A COAGULATION-FLOCCULATION PROCESS COMBINED WITH ADSORPTION USING ACTIVATED CARBON OBTAINED FROM SLUDGE FOR DYE REMOVAL FROM TANNERY WASTEWATER

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ABSTRACT

Coagulation-flocculation (CF) process studies on aqueous solutions of Acid Black 210 dye (AB-210), were performed to investigate efficiency at different pH, coagulant and polyelectrolyte doses, and sedimentation times. In the adsorption studies of the dye removal, the initial pH and isotherms studies were performed using an activated carbon prepared by microwave-assisted pyrolysis of Tannery sludge. This adsorbent material was characterized by isotherms of N_2 adsorption-desorption and density functional theory. Finally, the efficiency of the combined process CF followed by adsorption, was shown using a synthetic effluent identical to that produced in the wet-end process of the leather industry in industrial equipment. Effluent was collected from each treatment bath and analyzed for its physical properties and by ion chromatography.

The best conditions found in CF processes were: pH 10.0, sedimentation time of 60 minutes, coagulant dose of 71 mg L^{-1} ($Al_2(SO_4)_3$) and dose of flocculant (polyelectrolyte FX AS1) of 0.090 mg L^{-1} In the adsorption processes, the equilibrium data were best fit to the Liu isotherm model, presenting the maximum sorption capacity (Q_{max}) for AB-210 of 974.7 mg g^{-1} at 303.15K at pH 2.0. Using the synthetic effluent, the combined CF followed by adsorption of AB-210 dye demonstrated a removal of 85.2%, indicating that the combined process is efficient for real wastewater treatment.

Keywords: adsorption, coagulation-flocculation, dyes, leather industry, wet-end process.

1. INTRODUCTION

Tanneries process animal hide/skin through some or all stages and steps of leather production. Tanneries can be classified by the kind of raw material (hide, fell or skin) and the type of the tanning system, which depends on the tanning substance (mineral or organic). Tanneries can be categorized, according to the stages of production, as follows [1]: (a) Complete tanneries, which start from raw hide (green or preserved) and produce finished leather; (b) Beamhouse tanneries, that process raw hide up to the tanning step; (c) Tanneries for leather wet-end and finishing, which start from leather (wet-blue) and produce crust or finished leather.

The wet-end process includes dyeing, which is a key process for the leather industry, because it gives the desired color and appeal to the leather [2]. Dyeing contamination contributes to the elevation of chemical oxygen demand of wastewaters. Even at low dye concentrations these substances change the color of the water significantly, causing aesthetic damage. Water contamination caused by dye-related industries is constantly threatening ecological equilibrium and human health, therefore wastewater treatment improvements are becoming increasingly urgent [3-4].

Coagulation of dye-containing wastewater has been used for many years as its main treatment or pretreatment, due to its low capital cost [5], and coagulants based on hydrolyzing metal salts such as aluminum are widely used. To improve coagulation, the addition of polymers as flocculant aids has been shown to enhance the effectiveness of dye removal by enlarging the size of flocs and consequently causing rapid settling. When inorganic coagulants destabilize the system, polymers improve the rate of orthokinetic flocculation [6].

However, in order to maximize the efficacy of the isolated coagulation-flocculation process, in recent years other methods for wastewater treatment have been used in combination, including: nanofiltration [7], ozonation [8], photocatalytic oxidation [9], Fenton and solar Photo- Fenton processes [10], forward osmosis [11] and also adsorption processes [12-15].

Adsorption, is one of the most widely used methods because it is inexpensive, easy to handle and performs impressively in the removal of toxic dyes from industrial wastewater [16]. It has been widely studied for dye removal using different kinds of adsorbents and adsorbates [16-22]. In the leather industry, tannery solid waste has been used as an adsorbent in dye removal [2].

Taking cost and efficiency into account, previous studies have reported the combination of the coagulation-flocculation (CF) and adsorption processes, for the removal of tannic and humic acids [14] and reactive dyes [12-13] of

aqueous effluents.

Searching for alternative methods of treatment for dye effluents of the leather industry, specifically from the wet-end process, this paper presents research into achieving increased efficiency by using coagulation-flocculation followed by adsorption. This was accomplished using a novel activated carbon prepared by microwave-assisted pyrolysis of an organic precursor obtained from the sludge of a Tannery Wastewater Treatment Plant (ACT) and Commercial Activated Carbon (AC) in an aqueous solution of AB-210, and later applying it in wet-end tannery wastewater under similar experimental conditions as those of industrial processes.

2. MATERIALS AND METHODS

2.1 Solutions and reagents

A stock dye solution of 5,000 mg L^{-1} was prepared with distilled water, which was further diluted in the experiments. The pH of the solution was adjusted with 0.1 mol L^{-1} NaOH and/or 0.1 mol L^{-1} HCl using a Digimed DM-22 pH meter. The dye concentration was measured with a UV/visible spectrophotometer (T80 UV–VIS spectrophotometer, PG Instruments, Leicester, UK). Standard solutions of AB- 210 of between 10.00 and 190.00 mg L^{-1} were used for analytical calibration in parallel with deionized water, for the determination of the initial and final dye concentrations. If the absorbance was greater than 2.2, the necessary dilution was made with a solution of the appropriate pH. The coagulant used was aluminum sulfate ($Al_2(SO_4)_3$) and the anionic polyelectrolyte FX AS1 of FAXON Company, (Novo Hamburgo, Brazil, CAS:25987-30-8).

For coagulation-flocculation assays stock solutions of 50.0 mg L^{-1} of coagulant ($Al_2(SO_4)_3$) and 80.0 mg L^{-1} of polyelectrolyte were prepared.

2.2 Coagulation and coagulation-flocculation tests

To verify the effect of pH on the coagulation/flocculation process, aqueous solutions of 100.0 mg L^{-1} of AB-210, were prepared at pH values ranging from 1 to 10 using 0.1 mol L^{-1} HCl and/or NaOH. Using a Jar Test 218 LDB instrument, 700 mL of dye solution was treated with a fixed concentration of aluminum sulfate of 143.0 mg L^{-1} (2 mL) with agitation at 150 rpm for 5 min. A solution of 80.0 mg L^{-1} (1 mL) of polyelectrolyte was added and the agitation was maintained at 40 rpm for 15 min. After stopping the agitation, the final dye concentration was analyzed after 60 minutes of sedimentation time. All experiments using physical-chemical treatments of the aqueous dye solution were carried out in duplicate at room temperature.

For the test of the coagulant dosage, a dye solution of 100 mg L^{-1} at pH

10 was prepared. The experimental conditions for agitation and sedimentation were the same as for the pH tests, only varying the concentration of the coagulant doses between 14 mg L^{-1} and 214 mg L^{-1} without the use of polyelectrolyte. The amount of coagulant added to the Jar Test was determined using the mathematical expression (1):
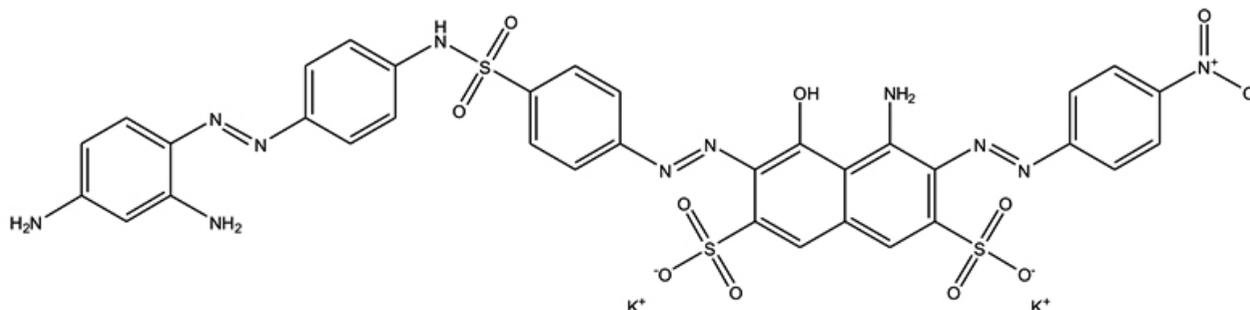
Figure 1. Molecular structure of the AB-210 dye.

$$\text{Sulfate Volume} = \frac{A*0.07}{B} \quad \text{Sulfate Volume} = \frac{A*0.07}{B} \quad (1)$$

where A, is the desired Al$_2$(SO$_4$)$_3$ concentration in the studied solution in mg L^{-1}, B is the sulfate concentration in mg L^{-1}, and 0.07 is a value representing the studied volume of 700 mL, using a settling time of 60 minutes.

The percentage of dye removal was calculated according to the following mathematical expression (Eq. 1):

$$\%Removal = 100. \frac{(C_o - C_f)}{C_o} \quad (2)$$

C_0, is the initial concentration of dye *(mg.L^{-1})* and C_f is the final dye concentration after the adsorption procedure.

The test of the polyelectrolyte dose was performed under the same experimental conditions, and the coagulant concentration was maintained constant at 71 mg L^{-1} to evaluate the effect of the polyelectrolyte addition. The volume of stock solution of polyelectrolyte at a concentration of 80.0 mg L^{-1} added varied from 0.2 to 6 mL (0.023 mg L^{-1}-0.686 mg L^{-1}), using a settling time of 60 minutes.

2.3 Preparation of activated carbon from tannery sludge (ACT)

The ACT was prepared by chemical activation of the sludge collected from a tannery wastewater treatment plant using zinc chloride and lime to form a paste (1:1 between the sludge and the inorganic material) and carbonized by microwave heating. The carbonized material was refluxed with 6.0 mol L^{-1} HCl, dried, ground and sieved to obtain the activated carbon [16-18].

The results of the gas-solid isotherms were analyzed in different ranges of pressures, using the BET method on which calculation of specific surface (p/p^0 range determined using the method proposed by Rouquerol et al. [23], and density functional theory (p/p^0 range 10^{-7}), which considered different pore models and the effects of surface roughness and heterogeneity (NLDFT and QSDFT), using the ASQiWin software [24-25].

While the calculation NLDFT has proven to be a reliable method for the characterization of a variety of materials ordered and structured, it has the drawback that it does not consider the geometric and chemical heterogeneity on the walls of the pores, assuming the structure behaves as a flat or even surface. Thus, there is a need for further study considering surface roughness, which is a characteristic in most carbonaceous materials. The QSDFT method was originally developed to take account of this and has been applied to slit-shaped pores, assuming typical models are microporous activated carbons [24-25]. However, the emergence of new materials with pore morphology, for example, predesigned and obtained by synthesis of various precursors, requires the development of new methods that take into account more complex geometric details (slit, cylindrical, spherical and combinations) [24-25].

2.4 Adsorption Tests

An aliquot of 20.00 mL of AB-210 solutions (10.00–1500.0 mg L−1) was added to a 30.0 mg of ACT activated carbon in different 50.0 mL Falcon conical tubes at different pH values (1.0–7.0). A temperature-regulated shaker (operating at 200 rpm) was used to agitate the adsorbent-adsorbate mixtures. After agitation at a specified time, the mixtures were centrifuged for 5 min for separation of the dye solutions from adsorbents [19,26]. After the batch adsorption experiment, the unadsorbed dyes were measured using a T90+ PG Instruments spectrophotometer at a maximum wavelength of 615 nm for AB-210 dye. The adsorbed quantity of dye per unit mass of activated carbon is given by Eqs. (3)

$$q = \frac{(C_o - C_f)}{m}. V \quad (3)$$

For the equilibrium studies, the Langmuir, Freundlich, and Liu models were used to analyze equilibrium data. The equations describing these models are shown below [27]:

$$q_e = \frac{Q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (5)$$

$$q_e = K_F \cdot C_e^{1/n_F} \quad (6)$$

$$q_e = \frac{Q_{max} \cdot (K_g \cdot C_e)^{n_L}}{1 + (K_g \cdot C_e)^{n_L}} \quad (7)$$

Where q$_e$ (mg. g^{-1}) is the amount of dye removed by ACT at equilibrium; C$_e$ (mg L^{-1}) is the dye concentration at equilibrium; Q$_{max}$(mg. g^{-1}) is the maximum adsorption capacity of the ACT; K$_L$ (L mg^{-1}), K$_F$[mg g^{-1}·(mg L^{-1})$^{-1/nF}$] and K$_g$ (L mg^{-1}) are the respective Langmuir, Freundlich and Liu equilibrium constants; nF and nL are the exponents of Freundlich and Liu models, respectively, (nF and nL are dimensionless) [28,29].

2.5 Statistical evaluation of kinetics and equilibrium models.

Usually for testing a given kinetic and equilibrium model, some statistical functions are tested. The best fit model is the one with the lowest value of Standard Deviation (SD) and the one in which the value of Adjusted Coefficient of Determination (R^2_{adj}) is closer to unity. Equations 8 – 11 depict the expressions of reduced chi-square, SD, Coefficient of Determination (R^2) and adjusted Coefficient of Determination (R^2_{adj}), respectively.

$$\text{Reduced Chi-squared} = \sum_i^n \frac{\left(q_{i,exp} - q_{i,model}\right)^2}{n_p - p} \quad (8)$$

$$SD = \sqrt{\left(\frac{1}{n_p - p}\right) \cdot \sum_i^n \left(q_{i,exp} - q_{i,model}\right)^2} \quad (9)$$

$$R^2 = \left[\frac{\sum_i^{np}\left(q_{i,exp} - \bar{q}_{i,exp}\right)^2 - \sum_i^{np}\left(q_{i,exp} - q_{i,model}\right)^2}{\sum_i^n\left(q_{i,exp} - \bar{q}_{i,exp}\right)^2}\right] \quad (10)$$

$$R^2_{adj} = 1 - \left(1 - R^2\right) \cdot \left(\frac{n_p - 1}{n_p - p - 1}\right) \qquad (11)$$

where $q_{i,\,model}$ is each value of q predicted by the fitted model, $q_{i,\,exp}$ is each value of q measured experimentally, $\overline{q}_{exp}$ is the average of q experimentally measured, n_p is the number of experiments performed and p is the number of parameters of the fitted model.

The reduced chi - squared is the residual sum of squares divided by the degree of freedom (n_p-p) (Eq. 8). The SD is the square root of reduced chi-squared (Eq. 9). Both Equations 8 and 9 are very useful for point to point evaluation of a given kinetic or equilibrium adsorption model, this is because for each experimental point there is a point in the model that corresponds exactly to the point on the curve (model). The lower the reduced chi-squared and the SD, the lower the difference between the values of experimental q ($q_{i,\,exp}$) and model q ($q_{i,\,model}$), therefore, the best fit is expected. However, it should be taken into account that it is not possible to compare the values of reduced chi-squared and SD among several kinetic and equilibrium isotherms that present other different concentrations or other conditions since the values of SD and chi-squared tend to increase as the concentration increases [28]. On the contrary, for the same set of experimental data, the values of reduced chi-squared and SD are useful to ascertain the best model since R^2 and R^2_{adj} are of low sensitivity (their values are limited to unity) [28].

2.6 Wet-end processing wastewater, characterization and treatments

To obtain wastewater with characteristics similar to those of the wastewater generated in the wet-end stage of the tannery industry, the wet-end process was carried out using a pilot-scale tannery drum (Master FLD-8 model) according to the formulation (**Table 1**), where the input percentage of the chemicals and water were based on the mass of wet-blue leather used (1.51 kg). Chemicals specialized to the leather industry were used (BASF; TFL; LANXESS).

The steps of the wet-end process were: washing, desacidulation, retanning, preliminary dyeing, fat liquoring and secondary dyeing. In each step the wastewaters generated were collected and refrigerated at -10ºC until they could be used in the wastewater treatment assays.

Table 1. Formulation for wet-end processing of wet-blue leather.

Percentage (%)	Product	Temperature (°C)C)	Time	Remarks
200	Water	40		
0.20	Surfactant (Eusapon LDE[1])		20'	Drain
150	Water	40		
1	Sodium formate			
0.5	Sodium bicarbonate		20'	
2	Desacidulation Agent (Sellasol NG[2])		60'	pH 5.20–5.50
100	Water	40		
5	Synthetic Tanning (Basyntan DLE[3])			
2	Retanning polymer(ReluganRV[4])			
2	Vegetable tannin (Mimosa extract[5])		60', 120'	Drain
100	Water	25		
2.5X	Acid Black 210[6])		60'	Drain
100	Water	60		
5	Oil (Lipoderm Licker LA-SLF[7])			
2	Synthetic Oil (Coriol L2T4[8])		60'	
1	Formic Acid		10'	pH =3.5 and Drain
200	Water	60		
1.5X	Acid Black 210[9]		30'	
X/2	Formic Acid		15'	Drain

[1,3,4,5,7,8]BASF; [2]TFL; LANXESS[6,9]

The generated wastewaters after each stage, were collected and analyzed for pH, conductivity, ionic chromatography and total organic carbon. Finally, they were mixed to obtain a composite wastewater for treatment.

Cation concentrations were determined using an Ionic Chromatography 883 Basic IC Plus Metrolab instrument using a Metrosep C4-150 column. The eluent used was 2.5 mM HNO_3 and 1.5 mM dipicolinic acid, with a flow-rate of 0.9 mL.min^{-1}, a pressure 6.3 MPa at room temperature, and a conductivity of 1196 µS/cm. This column allowed the determination of the following cations: lithium, sodium, ammonium, calcium and magnesium. All the analyses were performed using Milli-Q water for washing of the glass materials and for the respective dilutions.

The total organic carbon was determined using a Shimadzu TOC-L, instrument which uses the NPOC (non-purgeable organic carbon) method and the inlet gas was oxygen (O_2). All the analyses were performed using Milli-Q water for washing of the glass materials and for the respective dilutions.

The optimal conditions obtained for dye removal from aqueous solution (at 303 K) were used for the coagulation-flocculation and adsorption treatments of the wet-end composite wastewater, using 30.00 mg of ACT or AC being used for this combined treatment test.

The spectrum from 300 to 800nm were recorded for each treatment, and Microcal Origin 2015 software was used to determinate the percentage of dye removal using the calculated integral under the curve for each analyzed treatment process.

3. RESULTS AND DISCUSSION

3.1 Coagulation-flocculation process
Fig. 2 shows the dependence of the coagulation-flocculation and

sedimentation processes on initial pH. Aluminum sulfate at a fixed concentration of 143.0 mg L^{-1} was added to each vat in the jar test with agitation at 150 rpm for 5 minutes, followed by agitation at 40 rpm for 15 minutes after the addition of the polyelectrolyte at a concentration of 0.114 mg L^{-1}. Samples were collected 15, 30, 45 and 60 minutes after agitation ceased in order to evaluate the best settling time. In aqueous solution, Al^{3+} is a strongly hydrated ion and is found surrounded by six coordinated water molecules in an octahedral configuration. The highly positive charge on the central metal ion causes some polarization of the O–H bonds and there is a tendency for protons to dissociate giving one or more hydroxylated species [29]. The chemical reaction (3) represents this process, where the complexes of Al^{3+} ions in water act as weak acids [6]:

$$Al(H_2O)_6{}^{3+} \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H^+ \qquad (8)$$

For molecules such as the AB210 dye with a molar weight of 938.02 g.mol^{-1}, this reaction can lead to precipitation of the aluminum–dye complex [30], which was observed in the experiments.

Analyzing the data, 60 minutes settling time resulted in the best dye removal. In the acid pH range between 1 and 3, only 15.31% dye removal was achieved. However, above pH 4.0 the dye removal percentage increases quickly reaching 62.80% at pH 4.0 and was most efficient at basic pH with 93.2% removal at pH 10.0. This is likely because the auxochrome group of the dye molecule has a high degree of dissociation and thus the solubility of alum is also high [12].
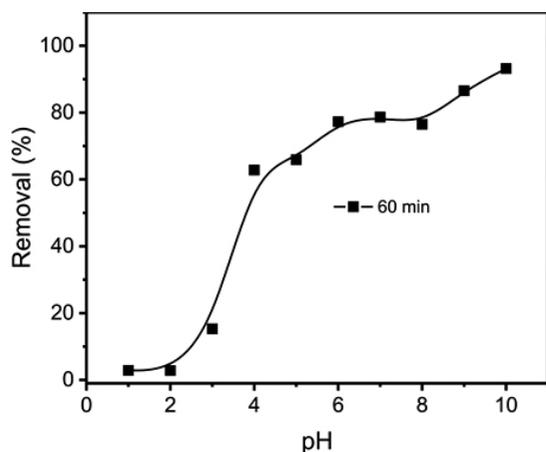
Figure 2. Effect of pH on the removal of AB-210 dye in the coagulation process ((Al$_2$(SO$_4$)$_3$) doses =143 mg. L^{-1}).

Fig. 3 shows the results obtained by varying the coagulant dosage from 15 to 215 mg L^{-1}. Between 15 and 50 mg L^{-1} the dye removal is low, however above 57 mg L^{-1} the dye removal increases quickly reaching 100% at 71 mg L^{-1}, at least in the case of the chromophore group of the dye, which is the part that is quantified spectrophotometrically. Between 71 and 215 mg L^{-1} the dye removal remained constant, reaching the equilibrium concentration.
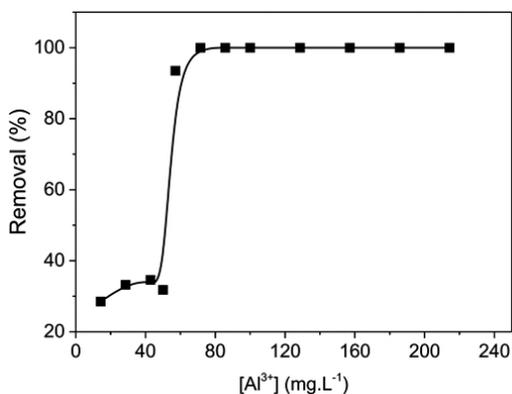
Figure 3. Effect of the Al^{3+} in the jar test on the removal of AB-210 dye (pH= 10.00).

The polyelectrolyte dosage was varied at the optimal coagulant dose of 71 mg L^{-1} and the optimum pH of 10 (**Fig 4**). With the polyelectrolyte addition it was observed that the flocs were bigger, facilitating the sedimentation process. For this reason, the chosen dose of polyelectrolyte was 0.114 mg L^{-1} ensuring 100% of the dye removal at the concentration studied and facilitating the physico-chemical process. The flocculant is a high molecular weight anionic polymer of polyacrylamide, produced with free radicals of acrylamide, which is essentially a common charge of sodium acrylate. The polyelectrolytes act to stabilize colloidal particles of great size, promoting sedimentation. Basically, polyelectrolytes enhance the rate of orthokinetic flocculation when added to a system already stabilized by inorganic coagulants [6].

The increase in flocs only happens when there is sufficient adsorption affinity between the polyelectrolytes and the floc surfaces. The flocs then undergo polyelectrolyte bridging or charge neutralization [31].
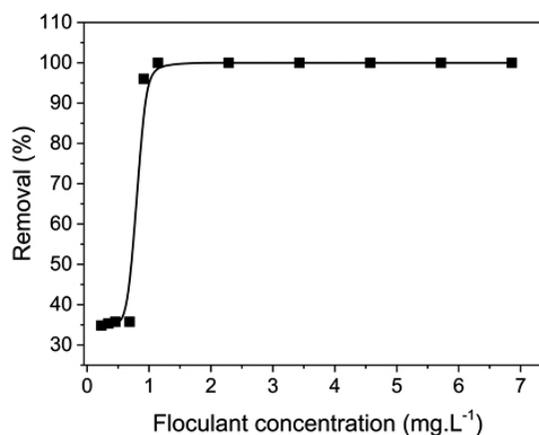
Figure 4. Effect of flocculant concentration (anionic polyelectrolyte) in the jar test for the removal of AB-210 dye (pH= 10.00 and 71.43 mg/L Al$_2$(SO$_4$)$_3$)).

3.2. Textural characterization of activated carbon from tannery sludge (ACT)

The obtained ACT had a surface area BET of 491.0 m^2 g^{-1}. As complementary study, this material was analyzed for the application of the method of Density Functional Theory (DFT), which has led to significant advances in the textural characterization of porous materials and provides information on the size of the pores in the range of micro- and mesopores.

Thus, for this analysis we considered data adsorption-desorption of nitrogen at 77 K (with a characteristic isotherm of micro-mesoporous activated carbon) **(Fig. 5)**, and applied both a NLDFT model as QSDFT [25] for a wide range geometry (slit, cylindrical and spherical) and combinations (slit/cylindrical, spherical/cylindrical and spherical/cylindrical/slit) for analysis. Of the different theoretical isotherms adjusted (not shown in this analysis), the errors obtained were correlated and it was found that the best fit was achieved with the QSDFT Carbon-N$_2$ (cylindrical/spherical) system in the field of adsorption (Er 0.17%) **(Fig. 6)**.
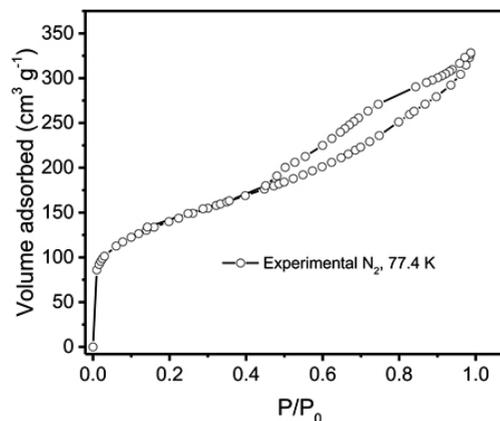
Figure 5. Nitrogen Isotherm adsorption of the activated carbon from tannery sludge (ACT) at 77.4 K
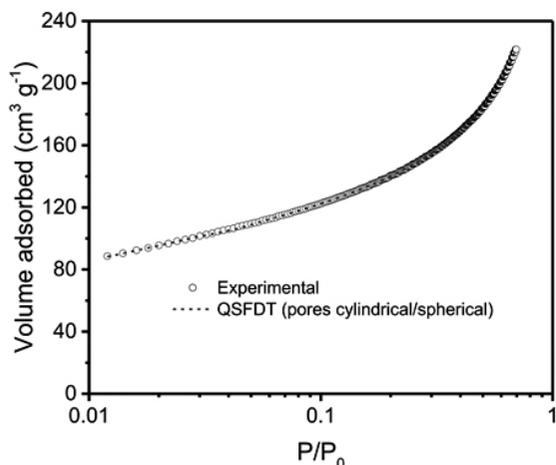
Figure 6. Experimental Nitrogen Isotherm and theoretical adjustment with QSFDT model for adsorption branch (logarithmic scale)

It is noteworthy that the materials have assumed spherical pores present during desorption, an evaporation process altered by the effect called "*pore blockage*". This assumption is therefore in the analysis with QSDFT carbon-N_2 (cylindrical / spherical), only the branch adsorption isotherm N_2 was considered to study the size and pore size distribution. Thus, one considers the correct delay in the condensation exists for a spherical pore type [24-25].

Finally, the appropriate model defined, considering the characteristic behavior of the pores of the sample, was used to make the pore size distribution **(Fig. 7)**. The peaks coincide with the pore sizes expected (down is observed in the boundary area micropore and peaks mesopores of different size) and predict the size distribution of micro and mesopores in the whole range of relative pressure (with a volume 0.33 pore cm^3 g^{-1} and characteristic width of 17 Å). Additionally, the best fit achieved with the QSDFT model suggests pores of roughness or tortuosity.
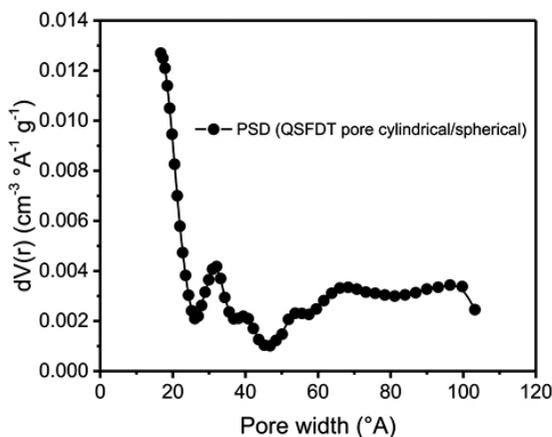
Figure 7. Pore size distribution of activated carbon from tannery sludge (ACT), QSDFT model in the branch of nitrogen adsorption isotherm

3.3 Influence of the pH on the adsorption process of AB-210 using ACT

Fig. 8 shows the influence of pH on the percentage of removal of AB-210 from ACT activated carbon in aqueous solution. In the pH interval between pH 2.0 and 6.0, the influence of pH on the adsorption percentage was not significant.

Considering the experimental evidence that at low pH such as pH 2.00–3.00 the activated carbons and the dye solutions are stable, and reports by other authors [19, 32-33], the adsorption of the AB-210 onto the activated carbon seems not be by electrostatic attraction, as the initial pH of the AB-210 leather dye solutions has practically no effect on the adsorption capacity [32].
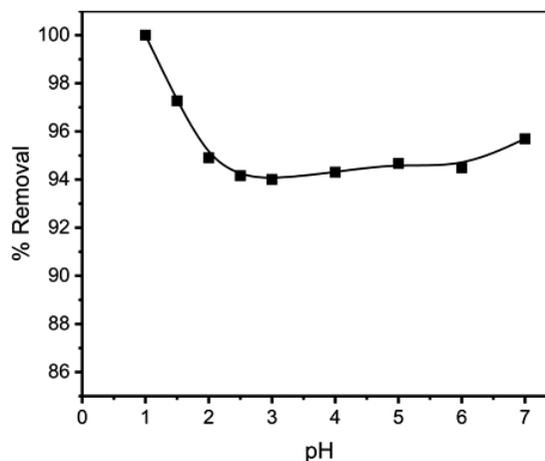
Figure 8. Effect of pH on the adsorption of AB-210 dye aqueous solution using the activated carbon from tannery sludge (ACT).

3.4 Equilibrium studies

Fig. 9 shows the equilibrium study at 303K performed to determine the maximum removal of the AB-210 dye using ACT. Table 2 shows the parameters adjusted from the equilibrium experiment on the adsorption of AB-210 using the Langmuir, Freundlich and Liu isotherm models. The use of R_{adj}^2 and SD for the analysis of the goodness of fit between the experimental data in aqueous solution and various non-linear adsorption models has been reported in the literature for the comparison of models of 2 and 3 parameters [28,34-36]. Based on R^2_{adj} as well as the SD, the best isotherm model was the Liu, that presented an SD value of 22.68 mg g^{-1}, which is lower when compared with the SD of Langmuir (38.60 mg g^{-1}), and Freundlich (29.04 mg g^{-1}). It could seem, to some readers that the Langmuir and Freundlich isotherm model was better fitted because at the higher q_e values obtained experimentally gets closer to the Q_{max} (theoretical) values of Langmuir isotherm, and also considering that R^2_{adj} obtained were 0.9583 and 0.9764 for Langmuir and Freundlich model, respectively. However, we reinforce that it is not correct to calculate the Q_{max} value based on the supposed plateau of the isotherm. Although several users of adsorption do it, this procedure is not correct. We do reinforce that q_e (experimental values) could not be directly compared with any Q_{max} values, because this is a theoretical parameter that is obtained from an isotherm model [28]. If someone already thinks that the plateau usually obtained in the experimental isotherms is the maximum saturation, this is just the q_e values obtained for higher concentrations of the adsorbate. The user should be born in mind that any experimental point of the isotherm (even at low adsorbate concentration), the system has attained the equilibrium. Therefore saturation of an adsorbent is quite different of a system attaining a equilibrium.

The maximum adsorption capacity according to the chosen model of Liu, was 974.7 mg g^{-1} at 303 K. It should be noted that the value of Q_{max} is a calculated value that is different from q_e values that were experimentally measured. Q_{max} is the maximum sorption capacity estimated by a given model. Observing the Liu isotherm at the equilibrium concentration of about 900 mg L^{-1} the complete saturation of the adsorbent was not attained yet, and this saturation would occur at higher values. However, considering that the initial AB-210 concentration (C_o) is much higher than the equilibrium concentration (C_e) left at the solution after the adsorption, it is not feasible to increase the concentration of the adsorbate even more, until saturation of the adsorbent occurs.

The fact that the Liu model was the best fit indicates that, due to the heterogeneity of the surface, this is a useful approach to study the behavior of the AB-210 on the surface in the range of concentrations worked. Since the Freundlich model is only appropriate to describe the low concentration region, it is not valid at higher concentrations, where the interactions of the dye molecules in the solution are likely to have a more important role, thus reducing the affinity of the dye towards the surface [37]. The Liu model is similar to the Freundlich isotherm at low concentrations of adsorbate, while at high concentrations it predicts an adsorption monolayer characteristic of the Langmuir isotherm [38].
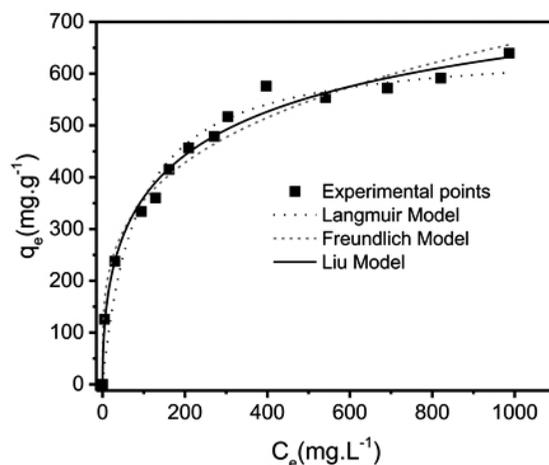
Figure 9. Adsorption isotherm at 303 K of AB-210 aqueous solution on ACT the activated carbon from tannery sludge (ACT)

Table 2. Parameters adjusted from the equilibrium experiments on the adsorption of AB-210 using the Langmuir, Freundlich and Liu models (303 K)

Langmuir		Freundlich		Liu	
Q_{max} (mg.g^{-1})	651.8	K_F (mg.g^{-1} (mg L^{-1})$^{-1/nF}$)	103.9	Q_{max} (mg.g^{-1})	974.7
K_L (L.mg^{-1})	0.01222	n_F	3.742	K_g (L.mg^{-1})	0.003458
				n_L	0.4990
Reduced $\chi 2$	1489.6157	Reduced $\chi 2$	843.4991	Reduced $\chi 2$	471.6445
R^2_{adj}	0.9583	R^2_{adj}	0.9764	R^2_{adj}	0.9856
SD (mg.g^{-1})	38.60	SD(mg.g^{-1})	29.04	SD (mg.g^{-1})	22.68

3.5 Wastewater from the leather wet-end process

Proportional volumes of the drained wastewater discharged from each step of the leather wet-end process performed in a pilot-scale drum were mixed to compose a test effluent **Fig. 10** shows the leather obtained and the drum used for the dyeing test and the wastewater collection. **Table 3** shows the results of the analysis of each wastewater.
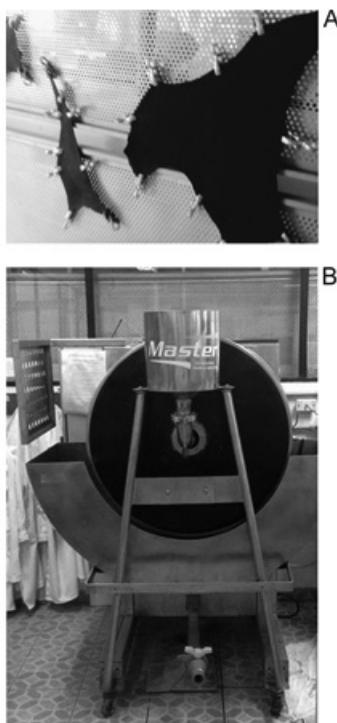
Figure 10. Experimental dyed leather (a) and pilot-scale drum (b)

Table 3. Characterization of wastewaters of the wet-end process

Stream of wastewater	pH	Conductivity (μS.cm^{-1})	TOC (mg.L^{-1})
Initial Washing	3.88	1094.7	615.5
Desacidulation	7.69	8.285	3401
Tanning	5.28	5.969	1823.5
Dyeing I	7.07	7.887	2522
Fat liquoring	3.52	5.413	4833
Dyeing II	3.50	4.967	2137.7

The final concentration of dye in the mixture of all wastewaters collected was 453 mg L^{-1}. Seeing as the precipitate obtained in the coagulation is a complex chemical containing coagulant and dye in aqueous solution, interference of the other chemical products added to the obtained effluent modify the complex formation equilibrium.

The coagulation-flocculation process is caused by the entrapment/enmeshment of the dye colloid into the gelatinous aluminum flocs, aggregated products of the hydrolysis of aluminum (III) ions, which are then removed by what is known as "sweep coagulation" [36].

However, this sweep coagulation is directly affected by interferents, because other cations like sodium, potassium, and formate compete for complexation with the chromophore group of the dye.

The composed effluent was adjusted to pH 10 with NaOH, and the coagulant volume was varied from 1071 to 7142.9 mg L^{-1} Considering the present interferents, and the ability of the polyelectrolyte to improve the coagulation process by forming large and heavy flocs, the volume of polyelectrolyte to add to the simulated effluent (5.27mL polyelectrolyte) was calculated according to previous studies with aqueous solutions. With this amount of polyelectrolyte and 4285 mg L^{-1} of coagulant, a clear precipitation was obtained in this effluent.

Ion chromatography was used to analyze the main cations in the wastewater (**Table 4**). These analyses were performed in duplicate and the reported values are the averages between them. In the initial effluent without pH adjustment the concentrations of sodium, ammonium, potassium and calcium were: 1736.170 mg L^{-1}, 145.55 mg L^{-1}, 23.442 mg L^{-1} and 107.111 mg L^{-1} respectively, deriving from the reagents of the desacidulation step and the composition of the wet blue leather.

Table 4. Chemical analyses of the composite wastewater from wet-end process before and after the treatments.

Composite wastewater	TOC (mg L^{-1})	Na$^+$	NH$_4^+$	K$^+$	Ca^{+2}
Initial	2024	1736.13	145.55	23.44	107.1
Initial adjusted at pH= 10.00	1567.7	1932.17	100.02	ND	ND
After coagulation-flocculation treatment	781.65	1454.88	80.52	ND	ND
After coagulation-flocculation and adsorption treatment with AC (Commercial activated carbon)	638.6	1345.42	73.397	ND	ND
After coagulation-flocculation and adsorption treatment with ACT (Activated carbon tannery sludge)	703.85	1502.84	83.236	ND	ND

The initial effluent shows an increase of the sodium ions amount compared with the composite wastewater, for the basic adjustment from 1736.13 mg L^{-1} to 1932.17 mg L^{-1}. Ammonium was reduced to 100.02 mg L^{-1}, possibly by ionic competence.

The effluent treated with the coagulation process showed a decrease from the initial cation concentrations of 24.70% for sodium and 19.49% for ammonium. The calcium and potassium precipitate completely with the addition of the coagulant, showing the high efficiency of this process.

However, the adsorption process performed at pH= 3.00 with AC evidenced an excellent polishing treatment, showing an adsorption of 7.52% of sodium ions, and for the ammonium ions the removal was 8.84% with the AC, compared to the treated wastewater with coagulation. On the other hand, with the ACT a slight increase in these ions was observed, possibly due to the trace composition of the sludge precursor that was maintained despite the leaching on the activated carbon.

From the TOC analysis, it was seen that through the coagulation process, the content of total organic carbon decreased to 50.1% of the initial content, and after the adsorption process with ACT an additional 5% reduction in TOC was seen. With AC an additional 9.16% reduction in TOC was achieved.

The area under the absorption bands between 300 and 800 nm obtained by the Microcal Origin 9.0 software was used to evaluate the percentage of dye removal from the initial effluent and the treated effluent by the physico-chemical process and subsequently also with the adsorption process. The dye removal through the coagulation process was 78.22%. From the initial concentration of the wastewater studies of 453 mg L^{-1} a residual concentration of 98.66 mg L^{-1} was obtained. Given the maximum adsorption capacity at the working temperature for the Liu model was 974.7 mg g^{-1}, the ACT could achieve additional dye removal, which was observed experimentally, obtaining a dye removal of 85.2% when the ACT was used for the adsorption and 88.64% with the AC.

Fig. 11 shows the absorbance spectra after the different treatments in these studies. They indicate that the combination of treatments provides an excellent alternative that can substantially improve the process. Aluminum sulfate as coagulant, anionic polyelectrolyte as flocculant and the activated carbon (ACT) used are excellent agents for the treatment of leather dye contaminated effluents.
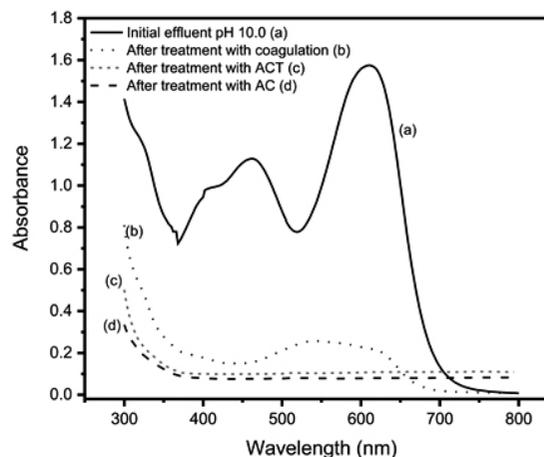
Figure 11. Absorption spectra of the initial effluent of leather wet-end process and after the treatments tested.

4. CONCLUSIONS

The combination of coagulation-flocculation with adsorption processes showed effective results in the removal of the tannery dye Black Acid 210 from aqueous solution and wet-end tannery wastewater.

The ACT was achieved with QSDFT Carbon-N_2 (cylindrical / spherical) system in the field of adsorption and presented roughness and tortuosity in its wall pores.

In wet-end tannery wastewater the combination of coagulation-flocculation and adsorption with ACT achieved 85.2% removal of the dye compared with AC that showed 88.64%. In addition, using the ACT, 68.44%, 13.44%, and 42.81% reductions were achieved for TOC, total sodium, and ammonium. Potassium and calcium were not identified from the solution after the NaOH addition for pH adjustment. For the combination process using AC, the results obtained were: 65.22% TOC removal, 22.5% total sodium removal, and 49.57% removal of ammonium.

ACKNOWLEDGEMENTS

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