will be discharged into the sewage system or surface water bodies are 2.0 mg/L total chromium and 0.2 mg/L chromium(VI).

Adsorption is a process by which chromium(III) can be removed from tanning wastewater. Even though such depollution has only been carried out at laboratory scale so far, acceptable results were obtained with various adsorbents [10-18]. The most effective solids for this purpose are characterized by the fact that they develop strong electrostatic interactions. Such interactions are related to a variety of physical and chemical events, which differ depending on the material examined (clays, activated carbon (AC), etc.). In order to illustrate the concept, a widely documented phenomenon



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in clays can be cited. During their genesis, the isomorphic substitution between cations of similar size but with lower electric charge occurs, proportionally increasing the attraction force of these minerals [6, 15, 18].

In AC, the removal is described by two mechanisms; the most widely known comprises an ion exchange on acid sites (carboxyl, lactone and lactol groups). The other is the product of the reaction between the negatively charged surface (delocalized π electrons in aromatic structures) and cations, forming π -d complexes [19-25]. This adsorbent is used to remove toxic materials dissolved in an aqueous medium, which is the reason why it was chosen for the present study [6, 8, 14, 19, 20, 22, 26]. Its maximum adsorption capacity for Cr^{3+} at 30°C (33.1 mg/g) was previously determined [14], as well as how the yield would be affected depending on the cation polymerization degree (monomer or dimer) [27].

Articles on the adsorption of chromium(VI) and to a lesser extent its desorption have been recently published [26, 28-30]. Obviously, the behavior established therein is not applicable to another species comprising an ion with an electric charge opposite in sign. For this reason, it was decided to use the above-mentioned industrial waste to assess the uptake of chromium(III) on AC and its recovery by elution with sulfuric acid.

2. Materials and Methods

Tanning wastewater was collected from a typical process using 33% basic chromium(III) sulfate ($\text{Cr}(\text{OH})\text{SO}_4$) and the complexing agent sodium formate (HCOONa). Proteinaceous materials and fats were separated by sieving (Tyler mesh sizes # 20 (840 μm); 200 (74 μm); and 325 (45 μm)), followed by ultrafiltration under a transmembrane pressure of 1.5 atm (Pellicon cassette filter with a 100,000 NMWL polysulfone membrane (PTHK00005)). The chemical analysis results of the sample obtained by this methodology are summarized in Table 1.

Table 1. Chemical Analysis of the Tanning Wastewater after Pretreatment via Sieving and Ultrafiltration

Component	g/L
Chromium(III)	1.09
Sulfate	10.36
Sodium	11.10
Chloride	9.57
Proteins	0.40
Fats	0.20
pH	3.42

The adsorption isotherms were made using nine solutions prepared by dilution (D_1 - D_9) of the cleansed effluent, thus keeping the relationship of all its constituents constant: 30 (D_1); 60 (D_2); 90 (D_3); 130 (D_4); 170 (D_5); 260 (D_6); 430 (D_7); 690 (D_8); and 1,090 (D_9) mg/L of chromium(III) (D_9 : mother liquid). To carry out the tests, laboratory grade AC (Anedra) was chosen. Its main properties were: 573 m^2/g BET- N_2 specific surface, 1.58 cm^3/g pore volume, and 5.18% ash. The surface functional groups were meas-

ured by the Boehm method [25]. In each determination, 500 mg of AC in 50 mL of NaOH 0.05 N or, alternatively, HCl 0.05 N was added, maintaining the suspensions in closed containers for 120 h. Both heterogeneous systems were shaken by hand six times a day, until a uniform distribution was achieved (4-5 min). When the contact time was over, the mixtures were filtered through No. 40 Whatman paper, and 20 mL aliquots of these liquids were titrated with either HCl 0.05 N or NaOH 0.05 N. The values obtained were 0.51 meq/g for acid sites and 2.51 meq/g for basic sites.

The original adsorbent was washed (W) with abundant distilled water, separated by filtration (F) through a No. 40 Whatman paper and dried (D) in an oven for 24 h at 105°C. Subsequently, it was dispersed in distilled water (5% w/v) and then it was poured slowly into solutions D_1 - D_9 (AC/aqueous solution ratio = 2.5 g/1.0 L = 2.5). The suspensions were stirred (100-180 rpm) and kept at a constant temperature ($T = 20, 30$, and 40°C) for 60 min. Once that period had elapsed, the sequence described above (W + F + D) was repeated in order to remove from the solid phase the retained substances that did not respond to the phenomenon under study. Chromium(III) adsorbed on AC and its content in the equilibrium solution (ES) for each stage (i) were determined by chemical analysis of both phases. The tanning agent bound to the adsorbent was extracted with sulfuric acid of different concentrations (0.8; 0.9; 1.0; and 2.0 N), at 70°C, 60 min contact time, and a solid/eluant solution ratio of 333.3 (33.3 g/0.1 L). Tests were conducted in duplicate for reproducibility.

Chromium(III) was evaluated by atomic absorption (AA) with an air-acetylene flame at $\lambda = 358$ nm when the concentration was lower than 10 mg/L and by volumetry for higher values. Colorimetry was the technique used to detect the presence of chromium(VI) in the original effluent and in the ES_i [31]. Sodium was measured by atomic emission (AE) with an air-acetylene flame at $\lambda = 589$ nm. The AA/AE evaluations were performed using a Jarrell Ash instrument. Chloride was quantified by the Mohr volumetric method with silver nitrate. The sulfate analysis was conducted by gravimetry, and barium chloride was added for precipitation [32].

Organic nitrogen was estimated by the Kjeldahl method (NOK), whereas the quantity of proteinaceous materials was calculated by multiplying the NOK by a specific conversion factor (5.51). The fat content was determined by means of dichloromethane extraction and solvent evaporation at 40-60°C until a constant weight was achieved [33]. The chromium(III) species in solution were identified by their absorption spectra (300-700 nm) with a Hewlett Packard 8453 spectrophotometer. The pH was measured on a Radiometer PHM201 pH meter equipped with a pHC3005 combined electrode.

3. Results and Discussion

3.1. Proteinaceous Materials and Fats

Proteinaceous materials (very small skin pieces together with denatured proteins) and fats become detached during the tannage process. The initial raw material for the manufacture of leather is the animal skin; from a histological perspective, its main compo-

ment is collagen. Such substance is composed of three polymeric chains of different amino acids in the shape of a triple helix. In contact with water, it is denatured, loses the original biological features and is divided into smaller fragments. The size of the particles formed is less than 150 nm. Regarding fats, once dried they are very difficult to remove, even by vigorous chemical treatments.

Exploratory tests revealed that the yield of the separation decreased by almost 3% in the presence of the above-mentioned organic constituents. This behavior was attributed to the fact that their dimensions prevented the access of chromium(III) to the active sites of the adsorbent. In order to improve the efficiency of this technique and avoid those materials that are detrimental to the reuse of AC, it was decided to aim at the highest elimination rate of such compounds. The original sample had 1.33 g/L proteinaceous materials and 1.18 g/L fats. After sieving, both contents decreased to 0.76 g/L and 0.53 g/L, respectively. The pretreatment was completed with ultrafiltration, and the final composition of the tanning wastewater is listed in Table 1.

3.2. Removal of Chromium(III)

Since chromium(III) binds to collagen at a temperature that does not exceed 40-50°C [34, 35], decontamination was carried out below such thermal values. Then, the isotherms on AC were determined at 20, 30, and 40°C with the liquid effluent mostly free of proteinaceous materials and fats (Fig. 1). By means of previous experiments, it was established that the suspensions remained homogeneous for stirring speeds between 100 and 180 rpm, whereas all solutions (D_1 - D_9) reached the equilibrium within 60 min. In our system, the three curves showed an infrequent evolution for the type of function they represent [18]. The region corresponding to very low equilibrium concentrations displayed sudden increases in chromium(III) uptake. Such percentages decreased gradually in more concentrated ES.

The pH in the successive aliquots before (D_1 - D_9) and after (ES_1 - ES_9) the tests at 40°C was determined in order to collect new evidence on the mechanism by which removal occurs (Fig. 2). The measurements were reported without corrections to compensate for the very different concentrations (ionic strength) of the solutes present in each case. The higher pH of the ES_i compared to the initial values indicated that, besides chromium(III), there was also a significant retention of H^+ . This fact would only be explained by its adsorption on the negatively charged surface of the AC (π -electrons) [20, 24, 25].

As the H^+ content in the medium decreases, the insertion of hydroxyl groups into the chromium(III) coordination sphere increases. The OH^- participates as a ligand of the complex ion; consequently, its electric charge tends to be neutralized. From a practical point of view, this group is a bridge between two chromium(III) cations. The continuation of this polymerization reaction reduces the solubility of the resulting species. The formate anion $HCOO^-$, coming from the complexing agent dissociation, is exchanged by the water ligand present in the chromium(III) dimer. Due to its stabilizing effect [35, 36], no phase change occurred at a high pH, as expected. After maintaining all the ES_i 's at rest for seven days, chromium(III) precipitation took place in the five samples with less residual acidity (ES_1 - ES_5).

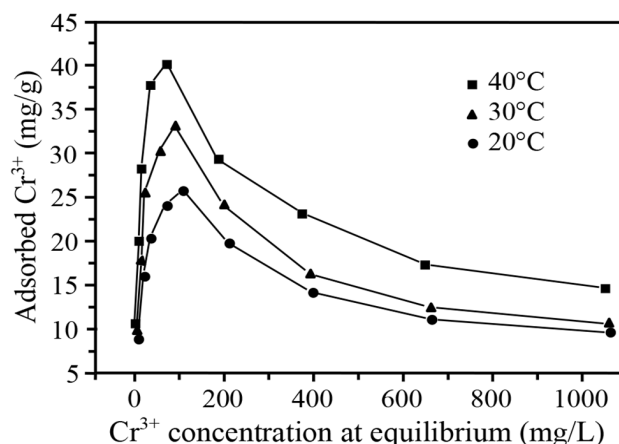


Fig. 1. Chromium(III) adsorption isotherms on activated carbon from tanning wastewater.

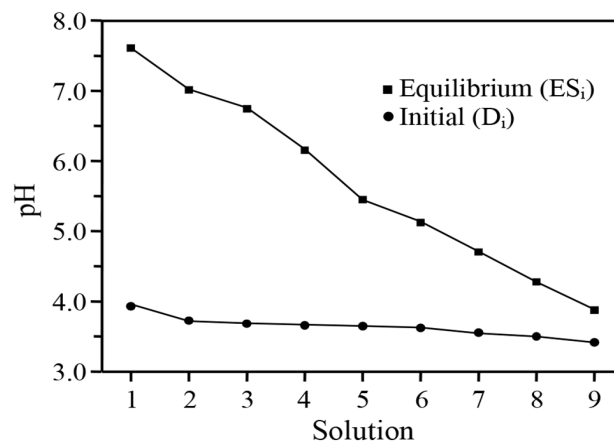


Fig. 2. pH of initial (D_i) and equilibrium (ES_i) solutions for the tests carried out at 40°C.

Absorption spectrophotometry in the 300-700 nm range of electromagnetic radiation is a simple technique that makes it possible to establish differences in the molecular structure of soluble substances. For Cr^{3+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$), visible bands are obtained because the 3d electrons move from their three orbitals of the lower energy subset to others of higher energy [37-40]. By means of a simple measurement, it was established that for $[Cr(H_2O)_6]^{3+}$ the above-mentioned d-d transitions should occur at 575 nm (~ 207 kJ/mol), 403 nm (~ 296 kJ/mol), and 270 nm (~ 442 kJ/mol) [37]. The last of these peaks is within the ultraviolet region. The remaining ions in the liquid effluent (sodium, chloride, sulfate) have more stable electronic configurations and maintain an unchanging baseline.

Fig. 3 shows the absorption spectra of ES_7 (375 mg/L) and ES_9 (1,053 mg/L) obtained from the tests at 40°C, together with that of the tanning wastewater (1,090 mg/L). In such curves, the two bands are shifted towards longer wavelengths compared to hexaaquachromium(III) $[Cr(H_2O)_6]^{3+}$, a response attributed to the fact that in all these systems the electronic structure of the cation would be a dimer $[(H_2O)_3Cr(OH)(SO_4)(OH)Cr(H_2O)_3]^{2+}$ [36]. As

regards ES₇ and ES₉, both peaks were only slightly displaced with respect to the initial effluent. This behavior would confirm that only minor alterations occurred in the conformation of the polymer after the adsorption on AC. In solutions ES₁-ES₆, the position of the maximums could not be established, because the chromium(III) complex ion was diluted. The loss of resolution was observed between ES₅ (73 mg/L) and ES₇ (375 mg/L).

The above-mentioned inconvenience was avoided by preparing a more concentrated solution whose pH was similar to that of ES₅ (maximum Cr³⁺ adsorption). The synthesis was performed by adding increasing quantities of sodium carbonate to D₉. In each case, the suspension was stirred for 60 min at 40°C, filtered through No. 40 Whatman paper, and the pH of the resulting liquid was measured. A value of 5.18, fairly close to that of ES₆ (5.14) and lower than in ES₅ (5.45), was achieved after pouring 1,600 mg/L of salt (~694 mg/L sodium). This dose was small compared to the 11,100 mg/L contained initially; therefore, the proportion of all constituents was almost unaltered. The first band of the replicated sample spectrum (Fig. 3) showed a highly flattened sector between 350 and 395 nm, so the position of the maximum could not be established. Furthermore, the second peak moved towards a shorter wavelength. The characteristics described confirm that the transformation of the chromium(III) dimer occurred due to the residual acidity of the medium. Then, it can be stated that the adsorption isotherms do not originate from a single species, which would explain the irregular shape determined.

The maximum chromium(III) uptakes were obtained with D₅: 40.2 mg/g at 40°C; 33.1 mg/g at 30°C; and 25.8 mg/g at 20°C. Consequently, the retention capacity of the adsorbent increased with temperature. Likewise, the cation concentration in the ES also decreased with a similar trend. The lowest value for the three thermal records tested corresponded to ES₁: 3.9 mg/L at 40°C; 5.6 mg/L at 30°C; and 8.1 mg/L at 20°C. These removal rates indicate that even the minimum content duplicates the 2.00 mg/L limit allowed for effluent discharge into the environment. The process yield was similar to that of other materials, but quite lower than those obtained with the two biomaterials that showed greater efficacy [27].

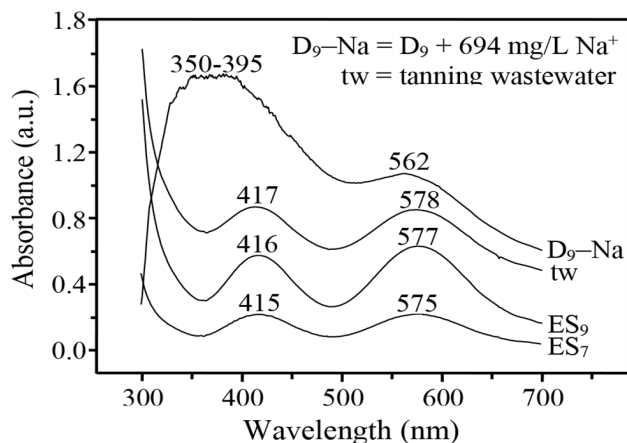


Fig. 3. Absorption spectra of equilibrium solutions ES₇, ES₉, of the tanning wastewater (tw), and of the solution D₉ with the addition of 694 mg/L sodium.

Initially, it was thought that the adsorption on AC could be due to an ion exchange mechanism with the participation of surface functional groups of a weak acid ($2 \text{ R-COOH} + [\text{Cr}_2(\text{OH})_2\text{SO}_4]^{2+} \rightarrow (\text{R-COO})_2[\text{Cr}_2(\text{OH})_2\text{SO}_4] + 2 \text{ H}^+$). Such an opinion was discarded because, if this were the reason, the medium pH should decrease as a consequence of proton release. On the other hand, the 40.2 mg/g (2.42 meq/g) of adsorbed chromium(III) cannot be explained on the basis of the 0.51 meq/g of acid sites determined in the adsorbent used. This suggests that the tanning agent-AC interaction would mainly occur through the basic sites. That is, π -d complexes between delocalized π electrons in aromatic structures and cations are formed [19-25]. According to these results, the Boehm method is considered more effective than the point of zero charge (PZC) measurement to quantify the adsorbent performance [14, 25].

3.3. Langmuir, Temkin, and Freundlich Models

An adsorption isotherm describes the ratio between the retained mass of a substance and its equilibrium concentration at constant temperature. The quantitative evaluation of our experimental results was carried out with the Langmuir, Temkin, and Freundlich isotherms [41-44]. The first of these models was originally developed to describe gaseous uptake on homogenous surfaces containing a finite number of active contact points (all are equivalent), but it also proved its efficacy in the analysis of solid-liquid systems. In its formulation, it was assumed that the adsorbed molecules do not interact with each other and that there is no steric hindrance either, such that

$$qe = \frac{K_L qm Ceq}{1 + K_L Ceq} \quad (1)$$

where qe is the adsorbed quantity of chromium(III) per gram of AC (mg/g), K_L is the Langmuir constant (L/mg), qm is the maximum adsorbed quantity of the complex ion in a monolayer (mg/g), and Ceq is the cation concentration (mg/L) in the ES. For its application, K_L must not to change in the entire range of concentrations studied. The inverse of Eq. (1) and the rearrangement of its terms make it possible to obtain the following linear mathematical expression:

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{K_L qm Ceq} \quad (2)$$

When the hypothesis is satisfied, $1/qe$ versus $1/Ceq$ is a straight line. The qm value is the inverse of the interception, and the equilibrium constant K_L is calculated from the slope ($1/K_L qm$) of this representation. As the concentration of the adsorbate in the liquid phase increases, a larger surface of the adsorbent is covered. The phenomenon continues until every active site in the solid is occupied, reaching a dynamic equilibrium at this point.

Some of the above-mentioned restrictions were considered in the Temkin model (Temkin and Pyzhev). Basically, this model takes into consideration the adsorbent-adsorbate interactions and it also indicates that the adsorption heat of the entire layer would decrease linearly as the surface is saturated. The linear form of the equation is

$$qe = \frac{RT}{b_T} \ln A + \frac{RT}{b_T} \ln Ceq \quad (3)$$

where A is the equilibrium binding constant (L/g), b_T is the Temkin constant related to the adsorption heat (J/mol), R is the gas constant (8.31 J/Kmol), T is the temperature in K, and the remaining terms have already been defined. A and b_T are obtained from the intercept and slope of the line qe as a function of $\ln Ceq$.

The evaluation of the isotherms was completed with the Freundlich model, which describes nonideal, reversible multilayer adsorption on heterogeneous surfaces. In such proposal, the mass of a retained substance is proportional to its concentration in the aqueous phase, even though it shows significant deviations for high solute contents,

$$qe = K_F Ceq^{1/n} \quad (4)$$

where qe (mg/g)- Ceq (mg/L) have the same meaning as in Eq. (1)-(3), K_F (mg/g/(mg/L)^{1/n}) is the Freundlich constant, and n is an empirical coefficient whose value is generally higher than 1 [19, 20, 44]. Its resolution is done by applying the logarithm

$$\ln qe = \ln K_F + \frac{1}{n} \ln Ceq \quad (5)$$

The intercept and the slope of line $\ln qe$ versus $\ln Ceq$ correspond to $\ln K_F$ and $1/n$, respectively. Table 2 includes the characteristic parameters of Langmuir, Temkin, and Freundlich for the three adsorption isotherms. The calculation was carried out with the five lowest equilibrium concentrations for each temperature, since no satisfactory agreements were achieved when higher values were included. The linearity of the curves was verified by the least squares method. In this way, it was established that the system fits more precisely the expression formulated by Langmuir. In other words, it is the one that best matches the experimental data. Besides, Temkin parameters (Table 2) indicate that the thermal

Table 2. Characteristic Parameters of Langmuir, Temkin, and Freundlich for the Chromium(III) Adsorption Isotherms on Activated Carbon

Parameters of each model	Temperature (°C)		
	20	30	40
Langmuir			
K_L (L/mg)	0.049	0.053	0.059
qm (mg/g)	31.6	41.3	54.2
r^2	0.998	0.984	0.994
Temkin			
A (L/g)	0.53	0.58	0.69
b_T (J/mol)	368	289	238
r^2	0.980	0.943	0.952
Freundlich			
K_F (mg/g/(mg/L) ^{1/n})	4.266	5.104	6.316
n	2.459	2.258	2.112
r^2	0.915	0.884	0.884

Table 3. R Values as a Function of the Temperature (T) and Initial Chromium(III) Concentration (C_{Cr0}) Allowing the Assessment of Langmuir Isotherm

T (°C)	R	
	$C_{Cr0} = 30$ mg/L	$C_{Cr0} = 1,090$ mg/L
20	0.405	0.0184
30	0.386	0.0170
40	0.361	0.0153

requirement (b_T) to perform the removal decreases with temperature, and based on the information that A (0.53 L/g-20°C; 0.58 L/g-30°C; 0.69 L/g-40°C) is lower than 8 L/g, the process can be qualified as of a physical nature [42].

It is known that Langmuir isotherms can be analyzed in terms of a "constant separation factor" or "equilibrium parameter" R [41, 45], which is defined as

$$R = \frac{1}{1 + K_L C_{Cr0}} \quad (6)$$

where C_{Cr0} is the initial chromium(III) concentration. Four possible cases can be recognized: favorable ($0 < R < 1$), unfavorable ($R > 1$), irreversible ($R = 0$), and linear ($R = 1$). The R 's determined are between 0 and 1 (Table 3), which confirms that adsorption occurs favorably in our operational conditions.

3.4. Removal of Sulfate, Sodium, and Chloride

The adsorptions of sulfate, sodium, chloride, and chromium(III) on activated carbon at 40°C for AC₁ (lowest Cr³⁺ concentration in an ES), AC₅ (highest Cr³⁺ adsorption), and AC₉ (highest Cr³⁺ concentration in an ES) are listed in Table 4.

The net surface electric charge of the adsorbent is negative (prevalence of basic sites); for this reason, it was assumed that sulfate binding would not be significant. However, the opposite was the case and a possible explanation would be that, for the range of equilibrium concentrations studied, the anion followed a similar trend to that of the tanning agent. This response would be explained if SO₄²⁻ was part of the chromium(III) complex ions with positive charges [34] and these cationic units were mostly retained on the surface of the solid. According to the interaction model described, the chromium:sulfate ratio was 4.20 (10.5/2.5) for AC₁; 3.76 (40.2/10.7) for AC₅; and 1.93 (14.7/7.6) for AC₉. Such results confirm that the chemical composition of the chromium(III)-bearing species changed, as was determined by visible spectrophotometry.

Table 4. Quantities of Chromium(III), Sulfate, Sodium, and Chloride Adsorbed at 40°C on Activated Carbon

Component (mg/g)	Activated carbon		
	AC ₁	AC ₅	AC ₉
Chromium(III)	10.5	40.2	14.7
Sulfate	2.5	10.7	7.6
Sodium	0.5	0.6	0.6
Chloride	0.7	0.8	0.9

At a low pH, certain adsorbed electropositive ions were partially dehydrated [46]. This led us to think that a fraction of the water in each hydrate was replaced by the negative electric charge of the adsorbent. Then, the ionic radii of chromium(III) (0.069 nm) and sodium (0.098 nm) would approximately show the distances to the points of contact on the interfacial plane. The attraction force between the AC and the cation decreases proportionally with the square of the distance at which the particle is (Coulomb's law). The difference between the inverses of the referred sizes raised to the second power ($1/0.069^2 = 210.0$ and $1/0.098^2 = 104.1$) is a possible explanation for the unequal uptake.

Retentions of chloride and sodium were similar, even though both monovalent ions have negative and positive electric charges, respectively. Chloride, unlike sulfate, is not a chromium(III) ligand found in compounds that are commonly present in tanning wastewater [35, 36]. To remove those substances that were not effectively bound and thus be able to guarantee a reliable value in the quantitative determination, the solid was washed with abundant distilled water before the chemical analysis. If, in addition, it is taken into account that the adsorbent and the chloride have a negative electric charge, it can be suggested that the anion would be fixed to the sodium initially retained on the AC.

3.5. Chromium(III) Elution with Sulfuric Acid

The reagent was chosen in order to evaluate the efficacy of the procedure to reuse the tanning agent. Various solid (g)/eluant (L) ratios were tested, and it was established that 333.3 was the most convenient. A high value makes stirring difficult and a low one dilutes the species desorbed. The contact time was chosen arbitrarily so that it matched the adsorption time (60 min) and under such operational conditions, it was necessary to raise the temperature up to 70°C. Even though this decision is inconsistent with the proposal to decontaminate at 40°C, in the end it was adopted, as the volume at this stage is considerably lower than at the previous one.

AC loaded with ~40 mg of Cr^{3+} /g was slowly poured into the acid solution, under vigorous shaking. Different H_2SO_4 concentrations were tested: 0.8; 0.9; 1.0; and 2.0 N. The sulfate content varied greatly with eluant normality, while the other ions remained constant. The chromium(III) recovery was higher than 98.0% for ≥ 1.0 N; below this acidity it began to decrease. The yield for 0.9 N was 96.5%; the solution thus obtained had the following chemical composition: 13.23 g/L chromium(III); 42.98 g/L sulfate; 0.16 g/L sodium; and 0.24 g/L chloride.

The $\text{Cr}/\text{SO}_4^{2-}$ ratio (13.23/42.98) was quite similar to the one that both ions have in $\text{Cr}_2(\text{SO}_4)_3$ 13.23/36.64. A concentration of 0.8 N or less becomes ineffective to perform the desorption. Compared with the starting effluent, it can be observed that the presence of NaCl decreased significantly, whereas that of sulfate increased almost four times. Consequently, the process described is suitable to retrieve a relatively pure chromium(III) salt from the wastewater. When our results are compared with those of other metals, we see that they are one of the highest [29].

Finally, the resulting AC capacity was analyzed. For that purpose, its surface functional groups were evaluated with the same methodology used for the physical and chemical characterization of the original material: 0.50 meq/g of acid sites (initial = 0.51

meq/g) and 0.05 meq/g of basic sites (initial = 2.51 meq/g). The foregoing shows that the solid contact points were only partially released. With the adsorbent regenerated and D_9 , a new test at 40°C was performed. Under these conditions, retention was less than 1/3 of the one displayed in Fig. 1. This behavior has not usually been reported in studies conducted with such technique [27, 29].

4. Conclusions

- A procedure was implemented to remove and recover the chromium(III) dissolved in a tanning wastewater. The route proposed comprises adsorption on activated carbon and elution with sulfuric acid.
- It was established that the chromium(III) adsorption isotherms at 20, 30, and 40°C on activated carbon had an irregular shape depending on the equilibrium concentration. The three curves showed a similar tendency, with a very fast initial increase in the quantity of cation uptaken. After reaching the maximum, they appreciably decreased as the tanning agent content in the equilibrium solutions was larger.
- Chromium(III) adsorption rose significantly with the temperature: 25.8 mg/g at 20°C; 33.1 mg/g at 30°C; and 40.2 mg/g at 40°C. The lowest cation contents in the respective equilibrium solutions were: 8.1 mg/L at 20°C, 5.6 mg/L at 30°C, and 3.9 mg/L at 40°C.
- It was determined that protons were also adsorbed, substantially increasing the pH of the liquid medium. Such a change affects the chemical composition of the chromium(III) complex ion and its electric charge, which explains the unusual representation of the isotherms.
- The Langmuir model allowed a better fit of the experimental data than the Temkin and Freundlich models.
- Sulfate retention was much lower than that of chromium(III), obtaining the maximum of 10.7 mg/g at 40°C. Sodium and chloride adsorptions were minimal. In summary, the process used was very efficient only for the removal of the tanning agent.
- It was found that the chromium(III) species bound on activated carbon were redissolved with sulfuric acid at 70°C. The tanning agent recovery depends on the eluant concentration. Adjusting its acidity to 0.9 N favored the formation of $\text{Cr}_2(\text{SO}_4)_3$ with a minimum content of SO_4^{2-} and NaCl.
- After chromium(III) desorption, the adsorbent cannot be reused since its basic sites remain inactive.

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