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Artigo

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Preparação e Caracterização de Compósitos de Argila Bentonita/Carvão Ativado e Aplicação de Planejamento Fatorial 2^3 em Estudo de Adsorção do Corante Azul de Metileno

Resumo: Nos últimos anos, um grande número de trabalhos envolvendo a preparação e utilização de compósitos de argila tem sido objeto de estudos científicos. Isto é decorrente de uma crescente preocupação social e ambiental, devido a alta taxa de esgotamento dos recursos de petróleo e novas regulamentações ambientais, as quais têm forçado a busca de novos compostos que não ofereçam riscos ao meio ambiente. Desta forma, neste trabalho descrevemos a preparação e caracterização de compósitos de argila/carvão ativado (AC) e dos seus precursores por técnicas como difração de raios X (DRX), microscopia eletrônica de varredura com espectroscopia dispersiva de energia (MEV-EDS), análise térmica (TG-DTA). O perfil de DRX dos compósitos mostrou características diferentes dos seus precursores argila e carvão ativado, ocorre um deslocamento dos picos de difração, sugerindo intercalação de carvão entre as camadas de argila. As condições ótimas para a adsorção do corante azul de metileno pelo compósito AC_{50} foram determinadas por planejamento fatorial. A maior eficiência de adsorção foi obtida nas condições de temperatura de 40 °C, pH 8,0, e força iônica igual a 0,01.

Palavras-chave: Argila bentonita; carvão ativado; compósitos; caracterização; planejamento fatorial.

Abstract

In recent years, several studies involving the preparation and use of composite clay have been the subject of scientific targets. This is due to an increasing social and environmental concern, due to high rate of depletion of oil resources and new environmental regulations, which are forced to search for new compounds that offer no risk to the environment. Thus, in this work we describe the preparation and characterization of composite clay/activated carbon (CA) and its precursors by techniques such as X-ray diffraction (XRD), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), thermal analysis (TG-DTA). The XRD profile of the composite showed different characteristics in relation to its precursor clay and activated carbon, a displacement of the diffraction peaks occurs, suggesting carbon intercalation between the clay layers. The great conditions for the adsorption of methylene blue dye by AC_{50} composite were determined by factorial design. The higher adsorption efficiency was obtained under the conditions of 40 °C, pH 8.0 and ionic strength equal to 0.01.

Keywords: Bentonite clay; activated charcoal; composites; characterization; factorial design.

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Preparation, Characterization of Bentonite Clay/Activated Charcoal Composites and 2^3 Factorial Design Application in Adsorption Studies of Methylene Blue Dye

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1. Introduction

Activated charcoal is the most popular and widely used adsorbent in water treatment and this has been attributed to the extensive surface area, micro-porous structure, high adsorption capacity and high degree of surface reactivity.[1-2] Also, activated charcoal has been successfully used as an adsorbent for removal of dyes from effluents. The adsorption of the dyes by this porous solid involves the transport of the dye from the solution and the diffusion of the dye molecules into the pores of the adsorbent.[3-4] The performance of the process of treatment with activated charcoal depends on the type of charcoal, as well as the characteristics of the effluent.[2-5] The ability of charcoal to absorb dyes has now been investigated and the results showed that the adsorption was very efficient. However, the contact time to reach equilibrium for adsorption of dyes on wastewater is generally great, due presence of other contaminants such as, acids or alkalis, salts, dissolved and suspended solids and other toxic compounds.[2-5]

Clays are of great importance as an alternative to the use of activated charcoal for adsorption of pollutants aquatic.[6] Clay is a rock that essentially consists of a group of minerals called clay minerals. Each different clay and each one of the four groups of ten clay minerals has a specific name and

different processes were also used to obtain the clay structure.[7] Clay minerals are hydrated silicates of Al, Fe, and Mg, with layered crystalline structures (phyllosilicates), made up of continuous sheets of SiO_4 tetrahedrons, arranged in a hexagonal shape, condensed with octahedral sheets of trivalent and divalent metal hydroxides.[8] Bentonites are clays of the montmorillonite group, whose members possess interlayer cations such as Na^+ and Ca^{2+}. Montmorillonite clays are some of the most abundant and most investigated clay minerals.[9]

The use of clay minerals to obtain composites through the interaction with organic compounds with specific functionalities has aroused scientific interest. This occurs because the most recent technologies require materials with a combination of properties that are not found in conventional materials such as pure clay and activated charcoal. Mineral/Carbon Material compounds (MCMCs) have been prepared by the combination of organic and inorganic components and constitute an alternative for the production of new multifunctional materials with a wide range of applications. These MCMCs are also interesting in the removal of dyes by adsorption. Dyes, even when present in small quantities, are visually detectable and cause serious aesthetic problems in river and lake water. The effluents of textile industries, dye manufacturing industries, and manufacturers of paper and pulp are highly colored.[10]

In addition to their aesthetic problems, most commercially-used dyes are resistant to biodegradation, photodegradation, and oxidation.[1] Dyes also significantly affect photosynthetic activity by reducing the penetration of sunlight; they are toxic to certain aquatic life forms due to the presence of exchangeable metals and chloride; some dyes are carcinogenic and mutagenic and can interfere in certain processes used to treat municipal waste water, such as ultraviolet disinfection.[1] Currently, adsorption is regarded an excellent method for wastewater treatment, particularly on dyes removal.[11]

Factorial design application on adsorption process has been observed in the literature. An example is the study in that the significance of the parameters pH, initial concentrations of Cr (IV) adsorbent and temperature were evaluated by experimental design with a reduced experiments number, minimizing costs and time.[12-13] In the present work, alternative composite materials resulting from the combination of bentonite clay and activated charcoal were prepared. The materials were characterized by different spectroscopic and thermal techniques and tested to evaluate their potential for adsorption of methylene blue dye. From the results, one of the composites was chosen for subsequent study of the optimization of the methylene blue adsorption process through factorial design in which the influence of factors such as ionic strength, temperature and pH was investigated.

2. Experimental

2.1. Materials

All chemical reagents used were of analytic grade, and the solutions were prepared with ultra-pure water. The clay used was bentonite clay (Argel T), supplied by Buntech Tecnologia de Insumos Ltda. According to the information provided by the supplier, the clay possesses thixotropic and anti-sedimentary properties. It is composed of oxides of aluminum, iron, and magnesium, and in a greater proportion, silicon. Moisture of materials was determined gravimetrically by desiccation in an oven at 110°C until constant mass and it were found moisture contents of 7.4 % and 2 % for clay and charcoal, respectively. The activated pine coal (pulverized) used was obtained from Alphacarbo Industrial (Guarapuava, Brazil). The dye methylene blue was used for the adsorption tests, and the absorbance measurements were performed using a Spectrum UV/Vis SP 2000 UV spectrophotometer.

2.2. Composites preparation

The composites were prepared using samples of pine charcoal ($Charcoal_{100}$) and Argel T clay ($Argel_{100}$). First, the starting materials were placed in an oven at 110 °C to dry, and after this, the clays were added to the charcoal in different percentages to create mixtures consisting of 85 % , 50 % and 15 % of dry clay. Then a clay-charcoal mixture was prepared, from an aqueous dispersion, using continuous stirring for approximately 15 minutes at room temperature. After this, the dispersion was allowed to rest for 24 h and it dried in an over at 110 °C also for 24 h. Then the samples were activate in oven at temperatures of 500 °C, 700 °C and 900 °C, for 30 minutes. The composite samples obtained were pulverized and standardized using a sieve number 70-400 mesh (ABNT - Brazilian Association for Standards and Techniques). According to the International Standards Organization, a 48-400 mesh (38-300 mm) sieve classifies materials as ultra-fine. The materials characterized and used in this work are referred to as follows: Argel T ($Argel_{100}$), activated charcoal ($Charcoal_{100}$), composite with 85 % of clay (AC_{85}) and composite with 50 % of clay (AC_{50}).

2.3. Materials Characterization

The X-ray diffraction pattern were performed using the powder method and a Bruker D2 Phaser diffractometer operated under the following conditions: 30 kV, 10 mA, copper source (kα, λ = 1.5418 Å); scanning step 0.02 (2θ), with time of 1.2 s per step; scanning range 3°-90° (2θ). Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) were performed in a thermal analyzer from Seiko, model 6300, under dynamic air atmosphere (50 mL min^{-1}), heating rate of 10 °C min^{-1}, from 25 to 1000 °C, Alpha alumina was used as a reference material for the DTA analyses. The infrared spectra were obtained using a Shimadzu FTIR-8300 spectrophotometer. The scanning conditions were 400-4000 cm^{-1} with 32 scans and resolution of 4 cm^{-1}. The samples were characterized in pellet form, with pellets made with 1 % of KBr. For X-ray fluorescence analysis, the measurement system was composed of a portable X-ray tube (Ag target, 50 µm Ag filter, 4 W), a Si-PIN detector (resolution of 190 eV for energy of 5.9 keV and a 25 µm Be window), with electronics for acquisition and evaluation of spectra. The measurement conditions were: 28 kV, 10 µA, Ag collimator, 500 s acquisition time. Scanning electron microscopy (SEM) images were obtained using a microscope Jeol, model 5900LV (Scanning Electron Microscope – Low Vacuum) equipped with EDS (Electron Dispersive Spectrometer) belonging to the Centro de Nanociência e Nanotecnologia César Lattes (C2Nano) at the Laboratório Nacional de Luz Sincrotron (LNLS), Campinas, São Paulo, Brazil. The samples were covered with gold, through the *sputtering* technique available in the C2Nano.

2.4 Factorial Design Study

The influence of variables such as pH, temperature and ionic strength on the methylene blue dye adsorption by the AC_{50} composite was investigated by a 2^3 factorial design. For the measurements, a UV-VIS spectrophotometer SP 2000 UV – Spectrum (LabGAT, Unicentro, Brazi), with 665 nm wavelength was used; this accords with the maximum adsorption of the methylene blue dye according to the literature (Neumann et al., 2000; Dural et al., 2011). Experiments were carried out employing methylene blue dye solutions with initial concentration equal 1000 mg L^{-1}, the adsorbent mass used was 200 mg, agitation of 150 rpm and controlled temperature in the shaker. Samples were centrifuged and the dye absorbance readings

were performed randomly for all level combinations presented in Table 1.

The effects of factorial design were calculated through: $E_f = (\bar{R}_+) - (\bar{R}_-)$ where $(\bar{R}_+)$ $(\overline{R}_+)$ and $(\overline{R}_-)$ are the averages at the (+) and (-) levels of the factors involved. The factor effects on absorption of the methylene blue dye by the AC_{50} composite were tested for the statistical significance by standard error and by probability normal graph analysis at 95 % confidence level. All the statistical analyses were carried out using the software "Minitab for Windows 16.2.2".

Table 1. Factors and levels of 2^3 factorial design study

Factors	Level (-)	Level (+)
Ionic Strength (mol L^{-1})	0.01	0.10
pH	3.0	8.0
Temperature (°C)	25	40

3. Results and discussion

The composite materials characterized in this study were those prepared at a temperature of 500 °C, which were denoted as AC_{85} and AC_{50}, with percentages of 85 % and 50 % of clay, respectively. The choice of these composites for the characterization studies was due the lower activate temperature used during preparation and the best efficiency on adsorption of methylene blue dye. Composite samples and their precursor´s materials ($Argel_{100}$ and $Charcoal_{100}$) were characterized by X-ray diffraction (Figure 1). It can be observed that the materials have a peak at approximately 2θ = 7.0°, indicating that they are layered material of the montmorillonite clay type. After activated of the materials at 500 °C, a change in the diffraction peaks was observed for the composites AC_{85} e AC_{50} in relation to the clay $Argel_{100}$, for low angles. This displacement suggests an increase in the interlamellar (d_{001}) spacing due to the process of intercalation of the charcoal between the layers of clay. It was observed that the d_{001} for A_{100} was 12.34 Å (peak 001); while for the composites the spacing was 13.85 Å for AC_{85} and 14.59 Å for AC_{50}.[14] Therefore, this interlamellar spacing is more pronounced for the composites when compared with the Argel clay. It was also noted that $Argel_{100}$ possessed a 2θ peak at approximately 14.58 Å, which was not present for the composites, suggesting the presence of charcoal in the composites.[15-16]

Studies performed by Rodrigues et al. (2004) with organoclay nanocomposites/rubber presented an increase in basal clay mineral distances showing interleaving of quaternary ammonium cations. This is in agreement with the observations verified for composites studied in this work, with incorporation of charcoal in clay structure.[16-17]

Thermogravimetric analysis (TG/DTG) was used to evaluate the thermal properties of the materials. Figure 2c and 2d exhibits curves responding to loss of mass for the AC_{85} and AC_{50} composites, respectively. It can be observed that the DTG curve obtained for the AC_{85} composite (Figure 2c) shows four events with a total loss of mass of approximately 15.4 % of the initial mass. The first mass loss equal to 5.4 % (between 40 and 200 °C) is attributed to the evaporation of 1.14 hydration or weak-bonded water molecules, for the AC_{85} composite) and 2.7 molecules of weak-bonded water for the composite AC_{50}. This probably occurs due to the presence of montmorillonite that exhibits the first region of loss of mass between 40 and 200 °C, corresponding to water elimination. The event can be attributed to the volatilization of weak-bonded water, present on the

surface of the agglomerates and between the aggregates. The second mass loss occurs between 200 and 550 °C and is related to the volatilization of solvation water (interlamellar), which is more strongly bonded. The third mass loss, between 500 and 700 °C, is related to the loss of structural hydroxyls, and it can be noted that events above 750 °C are present in all composites, showing a decomposition of the oxides present in the sample. Figure 2a and 2b shows the mass loss events for the precursors $Charcoal_{100}$ and $Argel_{100}$.[18]

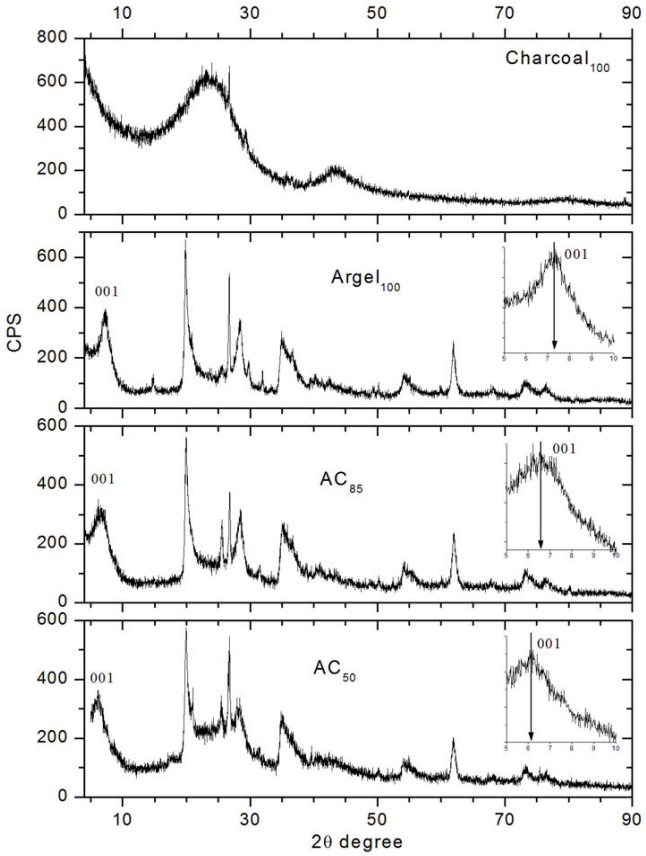

Figure 1. X-ray diffraction patterns of precursor's materials and composites: $Charcoal_{100}$, $Argel_{100}$, AC_{85} and AC_{50}

Differential thermal analysis is based on the difference of temperature between a sample and a reference to supply the parameters to relate endothermic and exothermic processes.[19] During the analysis of the samples, it can be observed that there is not uniformity in the loss or gain of energy, since there are two endothermic and two exothermic events. It can be seen that the endothermic events always precede the exothermic events. Therefore, in the first event there was probably only absorption of heat for evaporation of water derived from moisture absorbed by the material during handling and storage. The next event, which occurs between 200 °C a 600 °C was attributed to the dehydration of oxides present in the samples. It can be verified that the event that occurs between 600 and 800 °C is attributed to the liberation of water contained in the oxide structures and the last is due to the decomposition of these oxides.[5]

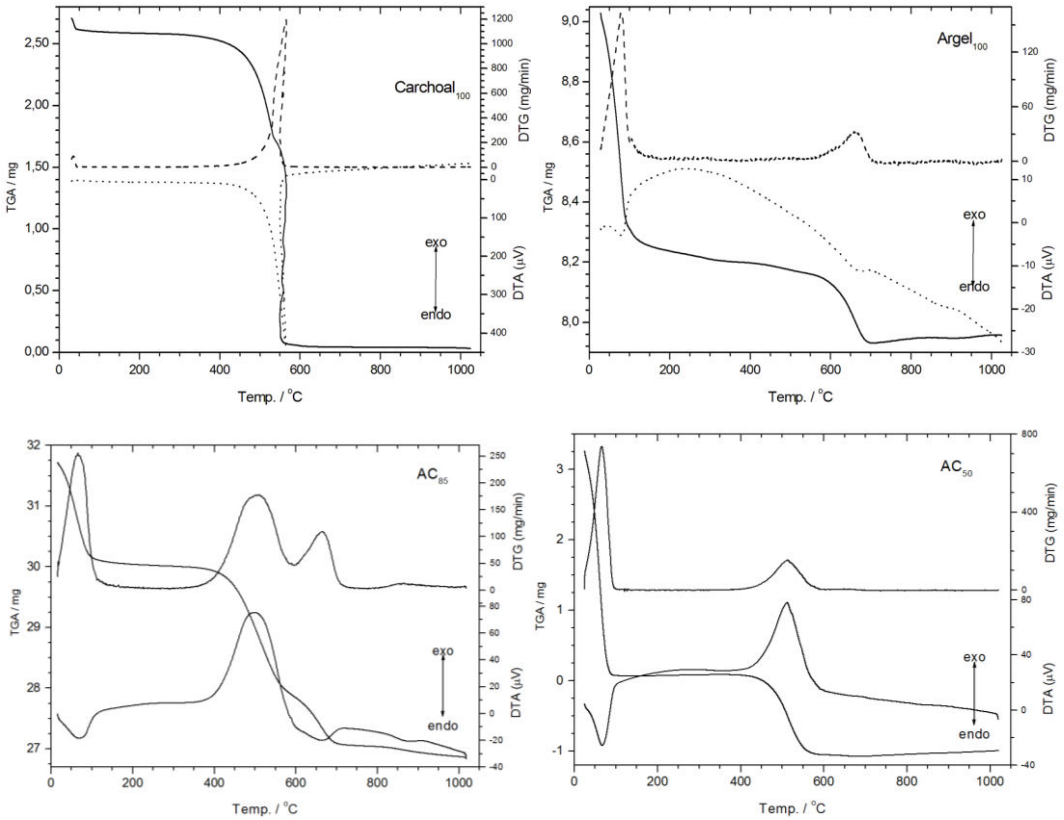

Figure 2. TG/DTA curves of precursor's materials and composites: $Charcoal_{100}$, $Argel_{100}$, AC_{85} and AC_{50}

Qualitative chemical analysis of the composites AC_{85} and AC_{50} and the precursors $Charcoal_{100}$ and $Argel_{100}$ were performed by X-ray fluorescence, and the elements identified (strontium, rubidium, yttrium, zirconium, copper, zinc and manganese) were present in trace amounts, in proportions smaller than 0.05 %. The chemical composition was determined by energy dispersive X-ray spectroscopy (EDS) and the results obtained are summarized in Table 2. Elements found in small proportions, but significant amounts were obtained directly using the software from equipment. Figure 3 shows the results obtained by EDS for the precursors and the composites highlighting the presence of the principal elements in the samples and confirming the presence of charcoal in the composites.

Table 2. Percentage (mass) of the principal elements presents in the composites and their precursors by EDS analysis

Sample	Mass (%)							
	Na	Mg	Al	Si	Ca	Fe	C	O
$Charcoal_{100}$	n.d.	0.07	n.d.	n.d.	0.71	n.d.	98.56	n.d.
$Argel_{100}$	2.09	1.49	10.18	40.26	1.13	4.94	ND	39.89
AC_{85}	0.53	0.46	2.91	9.27	0.87	2.23	61.26	22.16
AC_{50}	0.55	0.41	3.02	10.14	0.48	2.56	59.53	22.88

*n.d. – NOT DETECTED

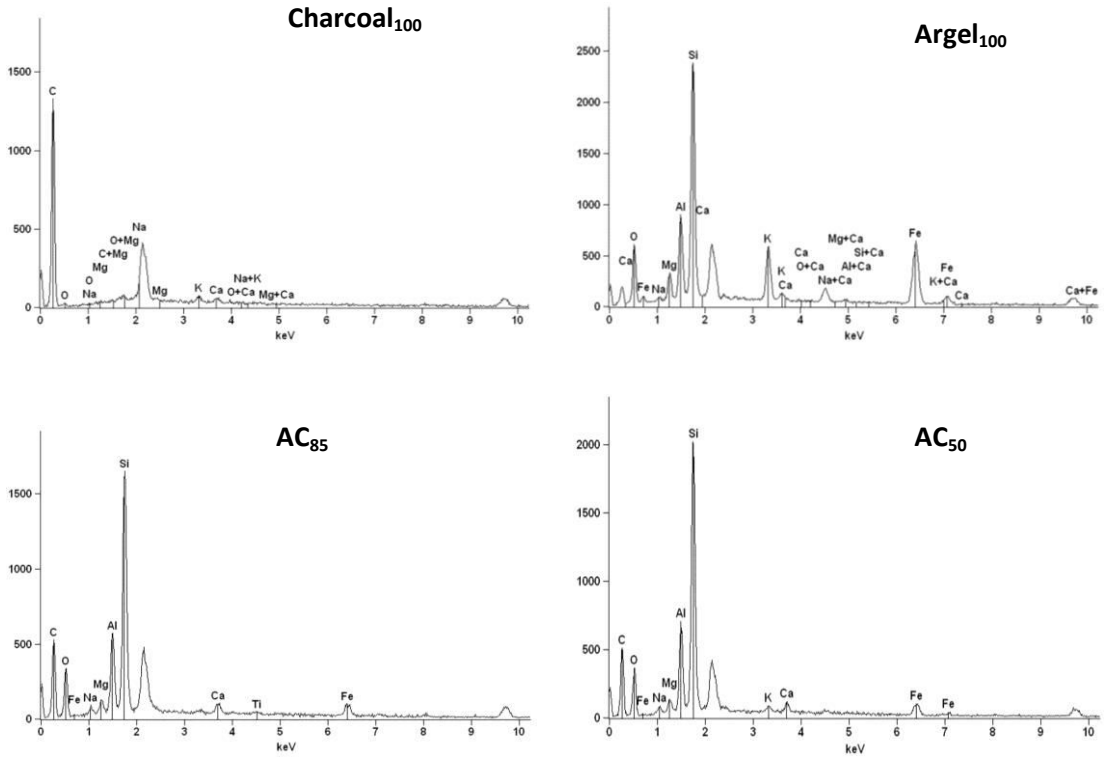

Figure 3. Chemical analysis by X-ray spectrometry energy dispersive (EDS) of precursor's materials and composites: $Charcoal_{100}$, $Argel_{100}$, AC_{85} and AC_{50}

The infrared spectra of the precursor´s materials and composites are shown in Figure 4. In these spectra, peaks can be observed at 3633 cm^{-1} for $Argel_{100}$ clay, in the composites we have peaks attributed to the clay (stretching OH-). At 3462 cm^{-1} present in the $Charcoal_{100}$ and 3430 cm^{-1} present in the AC_{50} composite (OH- vibrations (stretching). The band observed at 1650 cm^{-1} for the Argel clay and the AC_{50} composite is due to adsorbed water. The band at 1035 cm^{-1} observed in the Argel clay and composites are related to the Si-O vibrations.[20] Peaks characteristic of the octahedral sheets present in the clay can be observed between 522 cm^{-1} and 462 cm^{-1}.[21]

Figure 5 shows the SEM images of the activated pine charcoal (Figure 5a) and the Argel clay (Figure 5b). The charcoal evidences irregular shapes, such as those of broken glass, while the clay contains less irregular shapes of varying sizes. The clay evidences aggregates of uniform size and shape and of a porous nature, in the form of large rounded pieces with no sharp points.[20] In the electronic scanning micrographs of the samples of the composites (Figure 5c), it can be seen that these samples have charcoal on their surface, and that this is more perceptible in the AC_{85} composite. In the e AC_{50} composite (Figure 5d), various charcoal fragments can be observed on the clay surface, which was also confirmed by X-ray diffraction analysis, which showed a greater basal spacing between the layers.[3]

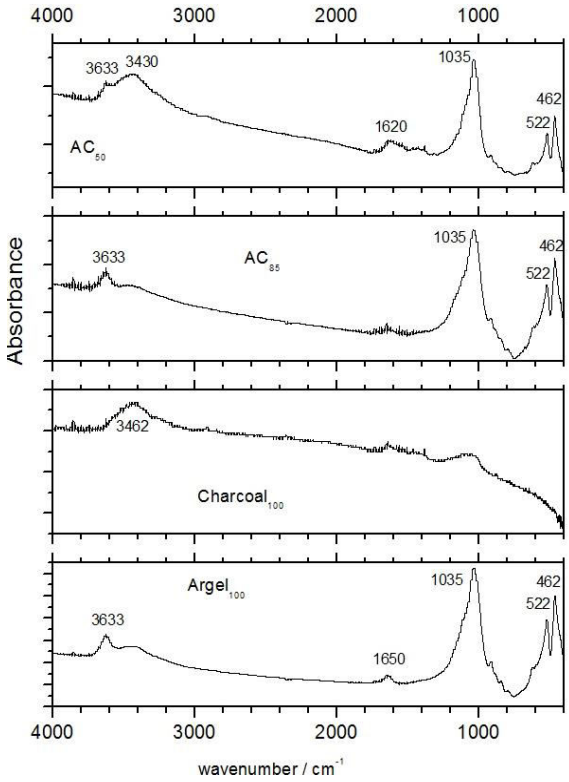

Figure 4. Vibrational spectra in the infrared region for the precursor's materials and composites: $Charcoal_{100}$, $Argel_{100}$, AC_{85} and AC_{50}

Various studies have been done to test the adsorption of dyes using clays and activated charcoal, and the object of the current study was to evaluate the application of composites obtained from these precursors for the adsorption of dye. The trials for adsorption of methylene blue dye by the composites obtained at different activated temperatures were performed with an initial pH of 5, solution of dye with initial concentration of 300 mg L^{-1}, temperature of 25 °C and stirring at 150 rpm for 3 h. The adsorption tests were performed for composites treated at different activated temperatures (500, 700 and 900 °C) and the results obtained are shown in Figure 6. The AC_{50} and AC_{85} composites showed better dye adsorption than the other composites prepared, showing greater efficiency in the removal of the dye methylene blue from the solution. The results of adsorption efficiency for materials AC_{50} and AC_{85} treated at 700 °C were 36 ± 13 % and 48.8 ± 4.0 % respectively, while for those treated at 900 °C were 37.6 ± 0.5 % and 67.1 ± 16.0 % respectively. On the other hand, the composites treated at 500 °C had an efficiency of 93.9 ± 5.7 % and 87.4 ± 1.6 % for AC_{50} and AC_{85} materials, respectively.

Therefore, the AC_{50} and AC_{85} composites were characterized and will be used in future studies of equilibrium of adsorption of methylene blue dye. Another relevant factor in the choice of these composites for the studies was the lower activated temperature used during preparation. AC_{50} and AC_{85} composites also showed better performance of adsorption than charcoal, which reinforces its industrial application, due to lower cost associated with clay. Methylene blue is a cationic dye in aqueous solution and so the adsorption of this dye is primarily influenced by surface charge on the adsorbent.[21-22] Silanol groups present on clay surface (Figure 4) become deprotonated with increase in the pH solution, thus increasing the number of negatively charged sites on composites, which favors the adsorption of methylene blue by the new materials compared to charcoal.[21]

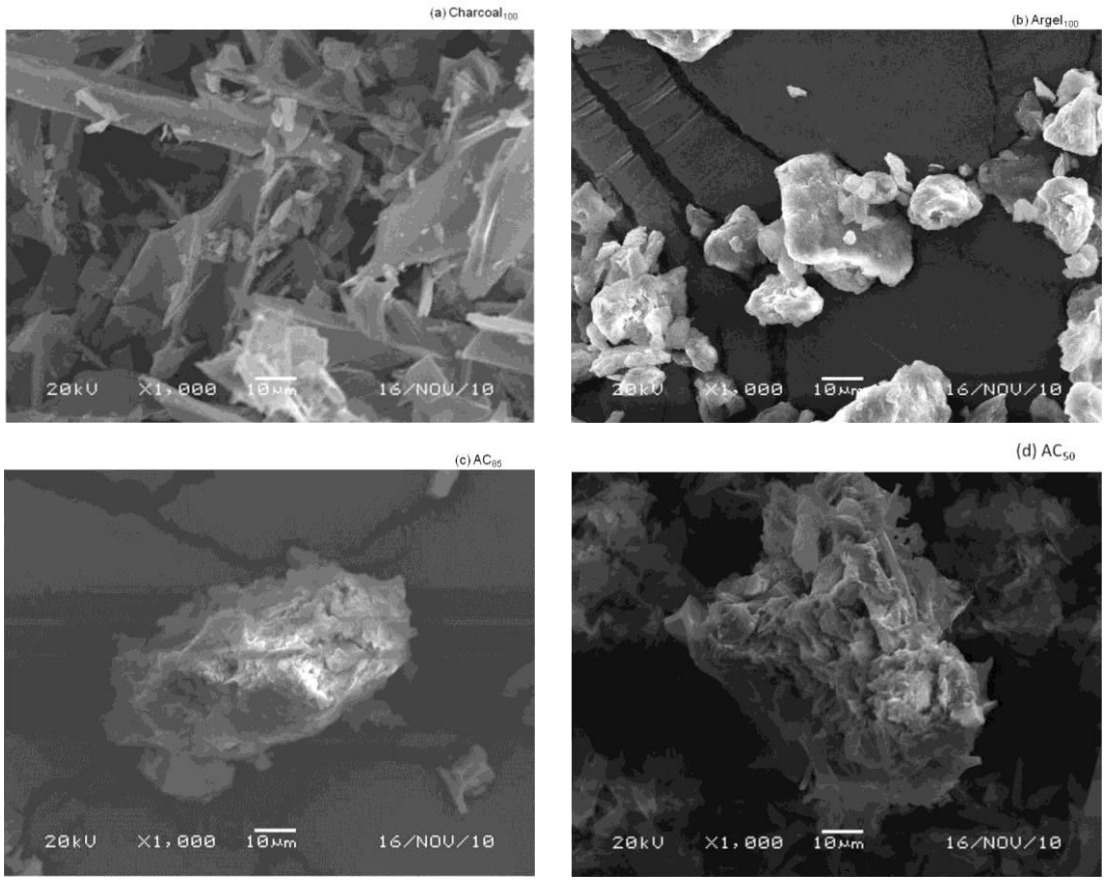

Figure 5. SEM images of the of precursor's materials and composites: $Charcoal_{100}$, $Argel_{100}$, AC_{85} and AC_{50}

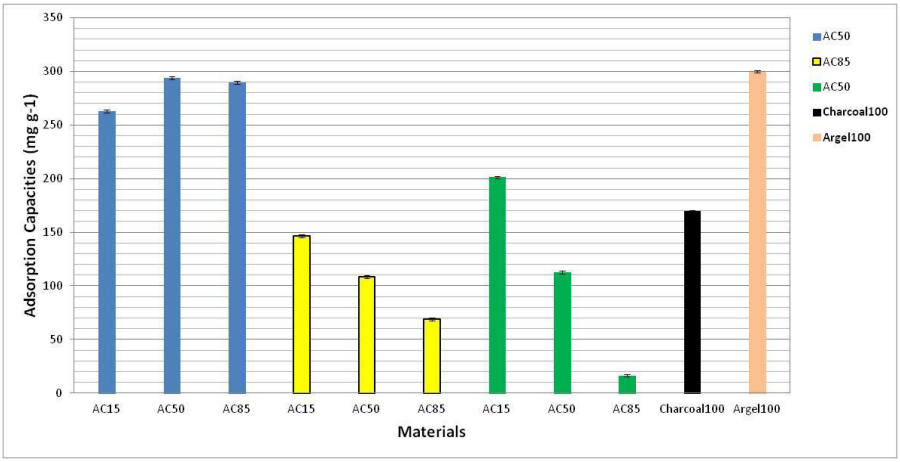

Figure 6. Comparison of the adsorption of metlhylene blue by the clay/coal composites

The composites prepared in this work have potential for application in studies of equilibrium adsorption of dyes and metal ions and, so these materials will be explored for this application. Therefore, a more complete study considering the application of factorial designs varying factors as pH, ionic strength and temperature for both composites (AC_{85} and AC_{50}) was performed,[22-23-24] in order to determine the influence of

these variables on the efficiency of methylene blue dye adsorption. Results obtained by application of the factorial design in the study of methylene blue dye adsorption by composite AC_{50} are shown in Table 3, and the calculated effects are presented in Table 4.

Analysis of Pareto's graph (Figure 7) and standard error at the 95.0 % confidence level of factorial design results (Tables 3 and 4) demonstrates that all factors are significant as well as the interaction effects between ionic strength and temperature, pH and temperature, and the interaction effect between the three factors (ionic strength, pH and temperature).

Table 3. Results of 2^3 factorial design applied to methylene blue dye adsorption by AC_{50} composite

Experiments	Ionic strength/M	pH	Temperature/°C	Averages of Adsorptive capacity (*q*) ± SD
1	0.01	3.0	25	204.45 ± 0.40
2	0.10	3.0	25	195.50 ± 0.20
3	0.01	8.0	25	200.68 ± 1.70
4	0.10	8.0	25	189.63 ± 0.30
5	0.01	3.0	40	229.26 ± 0.60
6	0.10	3.0	40	213.33 ± 0.60
7	0.01	8.0	40	230.30 ± 0.20
8	0.10	8.0	40	218.00 ± 0.20

Table 4. Effects and standard errors from 2^3 factorial design applied at methylene blue dye adsorption by AC_{50} composite

Effects	Estimates* ± SE
Global mean	210.14 ± 0.18
Main Effects	
Ionic strength (1)	-12.06 ± 0.36
pH (2)	-0.98 ± 0.36
Temperature (3)	25.16 ± 0.36
Second order interaction effects	
(1)x(2)	0.38 ± 0.36
(1)x(3)	-2.06 ± 0.36
(2)x(3)	3.84 ± 0.36
Third order interaction effect	
(1)x(2)(3)	1.43 ± 0.36

* Estimates higher than 0.83 are significant at 95.0% confidence level

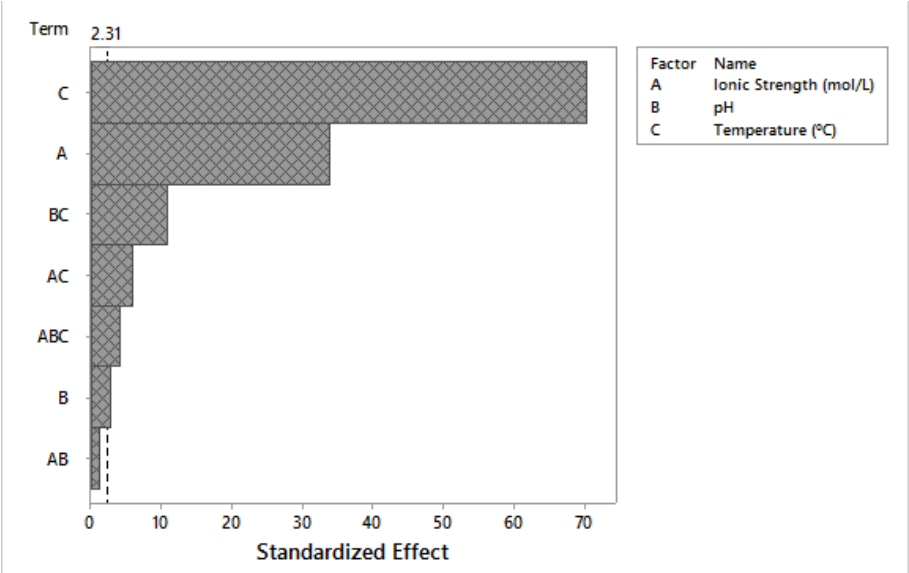

Figure 7. Pareto's graph for the standardized effects of the 2^3 factorial design at 95.0 % confidence level

Figure 8 suggests that the raising in temperature from 25.0 to 40.0 °C is significant to the adsorption of the methylene blue dye by the composite $AC_{50,}$ leading to increase of 25.16 mg g^{-1} in the adsorption capacity. This result indicate that an increase in temperature enables that a greater number of molecules of the methylene blue dye possess sufficient energy to interact with the adsorbent surface, decreasing the viscosity of the medium, and thereby increasing the mobility of the dye molecules in solution.[22-23] So, the adsorption process is favored.

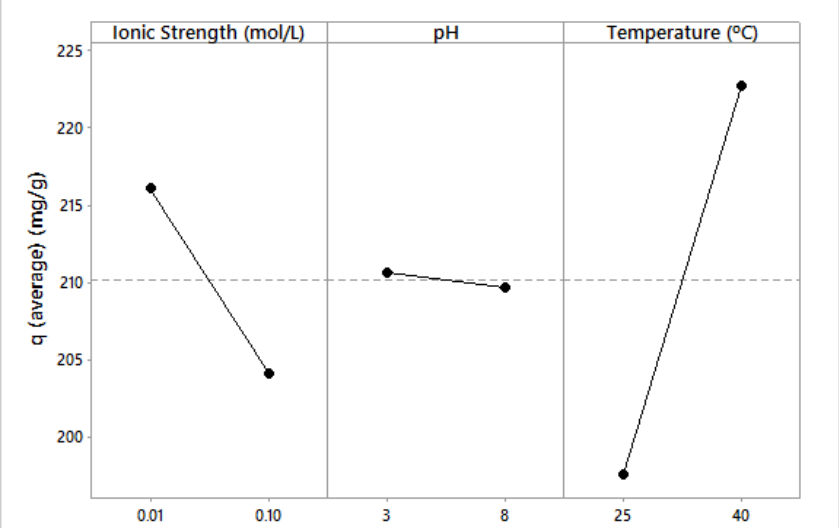

Figure 8. Graph for the interpretation of effects from 2^3 factorial design applied for the study of the methylene blue dye adsorption by AC_{50} composite

In Figure 8 is also illustrated the effect of ionic strength on the adsorption of methylene blue by AC_{50} composite. The increase on ionic strength from 0.01 to 0.1

resulted in a decrease of 6.12 mg g^{-1} of the dye amount adsorbed. When the electrostatic forces between the adsorbent surface and the ions of the salt are relatively strong, an increase in ionic strength would decrease the amount adsorbed.[24-25]

The change in pH of 3.0 to 8.0 had no important influence on the adsorption process (Figure 8). This result is quite interesting because it suggests that the application of AC_{50} composite in methylene blue dye adsorption can be performed without pH control, which increases the economic viability of this process.

In addition to the main effects, significant interaction effects were observed between the variables ionic strength and temperature, pH and temperature, and between the three factors. The factors cannot be analyzed separately because the effects of each depend on the levels of the other variables; this can be more readily explained by the lines shown in Figures 9, 10 and 11.

It can be observed in Figure 9 that the methylene blue dye adsorption in solution is raised (higher q values), when the pH is increased from 3.0 to 8.0 and when the ionic strength is decreased from 0.01 $mol.L^{-1}$ to 0.1 $mol.L^{-1}$. It suggests that the presence of salt, in the form of KCl favors the electrostatic interaction of the dye through the surface of the adsorbent similarly to results reported in the literature by Arafat et al (1999).

It can be seen from Figure 9 that the change in ionic strength of 0.01 to 0.1 causes a decrease in the amount of adsorbed methylene blue dye by composite. However, while at 25 ° C the reduction is of 10.0 mg g^{-1}, at a temperature of 40.0 ° C is of 14.0 mg g^{-1}. This shows that there is interaction between the variables ionic strength and temperature, and therefore they should not be analyzed separately.

Figure 10 enables the interpretation that at 40 °C and pH 8.0 there was increase in the capacity of adsorption of the methylene blue dye by AC_{50} composite. In order to justify this fact, it can be suggested that the increase in temperature improves the mobility of dye molecules, potentiating the adsorption process on the surface of the adsorbent. At pH 8.0, it is suggested that there is a higher number of negative loads on the surface of the adsorbent, thus favoring the adsorption of the methylene blue dye, a cationic dye. Another factor, documented in the literature, which justifies higher adsorption at pH 8.0 is the deprotonation of silanol groups present on the clay surface, which is explained by the increase in the electroforetic mobility at high pH values.[27]

Figure 11 illustrate the third order interaction effect for the variables: temperature, pH, and ionic strength. In this work it was observed that higher q values results in greater efficiency for the removal of methylene blue dye by AC_{50} composite. So it is noted that the factors that produce this response are: high levels of temperature and pH and level low of ionic strength.

However, in the experiment where the low levels of pH and ionic strength and high level of temperature are used it was obtained a response with a difference of only 1.035 units in the q value indicating that the pH did not significantly affect the adsorption of the dye methylene blue in the experimental region investigated by factorial design. The factors and their levels corresponding: temperature of 40 ° C, pH equal to 3.0 and ionic strength of 0.1 mol l^{-1}, produced a less efficient adsorption of dye methylene blue by AC_{50} composite.

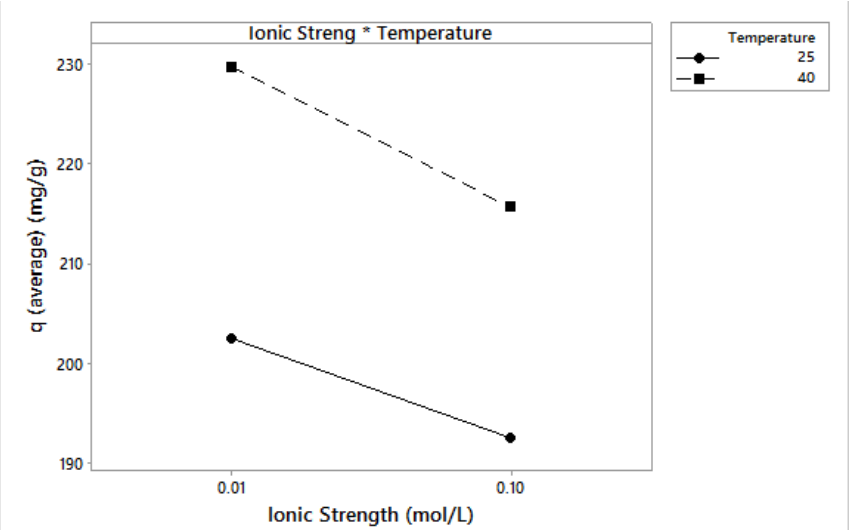

Figure 9. Graph of the interaction effect between ionic strength and temperature

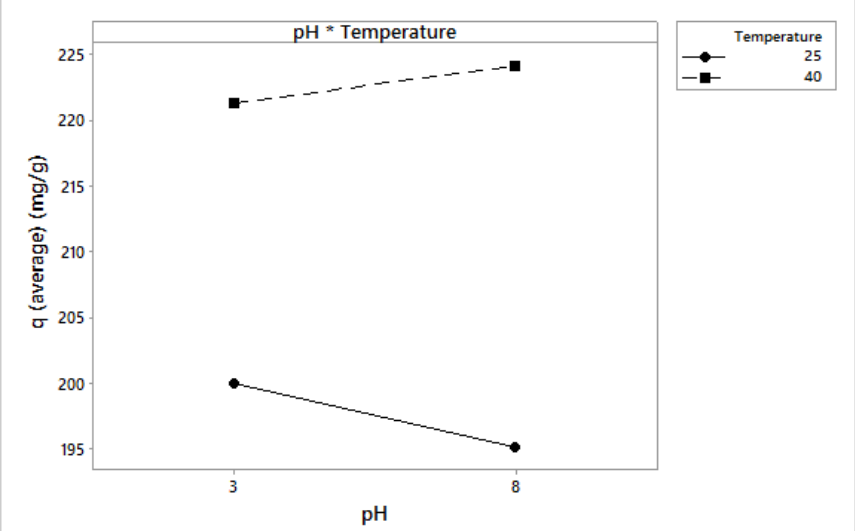

Figure 10. Graph of the interaction effect between pH and temperature.

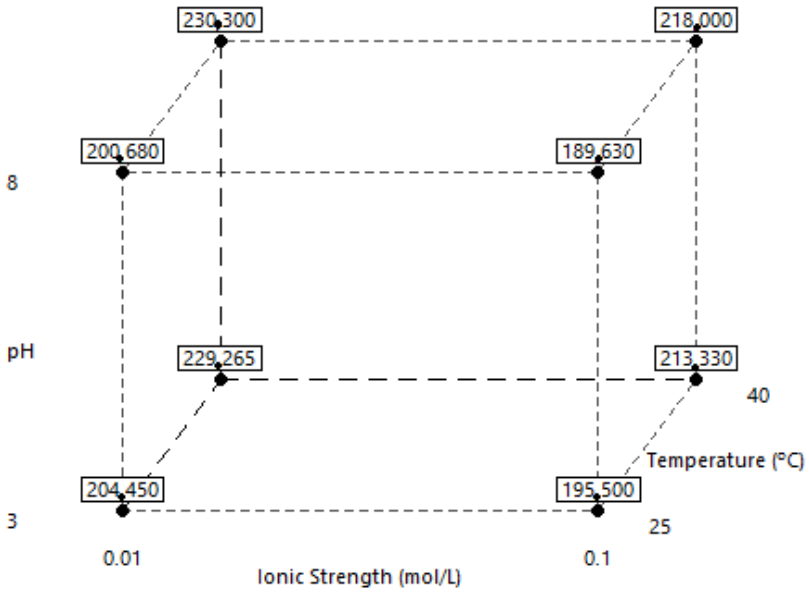

Figure 11. Interaction effect between temperature, pH and ionic strength for adsorption of methylene blue by AC_{50} composite

4. Conclusion

The characterization results showed the intercalation of activated pine charcoal between the layers of the bentonite clay Argel T and the thermal stability of the composites obtained was higher than the precursors. The composite prepared at a temperature of 500 °C showed a higher efficient adsorption of the methylene blue dye than others compositions prepared at the same temperatures such as the others temperature studied. All materials prepared at 500 °C showed better efficiency in removal of methylene blue than charcoal, suggesting enhancement of in their properties as adsorbent in general. The results indicate that the morphology, surface area and chemical composition of the composites play an important role in adsorption processes, especially for removal of dyes in wastewater. Factorial design results indicate that the variables temperature and ionic strength have strong influence in the adsorption of methylene blue dye by AC_{50} composite. The pH variable was not very important for the adsorption of the dye investigated; suggesting that for the process does not need to control pH, making it more attractive from an economic standpoint. The higher adsorption efficiency was obtained under the conditions of temperature 40.0 ° C, pH 8.0 and ionic strength equal to 0.01.

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