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Keywords: wastewater treatment, dye removal, Adsorption, activated sludge carbon, methylene blue

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Article

Preparation and Characterization of Activated Carbon Obtained from Water Treatment Plant Sludge for Removal of Cationic Dye from Wastewater

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Abstract: The proposal of this work was the preparation and characterization of activated carbons obtained from water treatment plant sludge (WTS) to apply as adsorbents in the removal of organic dye contaminants from wastewater. The activated carbons were produced with a combination of chemical activation and pyrolysis processes. The textural characteristics of both adsorbents presented a satisfactory superficial area and mesoporous structure. The presence of phenolic and carboxylic groups in the surface indicated a better adsorption of cationic adsorbates. When applied as adsorbents in the removal of methylene blue (MB) from wastewater, the maximum removal values obtained were up to 96%. The adsorption results showed that the adsorption was faster in the beginning and reached maximum around 30 min. The Elovich kinetic model and the Sips isotherm model presented the best fit to experimental data, which was checked by analysis of variance (ANOVA). The production of activated carbons from WTS is a sustainable and effective option in the removal of MB dye.

Keywords: methylene blue; activated sludge carbon; adsorption; wastewater treatment; dye removal

1. Introduction

The increase of industrial activities and water consumption has been causing environmental problems, leading to an environmental imbalance [1,2]. According to Natural Resources Defense Council (NRDC), 80% of the world's wastewater is discarded without a previous treatment. Every year, about 1 billion people get diseases caused by untreated water and more than 200 different species of marine life are harmed [3].

To obtain potable water, treatment is needed in order to remove undesirable components and contaminants. This process is accomplished in a water treatment plant (WTP), where a sequence of physical and chemical treatment processes is applied to eliminate particulate solids, organic compounds and harmful microorganisms. Only one WTP produces about 100 thousand tons of sludge a year as waste from this process [4–8].

When disposed into nature, this residue—called water treatment sludge (WTS)—causes environmental impacts that affect the quality of water and the health of animals and human beings [6,9]. Although legislation has been created to avoid improper disposal, nearby watercourses still contaminate the water.

This problem has been encouraging studies that focus on exploring the reuse options for this waste [10]. As the wastewater treatment has also been a concern [11–13], the use of residual sludge as a raw material for developing an alternative adsorbent has been studied, utilizing different methods [14–16]. Among the pollutants, the textile industry produces 200 billion liters of colored effluent a year [17]. These effluents contain hazardous compounds that cause damage to environment when incorrectly disposed into nature.

Organic dye pollution is a huge problem in various industries, such as textile, leather, plastic, paper, cosmetic, etc. According to NRDC, textile industries generate one-fifth of world's industrial water pollution, using 20,000 chemicals to make clothes [18], and methylene blue (MB) is one of the organic dyes widely used. The exposure to MB can cause health problems for human beings, such as vomiting, cyanosis, jaundice, shock and tissue necrosis [19].

Studies about dye removal have explored different methodologies [20–27]. Among these methods, adsorption has been becoming very popular due to its high efficiency, ease of operation and design [28]. The adsorption consists in transferring the pollutant from the liquid or gas phase to a solid phase. Consequently, the adsorbent is regenerated or kept without contact with the environment. Pursuing low cost, efficiency and eco-friendly techniques, different kinds of adsorbent materials have been used, such as activated carbon [16,29], carbon nanotubes (CNTs) [30–32] and graphene [33,34]. Puchana-Rosero et al. [11], Gonçalves et al. [12] and Deegan et al. [13] have investigated different methods to produce activated carbon for the removal of contaminants from aqueous solution obtaining satisfactory results, which indicates that residual sludge is a good precursor for adsorbent production.

The objective of this study was to produce and to characterize activated carbons using WTS as the raw material, proposing an alternative for reusing this waste. Another objective was to analyze the capacity and efficiency as an adsorbent in the removal of organic cationic dye (MB) from wastewater. The adsorption of MB dye was analyzed by using mathematical models of kinetic and isotherm submitted to statistical evaluation by ANOVA with 95% of confidence level.

2. Materials and Methods

2.1. Preparation of the Activated Carbon

The raw sludge used as primal matter was provided by the WTP (Water Treatment Plant) of Bagé, RS, Brazil (31°18'22.5" S 54°07'20.0" W). The sludge was oven dried (Nova Ética, model 109-1) for 48 h at 65 °C to remove the moisture. Afterwards, the sample was grinded (Marconi, model Croton) and sieved in an electromagnetic sieve shaker (Bertel, model 4830) to obtain particles with diameter lower than 495 µm. In this study, two different products were obtained, one of them resulting from sludge pyrolysis and the second from a combination of the chemical activation and pyrolysis processes.

The chemical activation was carried out by wet impregnation mixing precursors with activating agents at room temperature (1:0.8:0.2 WTS, zinc chloride and calcium hydroxide), drying, grinded and sieved the particles. Pyrolysis technique was applied using a stainless steel reactor at 550 °C for 30 min (heating rate of 3 °C min⁻¹) under N₂ atmosphere. The product obtained were called activated carbon (AC) and activated carbon originated from sludge paste (ASC).

2.2. Characterization of the Activated Carbon

The specific mass was determined by pycnometry of helium gas, under pressure of 17.5 psig utilizing Quantachrome Corporation (model Ultrapyc 1200e). Specific superficial area and pore volume were determined by Brunauer–Emmett–Teller (BET) technique, utilizing Quantachrome Instruments (model NOVA 4200e). The Fourier transform infrared spectroscopy (FT-IR) technique was applied, in order to characterize the chemical structure of the material. The analysis was carried out by FT-IR, with the use of a Perkin-Elmer spectrometer (model UATR Two), by the technique of attenuated total reflectance (ATR), with no need for previous preparation of the sample, in the gap of 400 to 4000 cm⁻¹ with 32 scanning per spectrum and resolution of 4 cm⁻¹. The thermal gravimetric analysis (TGA) was

obtained (Shimadzu, model TGA 50) utilizing N₂ gas as fluid. Surface morphology of the samples was analyzed by scanning electron microscopy (SEM) (Carl Zeiss, EVO MA10).

2.3. Kinetics and Equilibrium Models

Based on previous studies, the range of adsorbent dosage and concentration of the solutions were established. The equilibrium isotherms studies were determined with 50 mL of MB solution (5 to 500 mg L⁻¹) was added to erlenmeyers flasks, each of them containing adsorbent in the dosage of 40 g L⁻¹. The samples were subjected to agitation (Nova Ética, model 109-1) at 120 rpm for 40 min. The solutions were transferred to centrifuge tubes and centrifuged for 10 min at 3000 rpm to separate the solids from the MB solution. A spectrophotometer at wavelength of 665 nm was used to determine the absorbance at 25 °C. A calibration curve of MB dye solution at a range of 1–15 mg L⁻¹ was used to ascertain the residual MB concentrations.

The adsorption capacity and the percentage of MB removal were calculated using Equations (1) and (2), respectively:

$$Q = (C_i - C_f)/M * V \quad (1)$$

$$E = (C_i - C_f)/C_i * 100 \quad (2)$$

where Q is the adsorption capacity, C_i is the concentration before adsorption (mg L⁻¹), C_f is the concentration after adsorption (mg L⁻¹), M is the mass of adsorbent (g) and V is the volume of the dye solution (L).

The results of equilibrium isotherms data were fitted to mathematical models: Langmuir and Sips, presented in Equations (3) and (4).

$$q_e = (q_m * K_L * C_e)/(1 + q_m * C_e) \quad (3)$$

$$q_e = (q_m * K_s * C_e^{1/m})/(1 + K_s * C_e^{1/m}) \quad (4)$$

where q_e is the amount MB removed by adsorbent at equilibrium (mg g⁻¹); q_m is the maximum quantity of MB adsorbed per unit mass of the adsorbent (mg g⁻¹); K_L is the Langmuir constant of rate of adsorption (K mg⁻¹); K_s is Sips constant of energy of adsorption and m is the parameter characterizing the system heterogeneity (L mg⁻¹)^{1/m}.

The adsorption kinetic was carried out with similar procedure mentioned before, but with a concentration of 70 mg L⁻¹ of MB. The time of contact between the adsorbent and MB solution was 2, 5, 10, 15, 20, 30, 40 and 90 min. The models used to analyze kinetic data were: pseudo first order, pseudo second order, intra-particle diffusion and Elovich. The respective mathematical expressions of these models are presented in Equations (5)–(8).

$$q_t = q_e * [1 - \exp(-K_1 * t)] \quad (5)$$

$$q_t = q_e - [q_e/(K_2 * q_e * t + 1)] \quad (6)$$

$$q_t = K_{id} * t^{1/2} + C \quad (7)$$

$$q_t = 1/a * \ln(1 + a * b * t) \quad (8)$$

where t is the time of contact (min); q_t is the amount of MB adsorbed at time t ; q_e is the quantity of adsorbate adsorbed at the equilibrium (mg g⁻¹); k_1 is the pseudo first order constant (min⁻¹); k_2 is the pseudo second order constant (g mg⁻¹ min⁻¹); C is the concentration on liquid phase (L mg⁻¹); a is the initial rate of Elovich model (mg g⁻¹ min⁻¹) and b is the Elovich model desorption constant (mg g⁻¹).

The mathematical models parameters were determined through nonlinear regression and the use of quasi-Newton method. The models were evaluated by using the average relative error (ARE) and Chi-square (X^2), calculated according to the Equations (9) and (10).

$$ARE = (100/nm) \Sigma [(q_{exp} - q_{pred})/q_{exp}] \quad (9)$$

$$X^2 = \Sigma [(q_{exp} - q_{pred})^2 / (nm - NN)] \quad (10)$$

where q_{pred} is the value proposed by the model and q_{exp} are the values experimentally obtained, nm is the number of experiments observed and NN is the number of parameters in the model.

The analysis of variance of the models (ANOVA) was produced, and the statistical values were measured considering the Fisher value (F) at a confidence level of 95% for each adjustment.

3. Results and Discussion

Table 1 shows the values of the BET characterization, which analyzes the surface area BET (S_{BET}), pore volume (P_v) and pore diameter (P_D).

Table 1. Textural characteristics of activated carbon (AC) and activated carbon originated from sludge paste (ASC).

Sample	S_{BET} (BET Surface Area) ($m^2 g^{-1}$)	Total Pore Volume (cm^3)	Average Pore Diameter (nm)	Specific Mass (g)
AC	101.9	0.108	3.241	2.5231 ± 0.0014
ASC	100.3	0.271	10.81	2.7315 ± 0.0016

The specific mass was measured in order to relate the S_{BET} per mass unity. The activated carbons presented a similar S_{BET} , which can be related to the increase of P_V and P_d in ASC. The P_v and P_d were bigger to ASC than to AC, indicating that the incorporation of inorganic compounds used in the process of chemical activation were responsible for increasing the pores size [35,36]. This analysis has the function of determining the size and transitivity of adsorbate molecules on the internal surface of the adsorbent. Although, in spite of the difference of P_d , both carbons have indicated that the activation process produced mesoporous particles (between 2–50 nm) [37] and therefore, they can be used in the process of MB adsorption (0.59×1.38 nm) [38]. The ASC presented a higher S_{BET} than similar studies with $23.72 m^2 g^{-1}$.

Similar studies have produced activated carbon from WTS, obtaining a S_{BET} of $23.72 m^2 g^{-1}$ using chemical activation by H_3PO_4 [39] and $87.10 m^2 g^{-1}$ with thermal activation (pyrolysis) at $400^\circ C$.

The activated carbons chemical properties can also define their adsorption capacity, and the FT-IR of WTS, AC and ASC are presented in Figure 1, where the ordinates represents transmittance (%) and the abscissa correspond to wavenumber (cm^{-1}).

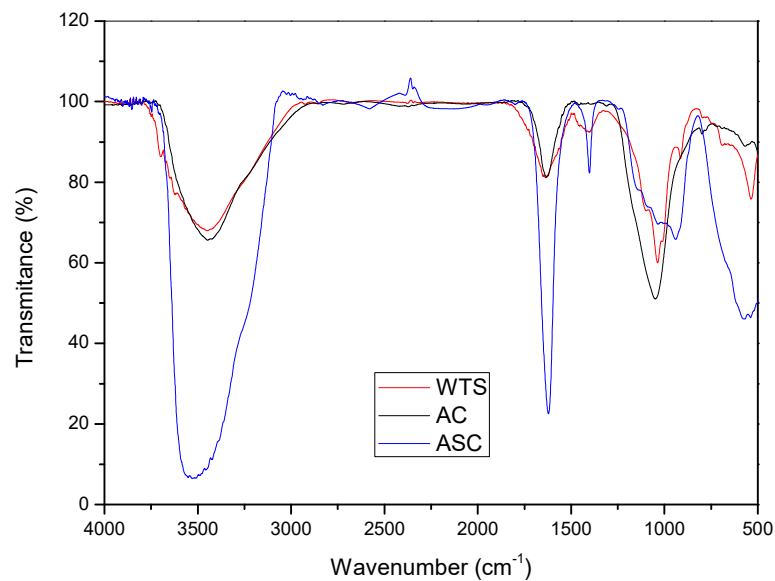


Figure 1. Fourier transform infrared spectroscopy (FT-IR) Spectrum of water treatment sludge (WTS), AC and ASC samples.

It can be easily observed that the bands were modified after pyrolysis. The ASC sample presents an increasing of O-H alcoholic and phenolic groups when compared to WTS and AC, represented by the intense band at 3400 cm^{-1} . The curves in the region at $3000\text{--}2500\text{ cm}^{-1}$ indicate the presence of C-H alkenes bonds which correspond to stretch vibrations. The carboxylic acids in the bands between $1700\text{--}1400\text{ cm}^{-1}$ indicate the presence of C = O of stretching. The evident band on AC sample at the region of $1000\text{--}1300\text{ cm}^{-1}$ can indicate the presence of C-O compounds. The $940\text{--}665\text{ cm}^{-1}$ band, more pronounced in ASC indicates the presence of bending O-H [16,40]. The adsorbents that were produced and raw sludge have functional groups with similar surfaces, however, the increase of phenolic and carboxylic groups on ASC sample indicates a better adsorption of cationic adsorbates, as the case of the dye used in the textile industry, the MB.

Figure 2 shows the thermal degradation profile (TG) and derivative thermal degradation (DTA) as a function of temperature for the WTS, AC and ASC samples.

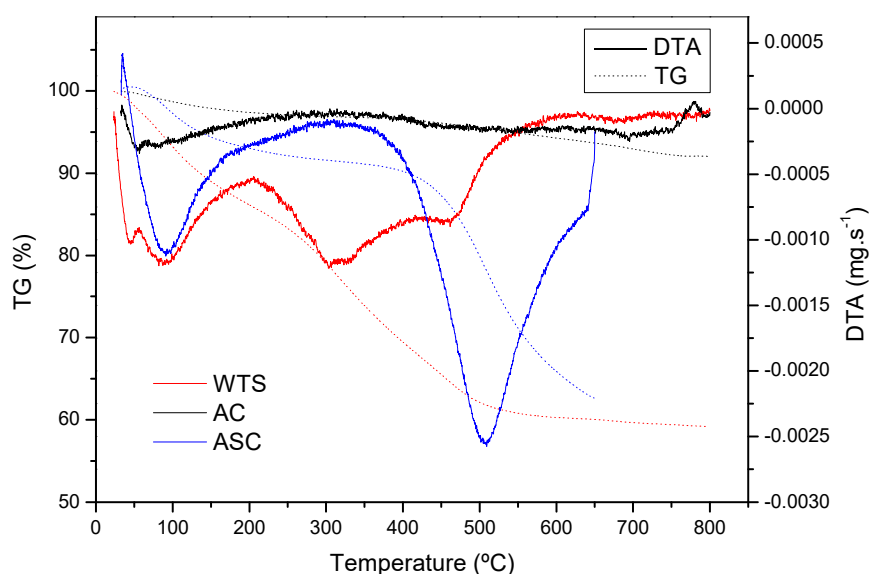


Figure 2. Thermalgravimetric curves.

In the thermogravimetric profiles the peaks of mass loss observed at temperatures lower than 100 °C is related to the absorbed moisture and crystallization of the inorganic in the precursor material. This mass loss is associated with the sludge clayey character and the presence of kaolinite, which is a characteristic of the sludge from WTS [9,41]. The decomposition of the carbonaceous matrix, reducing even more the mass of the sample in which WTS has been characterized by presenting a peak at 300 °C, due to the degradation of oxygen groups on the matter surface and the decomposition of organic matter. The AC has not presented mass loss peaks, which is explained by the complete combustion/pyrolysis of the volatile compounds present in the sludge during the thermal activation operation. The ASC has presented an evident mass loss peak at 500 °C, which is linked to the decomposition of carbonaceous skeleton, and probably to the remaining presence of zinc chloride and calcium hydroxide utilized in the chemical activation [16].

Figure 3 presents the WTS micrographs and Figures 4 and 5 show the activated carbons AC and ASC produced.

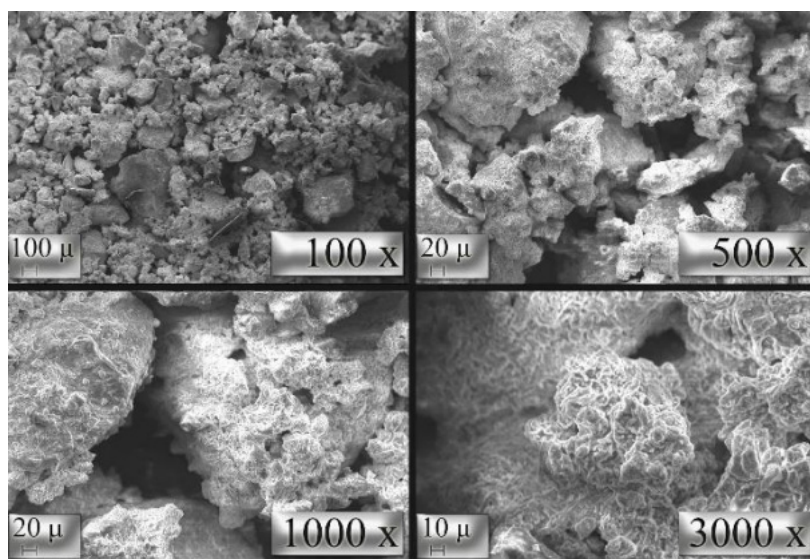


Figure 3. Scanning electron microscope (SEM) micrograph of dried sludge at a magnification of 100 to 3000x.

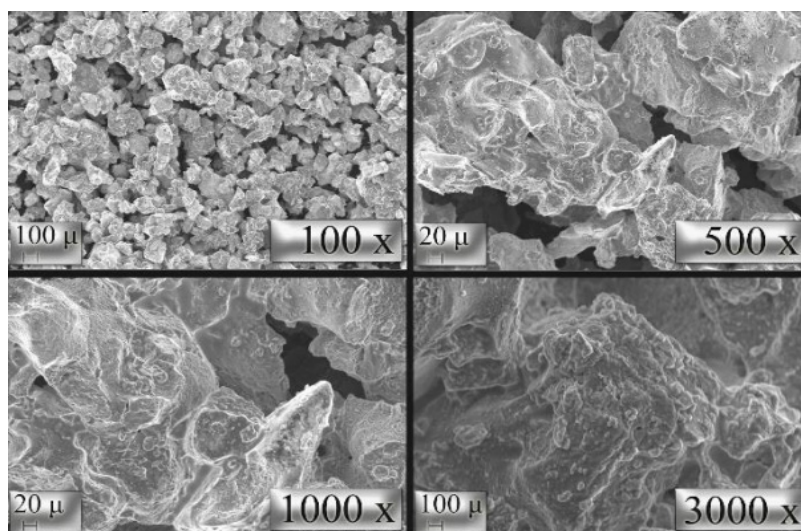


Figure 4. SEM micrograph of AC at a magnification of 100 to 3000x.

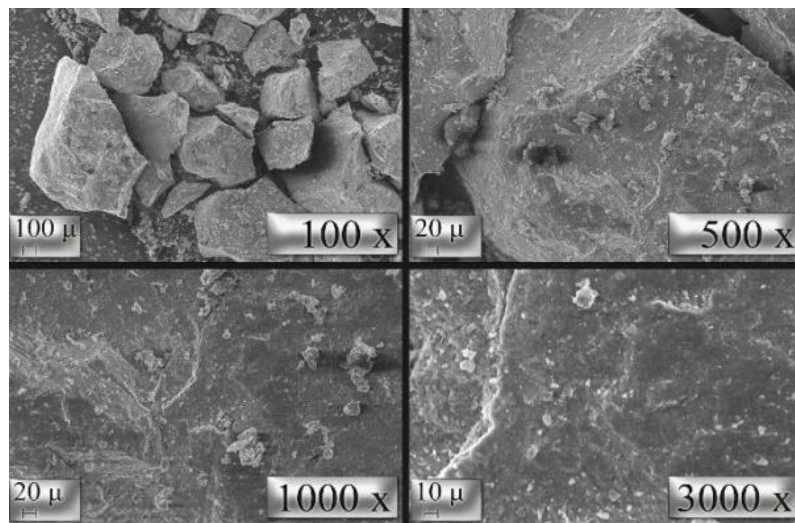


Figure 5. SEM micrograph of ASC at a magnification of 100 to 3000 \times .

Figure 3 shows that the sludge demonstrates irregular characteristics on its surface. Pyrolysis on the other hand, is utilized to increase the porosity of the precursor material, by removing the volatile compounds from these pores. Nevertheless, in Figures 4 and 5, it is possible to observe that AC and ASC have more elongated particles. Pushana-Rosero et al. [16] observed that the activated carbon samples chemically originated from sludge, have shown more appropriate superficial characteristics when submitted to acid leaching. The acid leaching removes the majority of the inorganic compounds, which can restrict access to the pores, as was observed in the ASC thermal gravimetric analysis. In addition, the acid leaching leads to a decrease of the particle sizes, augmenting its specific surface area. Therefore, further studies will be able to contemplate the effects of acid leaching in WTS activated carbon.

The adsorption of MB dye by the adsorbents happened quickly as it is shown on Figures 6 and 7, which presents the kinetic adjustment to the experimental data (in the range of 2 to 90 min) for the pseudo first order, pseudo second order, intraparticle diffusion and Elovich models from AC and ASC.

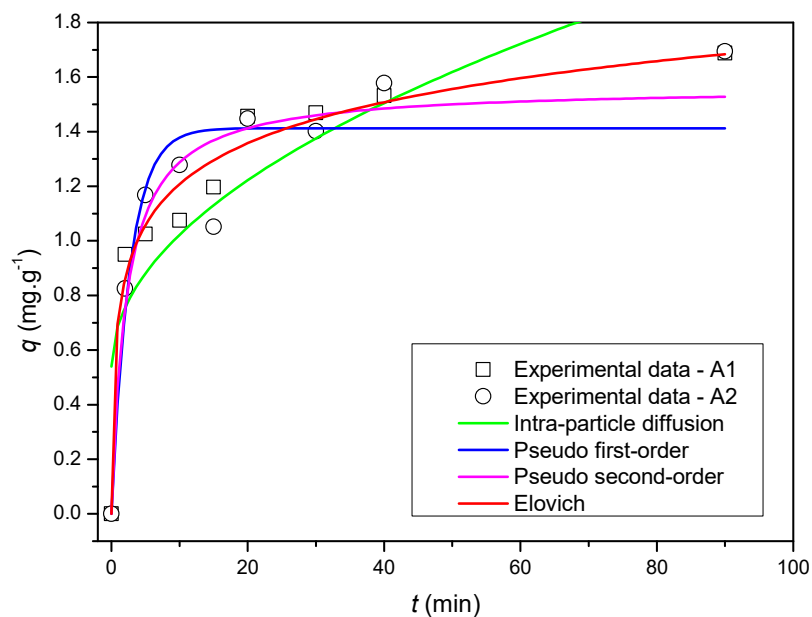


Figure 6. Kinetic models fitted to experimental data for AC.

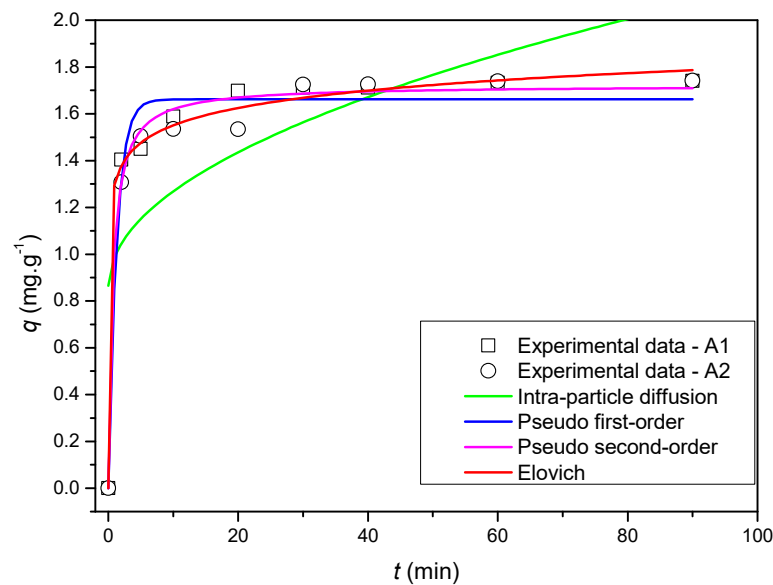


Figure 7. Kinetic models fitted to experimental data for ASC.

The results showed that the increase of contact between solid and liquid phases increase the MB adsorption. The maximum capacity of adsorption are 1.69 mg g^{-1} to AC (Figure 6) and 1.74 mg g^{-1} ASC (Figure 7), which corresponds to 96% and 99% of efficiency of removal, respectively. In 30 min of contact, more than 83% (1.46 mg g^{-1}) of adsorbate was removed when using AC and about 97% (1.72 mg g^{-1}) when ASC was used. The equilibrium was reached from ASC around 30 min. Similar studies obtained about kinetic adsorption: 90% of cadmium in 30 min was adsorbed using WTS activated with phosphoric acid [29]; around 98% of MB in 150 min using sewage sludge activated with sulfuric acid and pyrolysis at $625 \text{ }^\circ\text{C}$ [42], 50% of MB in 300 min using sludge from palm oil mill effluent activated with sodium hydroxide [43].

Table 2 shows the results obtained through the application of the kinetic models for the experimental data for AC and ASC in the adsorption of MB.

Table 2. Kinetic parameters of methylene blue (MB) textile dye adsorption onto AC and ASC.

Models	Pseudo First Order	Pseudo Second Order	Intraparticle Diffusion	Elovich
Adsorbent—AC				
Parameters	$q_e = 1.41$ $k_1 = 0.377$	$q_e = 1.56$ $k_2 = 0.297$	$k = 0.15$ $C = 0.539$	$a = 4.607$ $b = 5.66$
R^2	0.8646	0.9270	0.7307	0.9659
χ^2	0.0347	0.0187	0.0690	0.0087
ARE (%)	11.06	8.10	10.39	5.56
$\frac{MQ_R}{MQ_r}$	102.15	203.19	43.42	453.11
$F_{(R,r)}$	4.49	4.49	4.49	4.49
$\frac{MQ_{faj}}{MQ_{ep}}$	12.26	6.02	25.65	2.13
$F_{(faj,ep)}$	3.29	3.29	3.29	3.29
Adsorbent—ASC				
Parameters	$q_e = 1.66$ $k_1 = 0.789$	$q_e = 1.72$ $k_2 = 0.923$	$k = 0.13$ $C = 0.865$	$a = 9.321$ $b = 20,282.70$
R^2	0.9735	0.9897	0.5018	0.9935
χ^2	0.0082	0.0037	0.1548	0.0025
ARE (%)	4.55	2.55	12.48	2.16
MQ_R/MQ_r	586.77	1542.69	16.09	2390.51
$F_{(R,r)}$	4.49	4.49	4.49	4.49
MQ_{faj}/MQ_{ep}	6.62	1.77	147.21	0.69
$F_{(faj,ep)}$	3.29	3.29	3.29	3.29

Analyzing the results of Table 2 from AC and ASC the pseudo second order and Elovich models showed better correlation coefficients (R^2). Beyond the R^2 , lower values from ARE and X^2 indicate that the Elovich model was the best fit to describe experimental data. The statistical significance of the models was checked by a regression F test, where all the models showed a good fit. However, the best value was obtained with Elovich for both adsorbents did not show a lack of fit ($MQ_{faj}/MQ_{ep} < F_{(faj,ep)}$).

The Elovich model express an heterogeneous diffusion process, which is basically commanded by the diffusion factor and reaction rate, not by a simple first-order reaction [44]. It indicates that chemisorption processes have controlled the adsorption of MB on AC and ASC, similar results were presented by biochar from sewage sludge in the MB adsorption [45]. The parameter a , 4.607 ($\text{mg g}^{-1} \text{h}^{-1}$) for AC and 9.321 ($\text{mg g}^{-1} \text{h}^{-1}$) for ASC, corresponds to the rate chemisorption initial speed. The highest value obtained in parameter b for ASC indicates that this activated carbon has a bigger number of available sites for adsorption than AC. This interpretation is also corroborated by the textural characteristics of AC and ASC (Table 1).

The results of adsorption equilibrium data of MB textile dye onto AC and ASC at 25 °C are shown in Figures 8 and 9, and the results for the adsorption isotherm adjustments in the Langmuir and Sips models are presented in Table 3.

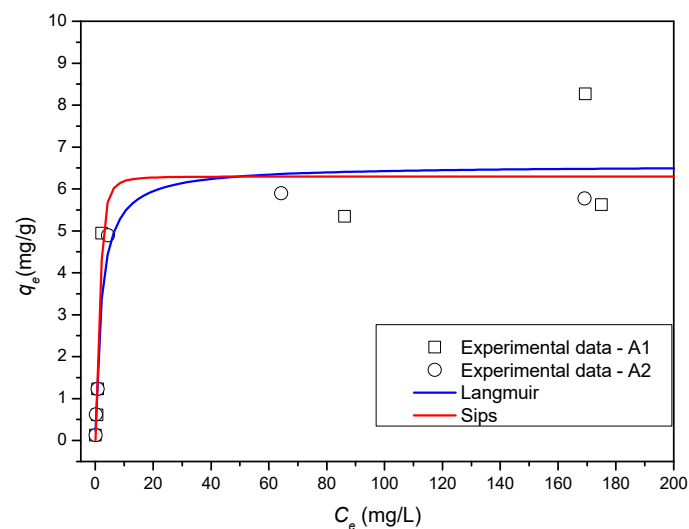


Figure 8. Adsorption isotherm of MB adsorption on AC at 25 °C.

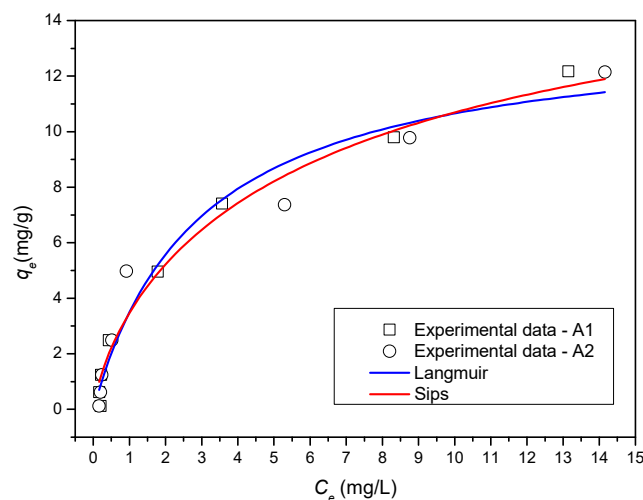


Figure 9. Adsorption isotherm of MB adsorption on ASC at 25 °C.

Table 3. Isotherm parameters for MB adsorption onto AC and ASC at 25 °C.

Models	Langmuir	Sips
Adsorbent—AC		
Parameters	$q_{max} = 6.56$ $K_L = 0.4877$	$q_{max} = 6.30$ $K_S = 0.4067$ $m = 0.4678$
R^2	0.9025	0.9268
X^2	0.8898	0.7319
ARE (%)	23.14	18.12
MQ _R /MQ _t	110.64	69.01
$F_{(R,r)}$	4.75	3.98
MQ _{faj} /MQ _{ep}	1.17	1.64
$F_{(faj,ep)}$	3.97	4.12
Adsorbent—ASC		
Parameters	$q_{max} = 13.79$ $K_L = 0.3398$	$q_{max} = 18.86$ $K_S = 0.2253$ $m = 1.3089$
R^2	0.9638	0.9775
X^2	0.6052	0.4858
ARE (%)	14.60	16.14
MQ _R /MQ _t	373.70	281.76
$F_{(R,r)}$	4.60	3.80
MQ _{faj} /MQ _{ep}	2.21	2.64
$F_{(faj,ep)}$	3.58	3.69

Figures 8 and 9 showed an increase on adsorption capacity at the first stage, which indicates the existence of compatibility between the adsorbent and adsorbate [46]. The AC and ASC isotherms characterize as type II and IV, however, according to showed in Table 1, the average pore diameter, both AC and ASC are mesoporous and this is a characteristic of isotherm equilibrium type IV [47]. This isotherm equilibrium type suggests the formation of multilayers of MB under the mesoporous adsorbent surface. Figures 8 and 9 also show that the C_e for ASC was lower than for AC, indicating a higher percentage of MB removal collated with AC, demonstrating the effect of chemical activation by ZnCl₂ in the production of ASC. Rozada et al. [48], studying the effect of ZnCl₂ activation on the production of activated carbon from sewage sludge using pyrolysis, obtained an increase in the adsorption capacity from 16.6 mg g⁻¹ to 137.0 mg g⁻¹.

The statistical significance of the models was checked by ANOVA and all models showed regressions significant without lack of fit. The values indicate that Sips is the most appropriate model to describe the equilibrium data, and indicates that the theoretical equilibrium adsorption capacity proposed by Sips model is similar to the experimental equilibrium adsorption capacity.

According to the parameters of m , the Sips model admits that the adsorption process of MB by ASC happened in a heterogeneous way ($m > 1$) and by AC in a homogeneous way ($m < 1$). The maximum adsorption capacities obtained to AC and ASC were, respectively, 6.2973 mg g⁻¹ and 18.8628 mg g⁻¹, both results agreed with FT-IR analysis (Figure 1). The improvement in the adsorption capacity of ASC indicates that chemical activation by zinc chloride is effective in the production of adsorbent from WTS for the removal of MB.

4. Conclusions

The WTS demonstrated to be an efficient precursor for production of activated carbon by the chemical activation with zinc chloride and pyrolysis operation at 550 °C. The activated carbons showed high results of surface area (around 100 m² g⁻¹) and pores size were classified as mesoporous, which justifies their potential of application in the removal of MB cationic dye. ASC showed higher presence of phenolic and carboxylic groups on the surface, which represents a better adsorption of cationic

adsorbates. The Elovich model describes better the kinetic process for AC and ASC, presenting statistical significance checked by a regression F test and did not show lack of fit. The maximum removal of MB to AC and ASC are 96% and 99%, respectively. For the adsorption isotherm, the model that best describes the adsorption data, checked by ANOVA, is the Sips model for both adsorbents, presenting a q_{max} of 6.30 mg g⁻¹ to AC and 18.86 mg g⁻¹ to ASC, which is a proof that the use of WTS as raw material for the production of carbon activated is an eco-friendly way to recycle this residue.

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