

Removal of Chromium Cr(Vi) of Tanning Effluent with Activated Carbon from Tannery Solid Wastes

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Abstract: This study offers an integrated process for treatment and recycling of tannery waste, it has a dual purpose. First the activated carbon (AC) has been prepared from leather shaving (LS) and goat hair (GH) by physical activation. Both the raw material and the prepared activated carbon were analyzed by DTG, TGA, and SEM. The adsorption tests of methylene blue (MB) and iodine onto the raw material and the prepared adsorbent were carried out and it was found that the adsorption capacity of the activated carbon was enhanced by the physical activation. The AC was then characterized by BET surface area and Fourier transform infrared spectroscopy (FTIR). The BET surface area was found to be 491.05 and 242.60 m²/g for ACs prepared from LS and GH respectively and the functional groups on the adsorbent surface were mainly CN, NH, OH, CO and CS. Secondly, the performance of the prepared AC was assessed by adsorption of chrome (VI) from a synthetic solution, and then the chrome (III) present in the tanning effluent. The results revealed a decrease of chromium by 78% and 73% for the activated carbons prepared from (LS) and (GH), respectively.

Keywords: Leather Shaving, Tannery, Activated Carbon, Adsorption, Chrome

1. Introduction

Tanneries industries generate a lot of waste that has negative impact on the environment and human health. The threat is the dumping of its solid and liquid waste that contains dangerous leftovers such as proteinaceous colloids, fats, tannins, flesh and hair, as well as toxic elements such as sulfides and chromium. All these "tailings" are a source of pollution and wastage that the leather industry cannot afford specially during this crisis period that lasted for several years, and is going from bad to worse. Note that 4 million tons of solid wastes per year are released by the global tanning industry [1]. According to some estimations, approximately 0.8 million tons of chromium are generated by tanning industry annually worldwide [2]. For the city of Marrakech (Morocco) pollution by the tannery industry due to the release of heavy metals in the environment, mainly

chromium, is estimated at 40 tons of chromium generated per year, which can easily result in disrupting the biological degradation of effluent [3]. When chromium Cr (III) is released in the nature, it is oxidized to hexavalent chromium Cr (VI) form which is known to be both acutely and chronically toxic to human, even when present in low concentrations. This form of chromium Cr (VI) has been considered as one of the sixteen most toxic pollutants. It is therefore important to remove both Cr (III) and Cr (VI) from the contaminated water before it is discharged.

In recent years adsorption process has been widely used for the treatment of the tanneries wastes. For instance chromium-collagen wastes were used to remove tannins from wastewater [2], the diatom *Planothidium lanceolatum* (Brébisson) Lange-Bertalot (*P. lanceolatum*) was used for

biosorption of hexavalent chromium [Cr (VI)] from aqueous solutions [3], powder of potato peelings [4] and an activated carbon prepared from coconut tree sawdust [5] were also used as adsorbents for removal of chromium [Cr (VI)] from aqueous solution, while leather waste was employed as adsorbent to remove dye from solution [6]. In this work, the solid waste from the tanneries is transformed into active carbon in order to enhance its adsorbent capacity for the chromium (VI) ions removal. Activated carbon is a carbonaceous material with highly developed internal surface area and porosity; it is widely used in industries for air and water treatment, in medicine as anti-toxin and in research as a catalyst and support to catalysts [7]. The use of activated carbon to remove chromium from tanneries wastewater is an effective method for removing chromium ions from aqueous solution before disposal.

In this study, the waste of leather shaving (LS) and goat hair (GH) from a traditional tannery "Bab Lakhmiss" in Marrakech (Morocco) was transformed into activated carbons, which were then used for adsorption of chromium ions from tanneries wastewater. The adsorption capacity of the carbons prepared was also investigated.

2. Materials and Methods

2.1. Raw Material

The tannery wastes used in this study were obtained from a traditional tannery in Marrakech figure 1. Before the experiments of carbonization, the wastes LS and the GH was cut into small pieces, washed with a distilled water under stirring for one day, and finally dried in an oven at 105°C until reaching constant weight.

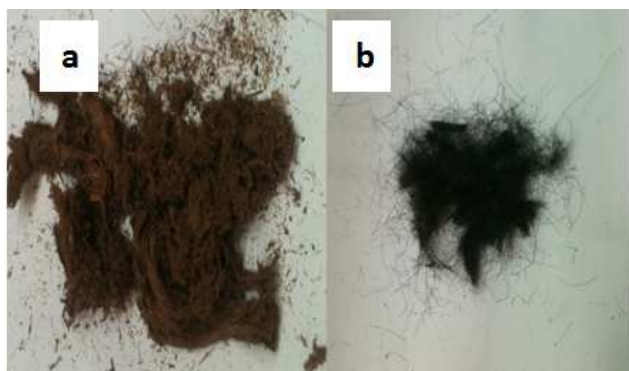


Figure 1. Leather shaving (a) and goat hair (b) extract from effluents of a traditional tannery "Bab Lakhmiss" in Marrakech (Morocco).

2.2. Experimental Procedure of Manufacturing Activated Carbon

10 g sample of raw material is placed in a sample holder that is put in the oven. It is brought under a nitrogen flow of 100 mL/min at a heating rate of 15°C/min to a temperature of 500°C which is maintained for 60 min as residence time. After carbonization, the activation process is carried out under a nitrogen flow of 100 mL/min, with a heating rate of

10°C/min to reach the desired activation temperature, and then the sample is placed under steam flow rate of 0.1 mL/min, which was maintained for the desired residence time. Activated carbon is recovered, washed with distilled water for 12 hours to remove the ash, then dried, weighed, ground and kept for adsorption tests. The total yield of sample is calculated by the following equation:

$$Yield = \left(\frac{m}{M} \right) \times 100 \quad (1)$$

where M (g) is the mass of the raw material, m (g) is the mass of obtained AC.

2.3. Characterization Method

DTG and TGA analyses were performed on the raw material with a temperature between 25 and 850°C. High-resolution images of the raw material were obtained by the scanning electron microscope (SEM).

The textural characteristics of the selected samples of ACs prepared were obtained using adsorption/desorption of nitrogen at 77 K. The surface area and pores sizes were calculated by the equation of Brunauer-Emmett-Teller (BET). The surface morphology of the selected active carbons was obtained using the scanning electron microscope (SEM). The functional groups of the selected active carbons were analyzed by Fourier transforms infrared spectroscopy (FTIR).

2.4. Adsorption Experiment

2.4.1. Iodine and Methylene Blue

The ability of the AC prepared to remove iodine and methylene blue from a synthetic aqueous solution was determined. Standard iodine solution was added over activated carbon (10 mg) and after an equilibration time of 4 h, the residual iodine concentration was determined by titration with standard sodium thiosulfate using starch as an indicator. The same quantity of carbon samples were mixed with methylene blue MB in 100 mL stoppered Erlenmeyer flasks. Batch adsorption experiments were carried out in the shaker (200 rpm) at room temperature for 4 h. The solutions were filtered and the concentration of methylene blue was determined by UV spectrophotometer (660 nm). The AC with improved adsorption capacity of MB and iodine was then chosen in order to finally test for adsorption with respect to chromium (VI) and chromium (III).

2.4.2. Adsorption of Chromium (VI) and Tannery Effluent (Cr (III))

Batch adsorption studies for the removal of chromium (VI) by AC prepared from LS and GH were conducted to determine pH effect and were performed by mixing 0.01 g of AC with 100 mL of synthetic solution of chromium (VI) in 250mL bottles that were left under stirring for 4 hours at 30°C.

For chromium (VI), at the end of stirring the filtrates were analyzed by reaction with 1,5-diphenylcarbazide monitored by measuring absorbance at 540 nm using a UV-visible

spectrophotometer.

For the chromium (III) tanning raw effluent samples, a treatment was specifically performed to separate out particles present in liquid phase by filtering on filter paper. After the separation process the aqueous solutions were analyzed to determine the concentration of chromium and were then subjected to adsorption in the same conditions as those applied for the synthetic solution of chromium. All the adsorption experiments were conducted at 18°C and the samples shaken at the rate of 200 rpm. For all the tests the adsorption capacity is calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (2)$$

where C_0 (mg/L) is the initial concentration of adsorbate (Methylene blue, Iodine and Chromium Cr(VI)), C_e (mg/L) is equilibrium residual concentration of Methylene blue, Iodine and Chromium in solution, V is volume of solution (L), and w (g) is mass of the selected AC.

3. Results and Discussion

3.1. Analysis of Raw Material

3.1.1. DTG and TGA Analyses

TGA analysis indicated thermal events associated with the mass change between 25-850°C, figure 2a. For LS it shows a first variation between 40.5 to 175°C which corresponds to a decrease in mass of 7.6%, due to evaporation of water. The weight loss was more significant from temperature 175.5 to 631°C; this is due to removal of volatile organic substances and moisture, with a weight loss of 52.1%. Beyond 631°C the mass varies slightly depending on the temperature. For DTG analysis, figure 2b, which is a thermal analysis technique to measure the endothermic and exothermic transitions as a function of the temperature, the analysis shows a peak between 38 to 318.7°C which corresponds to a first departure of water according to an endothermic reaction ($\Delta H = 693.5$ J / g), then the start of release of volatile organic materials according to an endothermic reaction ($\Delta H = 617$ J / g). For GH, the TGA curve (figure 2a) shows that the bristles have two events characteristic of mass loss, due to the thermal behavior of the material. The first event is observed between 42.5 to 183°C, which is due to the release of water and a mass loss due to the degradation of hair microfibers with a loss of 9.3%. The second loss observed between 185 to 571.98°C is due to the degradation of hair, which leads to a carbon chain of keratin with a loss of 55.5%. Complete degradation of the keratin and hair structure happens at 700°C [5, 6]. For DTG analysis, figure 2b, the first degradation is related to the loss of water as well as organic matter, it takes place according to an endothermic reaction ($\Delta H = 816.214$ J/g) followed by another endothermic reaction ($\Delta H = 330.411$ J/g) due to the degradation of hair microfibers.

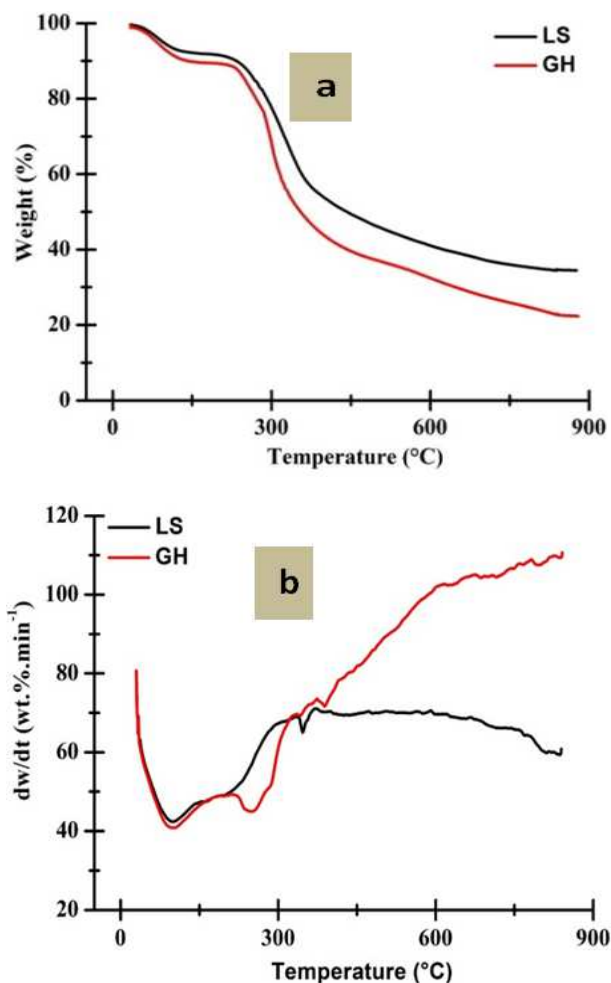


Figure 2. TGA/DTG curves of an untreated leather shaving and goat hair; a is TGA and b is DTA of both raw materials before transformation into activated carbon.

3.1.2. Adsorption Analysis on Raw Materials

The adsorption capacities of the raw materials towards iodine and MB are shown in table 2. The results show that adsorption occurred at the surface of the both raw materials possibly on the functional group available at the surface of LS and GH, for example $-CO-$, $-CO-NH-$, and $-NH_2$. This can explain the low values of MB and iodine found for LS and GH. The transformation of these raw materials into AC is expected to enhance the adsorption capacity by creating porous sites and more functional groups at the surface.

3.2. Preparation and Characterization of AC

3.2.1. Yield Analysis of AC

Tables 1 and 2 present the conditions (final temperature, residence time, and yield) of preparation ACs. Analysis of the AC from LS (table 1) shows that the increase in temperature from 750°C to 850°C with a fixed residence time is accompanied by a decrease in the final yield. Leaving the temperature fixed, the yield decreases with increasing residence time (activation) from 60 min to 90 min. It can be concluded that the increase in the temperature and the residence time leads to a decrease in the final yield, due to

the intensification of gasification reactions and therefore the loss in weight of the obtained carbon. It is known that the lower the yield, the more microporous is the adsorbent and the higher the specific surface area. The analysis of GH yields (table 2) shows that the increase of residence time (activation) from 30 to 60 min led to a decrease in the final yield; leaving the residence time (activation) fixed, increasing of temperature from 750°C to 800°C does not lead to a large change in performance. This leads to the conclusion that with these conditions of AC preparation from GH, the performance is mainly controlled by the residence time (activation) caused by the reactions of carbon with the

oxidizing medium.

Table 1. Preparation parameters and adsorption capacity of Methylene Blue and Iodine for activated carbon from LS.

Samples	Final temperature (°C)	Residence time (mn)	Final yield	Q _{ADS} MB (mg/g)	Q _{ADS} I ₂ (mg/g)
LS				110.4	586.9
AC ₁	750	60	15.22	387.7	576.53
AC ₂	750	90	11.35	583.4	610.28
AC ₃	850	60	10.14	450.2	706.89
AC ₄	850	90	4.7	505.35	190.36

Table 2. Preparation parameters and adsorption capacities of Methylene Blue and Iodine for activated carbons from GH.

Samples	Final temperature(°C)	Residence time (mn)	Final yield	Q _{ADS} MB (mg/g)	Q _{ADS} I ₂ (mg/g)
GH				218.1	80.7
AC ₅	750	30	17.16	278.1	613.27
AC ₆	750	60	12.3	385	694.8
AC ₇	800	30	17.85	345	645.31
AC ₈	800	60	11.84	392.95	190.4

3.2.2. Adsorption Tests for MB and Iodine

(i) Tests for MB

The results obtained for AC from LS are summarized in table 1. It can be observed that the adsorbed amount increases generally with increase of residence time of activation, and also increases with increasing temperature. According to Fiessinger *et al.*[7, 8] and Wiesner *et al.*[9], adsorption of organic compound mainly concern mesopores and macropores, then the enhancement of residence time and temperature increases the pore diameter. It can be noticed that the amount of MB adsorbed increases significantly when the raw materials are transformed into AC.

(ii) Tests for Iodine

The influence of activation temperature and the activation residence time are also examined for adsorption capacity of iodine. Results are shown in tables 1 and 2. It is clear that uptake of iodine in aqueous solution were improved during the transformation process of raw materials into ACs. However, in these tables, we observe for all the samples that the amount of iodine adsorbed increases significantly with increase of temperature and activation residence time during preparation, except for ACs obtained for temperature up to 800°C and the residence time equal to 90 min, AC₄ and AC₈ for which the iodine numbers are about 190 mg/g. For the sample prepared by the residence time less than or equal to 60 min the adsorption capacity is higher, meaning that ACs prepared contained an important amount of micropores. This can be attributed both to the structure of raw material and to the use of steam within the activation process; steam was observed to generate a narrow but more extensive microporosity.

The adsorption of MB and Iodine shows that the

transformation of raw materials into AC using steam generates micropores and mesopores, existing mesopores serving as gateway to micropores. For samples AC₄ and AC₈, increasing temperature and residence time widens micropores to give mesopores or macropores. Sample AC₃ and AC₆ show highest values of iodine; this allows us to calculate their surface area and pore volume using BET analysis, Table 3.

Table 3. BET analysis performed on activated carbons obtained from LS after physical activation at 850°C during 60 minutes AC₃ and activated carbon obtained from GH after physical activation at 750°C during 60 minutes AC₆.

Samples	Surface areas (m ² /g)	Total pore volume (cm ³ /g)
AC ₃	491.05	0.421
AC ₆	242.60	0.138

3.3. Analysis of AC₃ and AC₆

3.3.1. SEM, BET and IR Analyses

Typical SEM micrographs of the surfaces of AC₃ and AC₆ are illustrated in figure 3. The surface morphology of the carbon atoms shows that the carbon atoms of the surfaces are heterogeneous with an irregular pore structure. Pores of different sizes and forms have been observed in these images.

The IR spectra of activated carbons obtained from leather shaving (LS) and goat hair (GH) are superimposed and represented in figure 4. The IR spectra for AC from LS as well as from GH reveal the presence of characteristic band at (2420, 3430) cm⁻¹, which corresponds to NH or OH [10-13], while the bands located at 1460 cm⁻¹ and 1100 cm⁻¹ are attributed to C=C vibration and CO respectively, in relation to 2350 cm⁻¹ which corresponds to CN nitrile. But in the spectrum of AC from GH, there are also peaks at 594 cm⁻¹ and 870 cm⁻¹ corresponding to CS and aromatic CH respectively [13-16].

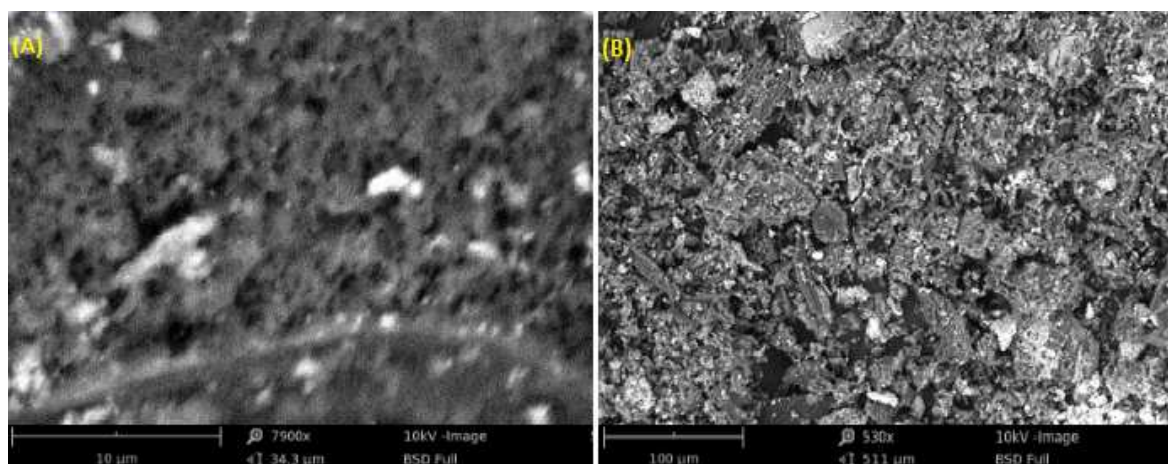


Figure 3. The SEM micrographs of activated carbon, (A) activated carbons obtained from LS after physical activation at 850°C during 60 minutes AC₃ and (B) activated carbon obtained from GH after physical activation at 750°C during 60 minutes AC₆.

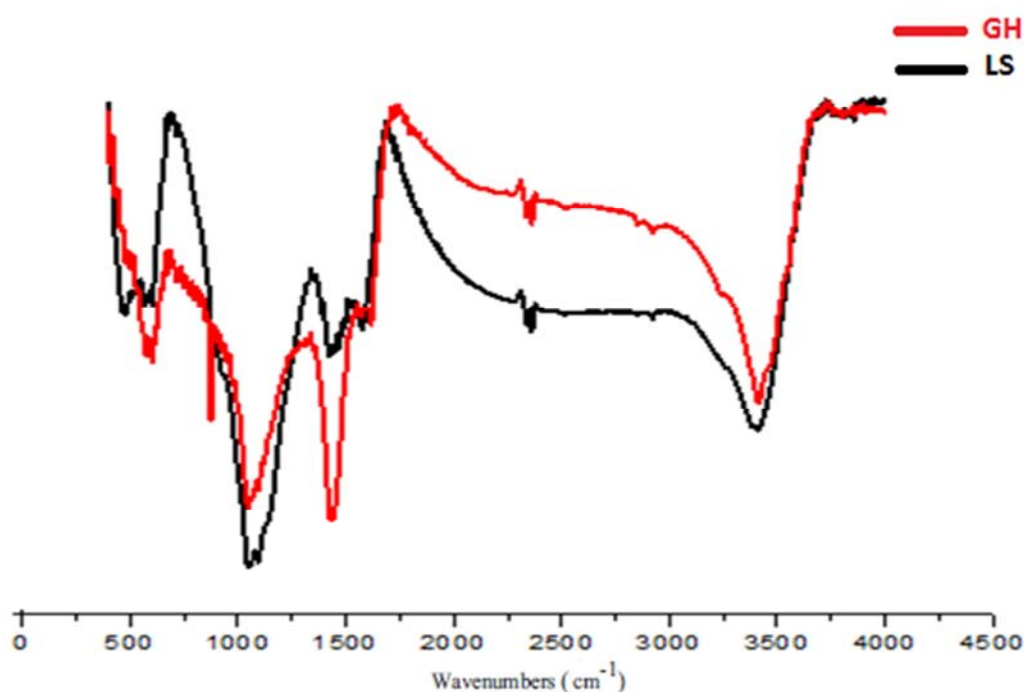


Figure 4. The FT-IR spectrum of activated carbons obtained from LS after physical activation at 850°C during 60 minutes AC₃ and activated carbon obtained from GH after physical activation at 750°C during 60 minutes AC₆ before Cr(VI) sorption.

3.3.2. Adsorption Cr (VI)

The curves given in figure 5 represent the change in the adsorbed amount (mg/g) as a function of pH. It can be noticed that the adsorbed amount increases with pH until a maximum value for the pH = 3 (57.71 mg/g for the AC from LS and 50.8 mg/g for the AC from the GH) and then declines at pH = 5, because the degree of protonation of the surface is reduced gradually, leading to the reduction of adsorption. In acidic medium, the surface of the adsorbent is highly protonated and promotes the adsorption of Cr (VI) in its anionic form. When the pH = 3 we find that the adsorption of the predominant form $\text{Cr}_2\text{O}_7^{2-}$ is important. This suggests that the adsorption cannot be

by electrostatic forces (physisorption) but rather by chemical forces via an electron exchange between the activated carbon and $\text{Cr}_2\text{O}_7^{2-}$ ion [17-19]. This leads according to Padaki Srinivas Rao et al. [20] to a reduction of chromium (VI) to chromium (III) by the catalytic action of carbon. Below pH = 3, we noticed a decrease in the amount adsorbed to a minimum value at pH = 1; the adsorption capacity was decreased by about 8 times, with the decrease of pH from 3 to 1. This decrease was attributed to the various complexes that Cr (VI) can form in aqueous solution. Under the acidic conditions (pH < 1.6), chromium is transformed in its neutral form H_2CrO_4 which decreases its adsorption capacity on the activated carbons.

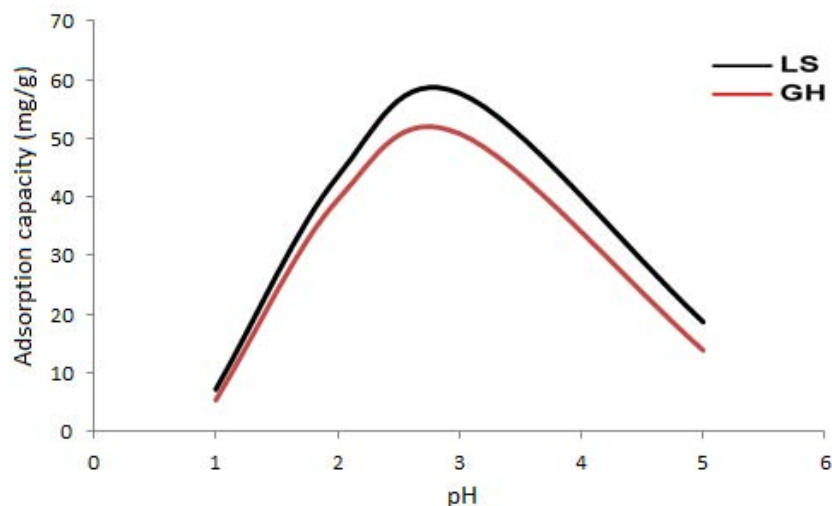


Figure 5. Effect of pH for the adsorption of Cr(VI) onto activated carbon prepared from LS and GH. Conditions: during 4 hours, 0.01g/250 mL, at 30°C.

3.3.3. Adsorption Cr (III) of the Effluent from Tannery

The completion of the adsorption tests on the solution of tannery effluent after treatment and oxidation of chromium (III) to chromium (VI), allowed us to find a concentration of 3.215 g/l with the spectrophotometer. This tannery effluent is discharged into the waste water after each chromium tanning operation.

In order to reduce the concentration of chromium in the effluent from tanneries, we realized the Protocol shown in figure 6. After treatment we got the adsorbed quantity and elimination rates. In the prevailing condition pH = 6, chromium is present in $\text{Cr}(\text{OH})_2$ form [21]. The latter is adsorbed on the activated carbon from LS which leads to a removal rate of 78%, and for AC from GH to a removal rate of 73%.

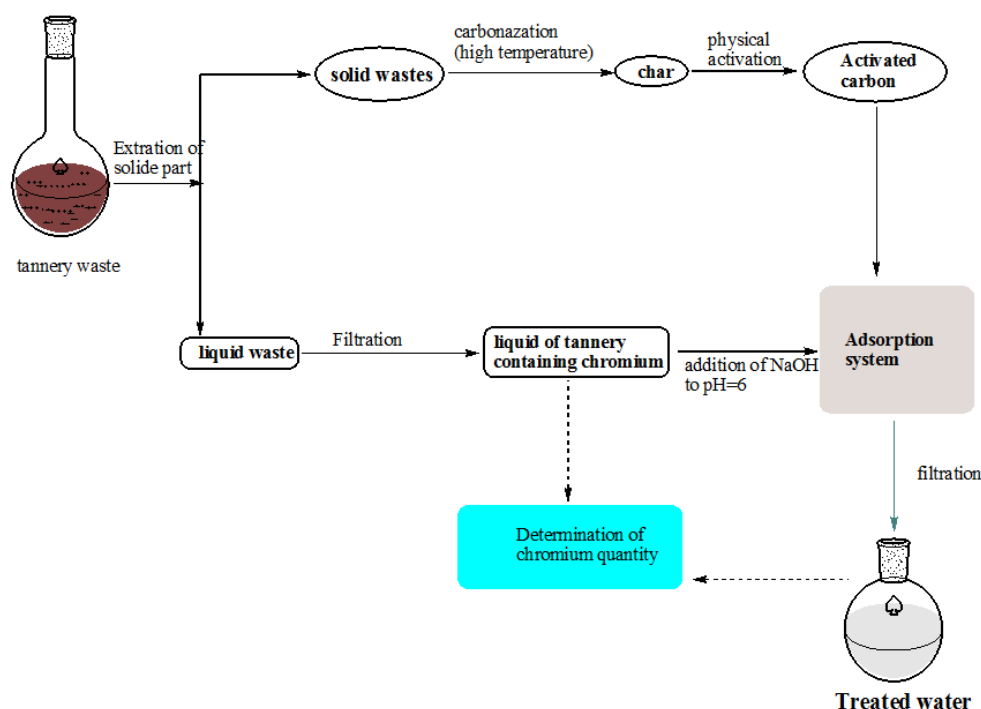


Figure 6. Schematic representation of the transformation of solid waste of tannery effluent into activated carbon and the removal of Cr(VI) from tannery effluent.

4. Conclusion

The adsorption tests showed that activated carbons prepared from the tannery wastes, are good adsorbents for methylene blue, iodine and Cr (VI). The protocol that we

presented for the removal of chromium (III) in the tannery effluent with the prepared activated carbon, has allowed us to eliminate 78% of the concentration of chromium (III) in the tannery effluent, this with the activated carbon based on the shaving leather, and 73% with the activated carbon based on the goat hair, with a surface that exposes various functional

groups responsible for the adsorption. Thus these tannery wastes can be valued by decreasing their accumulations in nature as pollutants, and also by transforming them into activated carbons in order to remove the pollutants or recover the metals accumulated in the wastewaters.

Authors' Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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