Kinetic adsorption study of textile dye “Reactive yellow BF-4G 200%” through adsorption using natural and activated smectite clays

Kinetic estudo da adsorção de corantes têxteis "Reactive amarelo BF-4G 200%", através de adsorção utilizando naturais e argila esmectítica ativada

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(Recebido em 19 de abril de 2012; aceito em 11 de julho de 2012)

The main objective of this study was to evaluate Reactive Yellow 4G-BF-200% dye removal process through adsorption on smectite clays in their natural, chemically activated and thermally activated forms. A solution of 20 mg/L of dye was prepared and the mass of smectite clay used was set at 0.2 g smectite for each smectite clay employed. An adsorption kinetics was developed according to a 2^2 factorial design in which samples containing adsorbent and adsorbate were submitted to finite bath assays in shaker IKA KS 130-WEBER at room temperature (25°C), being conducted at intervals of 0-600 minutes using NaCl P.A, which participates in the process of conduction, fixation the trapping of the dye in the clay pores. The results of 98.05, 86.4 and 95.1% were obtained as removal percentages for natural, chemically and thermally activated smectite clays, respectively. These results showed that chemical and thermal activation were not efficient when compared with results found for natural smectite clay, according to the method used. Based on the kinetic results obtained, it was possible to test the Lagergren’s pseudo-first-order and pseudo-second-order kinetic models, the latter being the most appropriate. The use of smectite clay as adsorbent seems to be an efficient and economically viable method for the treatment of textile effluents.

Keywords: Smectite clay; adsorption; textile effluent

O objetivo principal deste estudo foi avaliar reativa processo de remoção Amarelo 4G-BF-200% de corante através de adsorção em argila esmectítica em suas formas naturais, ativado quimicamente e termicamente ativados. Uma solução de 20 mg/L de corante foi preparada e da massa de esmectita argila utilizada foi fixado em 0,2g para cada argila de esmectita empregada. Uma cinética de adsorção foi desenvolvida de acordo com uma Planejamento fatorial 2^2 em que as amostras contendo adsorvente e adsorvato foram submetidas a ensaios de banho finito no IKA agitador KS 130-WEBER à temperatura ambiente (25°C), sendo conduzida em intervalos de 0-600 minutos usando NaCl PA, que participa no processo de condução, o aprisionamento de fixação do corante nos poros de argila. Os resultados de 98,05, 86,4 e 95,1% foram obtidos como percentagens de remoção para naturais, argilas de esmectita quimicamente e termicamente ativadas , respectivamente. Estes resultados mostraram que a ativação química e térmica não foram eficazes quando comparados com os resultados encontrados para argila de esmectita natural, de acordo com o método utilizado. Com base nos resultados cinéticos obtidos, foi possível testar a Lagergren de pseudo-primeira ordem e pseudo-segunda ordem modelos cinéticos, sendo

este último o mais adequado. A utilização de argila de esmectita como adsorvente parece ser um método eficiente e economicamente viável para o tratamento de efluentes têxteis.
Palavras-chave: argila esmectita; adsorção; efluente têxtil

1. INTRODUCTION

Industrial effluents are a major cause of environmental pollution. Effluents discharged from industries that use dyeing processes are highly colored[1] because dyeing and finishing processes in the textile industry generate waste with high content of color and organic compounds. Synthetic dyes are aromatic compounds that are incorporated into various functional groups and are widely used in textile, leather, paper, plastic and other industries. Some of these dyes may pollute the environment and produce carcinogens and toxic chemicals[2].

Dyes are designed to resist rupture over time when exposed to sunlight, water, soap and oxidizing agents. Due to their complex structure and synthetic origin, they cannot be easily removed by conventional physical, chemical or biological effluent treatment processes such as flocculation-coagulation, ozonation and aerobic or anaerobic digestion[3, 4]. These processes are expensive and may lead to the generation of sludge or by-products[5].

Among the available physical methods, the adsorption process is one of the most efficient methods for removing dyes from wastewaters, especially if the adsorbent is inexpensive and readily available[6]. Activated carbon is the most widely adsorbent used for removing dye, but it is very expensive[7]; therefore, many low-cost adsorbents have been proposed as alternatives such as peat[8], sepiolite[9,10,11], bentonite[12,13], zeolite[14], montmorillonite[15], chitosan and nanocomposite[16], and pine sawdust[17].

Compared with other wastewater treatments, adsorption as separation and purification technique has shown to be one of the most effective relatively inexpensive methods for removing dyes, offering some advantages such as high efficiency, simple operation and easy recovery and reuse of the adsorbent[18,19]. Adsorption is a powerful physicochemical process for the treatment of wastewaters, which involves the passive separation of adsorbate from an aqueous phase onto a solid phase[20, 21]. After adsorption, the dissolved dye molecules are adhered on the adsorbent surface, and the depleted adsorbent may be recovered for reuse purposes.

The color removal efficiency is affected by many physicochemical factors such as type and structure of the dye, chemical nature and properties of the adsorbent surface, and most importantly, the dye-adsorbent interaction. It is also affected by operational conditions such as the dye concentration, dosage of adsorbent, contact time, solution temperature, pH, and ionic strength[20].

Clays have high adsorption capacity due to their lamellar structure that offers high specific surface area[22] and the possibility of adsorbing ions and organic polar molecules into particles of the external site and in intercalary positions[23, 24].

This study evaluated the adsorption of textile dye Reactive Yellow BF-4G 200% onto natural, chemically activated and thermally activated smectite clays. The dye chemical structural is shown in Figure 1.

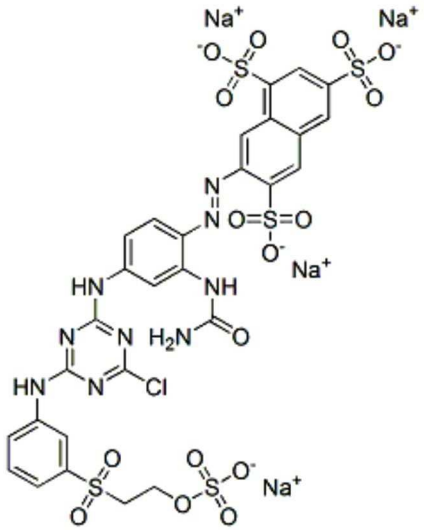

Figure 1: Chemical structure of textile dye Reactive Yellow BF-4G 200%.

Adsorption conditions such as rotational speed, contact time and the mass of the fixing agent (NaCl) were analyzed in this study. The fixing agent is responsible for conducting the dye to the clay layers, thus being able to increase the cation exchange capacity (CEC). The adsorption capacity of clays used for this dye was also assessed using the adsorption isotherm technique.

A 2^2 factorial design was used to examine possible interactions and variations in the adsorption process, which is of easy application and produces satisfactory results, using a smaller number of trials.

The experimental data were analyzed using the Langmuir and Freundlich isotherms, since these models are the most used in literature for the process under study to determine which isotherm best represents the process carried out, although other adsorption isotherm models can be tested, for example, the BET model (Braunauer, Emmet and Teller).

2. MATERIAL AND METHODS

2.1 Chemicals and reagents

The adsorbent used in this study was smectite clay obtained from the gypsum production region of Araripe-PE (Brazil). Clay with particle size of 35 mesh was used in its natural, chemically activated and thermally activated forms.

Chemical activation was performed by adding 0.255 L HCl (50% by volume) to a mass of 150 g of natural smectite clay. Then, the mixture was exposed to sunlight for a period of about 30 days, considering that there was complete liquid evaporation.

The thermal activation was performed at 300°C for a period of 24 hours.

The dye Reactive Yellow 4G BF-200% was provided the “Céu Azul” laundry, located in the municipality of Toritama-PE (Brazil). The other reagents used were of analytical grade from FMaia.

2.2 2^2 factorial design

Initially, 20 mg/L of dye Reactive Yellow 4G-BF 200% solution at pH 6.47 was prepared. The mass of smectite clay was fixed at 0.2 g for each clay used (natural, thermally activated and chemically activated) and the other variables were applied according to the 2^2 factorial design based on results obtained by[25], as shown in Table 1.

Table 1: 2^2 Factorial design applied to the experiment.

Variables	Levels		
	Lower (-)	**Center point (0)**	**Higher (+)**
NaCl (g)	**2,0085**	**5,512**	**8,340**
Rotation (rpm)	**200**	**300**	**400**

Assays were performed in duplicate. Each type of smectite clay (natural, chemically activated and thermally activated) was mixed with NaCl P.A. and the mixture was added of 50 mL of synthetic dye. Then, the tests were carried out in finite bath shaker IKA KS 130-WEBER for a total time of 5 hours.

After this time, the solutions were vacuum filtered on millipore filter paper (Millipore membranes). The final concentration of synthetic effluent was determined using a UV-Visível Genesys 2 spectrophotometer.

By means of spectrophotometric analysis, the percentage of color E removal (%) and the maximum adsorption capacity *q (mg/g)* for each clay studied were determined, according to equations (1) and (2):

$$q = \frac{(C_0 - C_e)}{W} \tag{1}$$

where C_0 and C_e (mg/L) are the initial and final dye concentrations at equilibrium of phases, respectively, V (L) is the dye solution volume, and W (g) is the adsorbent mass.

$$E\% = \frac{(C_i - C_f)}{C_i} x100 \tag{2}$$

where C_i is the initial dye concentration and C_f is the final dye concentration.

2.3 Kinetic study

From the results obtained with the 2^2 factorial design, a kinetic study for the three clays separately was developed. For this, 25 mL of a dye solution with concentration equal to 20 mg/L (pH 6.47) was mixed with 0.2 g of clay and 8.340 g NaCl. The mixture was kept in contact for a period from 0 to 600 minutes under shaking at 200 rpm at room temperature (25°C).

Upon completion of the tests, the samples were removed and filtered through a Millipore membrane. Then, the final pH of the post-kinetics solution was measured in pH meter. The kinetic efficiencies were assessed by measuring the dye concentration in the solution using a spectrophotometer.

The investigation of a possible adsorption mechanism led the pseudo-first-order and pseudo-second-order adsorption models to be tested. The first-order expression shown by Lagergren[26] is given by Equation (3):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

in which q_e and q_t are, respectively, the amount of dye adsorbed on the adsorbent (mg/g) at equilibrium at time t, and k_1 is the adsorption rate constant. Integrating Equation (3), after

applying the initial condition of $q_t = 0$ at $t = 0$, the linear form in the equations (4) and (5) is obtained:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2,303} \tag{4}$$

or

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

From Equation (4) the straight line $\log(q_e - q_t) \times t$ was drawn, which slope of the line was used to determine constant k_1. The expression of the second-order kinetic model is given by Equation (6).

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{6}$$

where k_2 ($mg.g^{-1}min^{-1}$) is the second-order adsorption constant. Similarly, equation (7) can be obtained after integration to obtain the linear form.

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \tag{7}$$

The intersection of 1/qt against t was used to calculate the second-order constant k_2 and the slope of the line was used to calculated q_e. The initial adsorption rate h is given by Equation (8):

$$h = k_2 q_e^{\,2} \tag{8}$$

3. RESULTS AND DICUSSION

3.1 Factorial design

The values obtained in the factorial design for color removal percentages were 96, 96.5 and 95.8% for natural, chemically and thermally activated smectite clays respectively. It was found that the result obtained for the chemically activated clay was slightly better than the others, using 8.340 g of NaCl, and rotation of 200 rpm. For being the best result obtained in the factorial design, they were used in the kinetic study.

The results of the factorial design are shown in Figures 2 and 3.

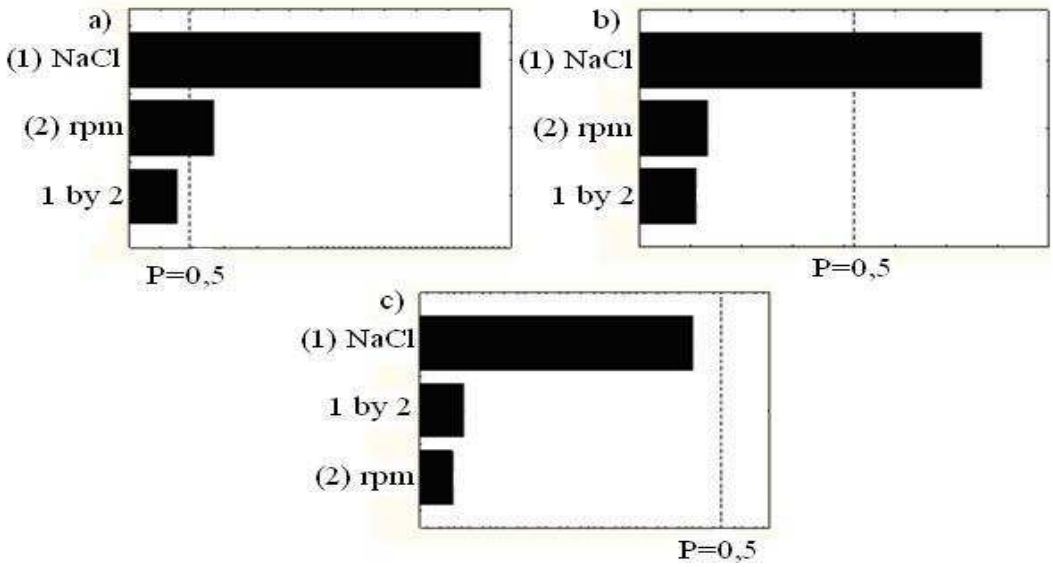

Figure 2: a) Pareto chart for natural smectite clay, b) chemically activated and c) thermally activated smectite clay

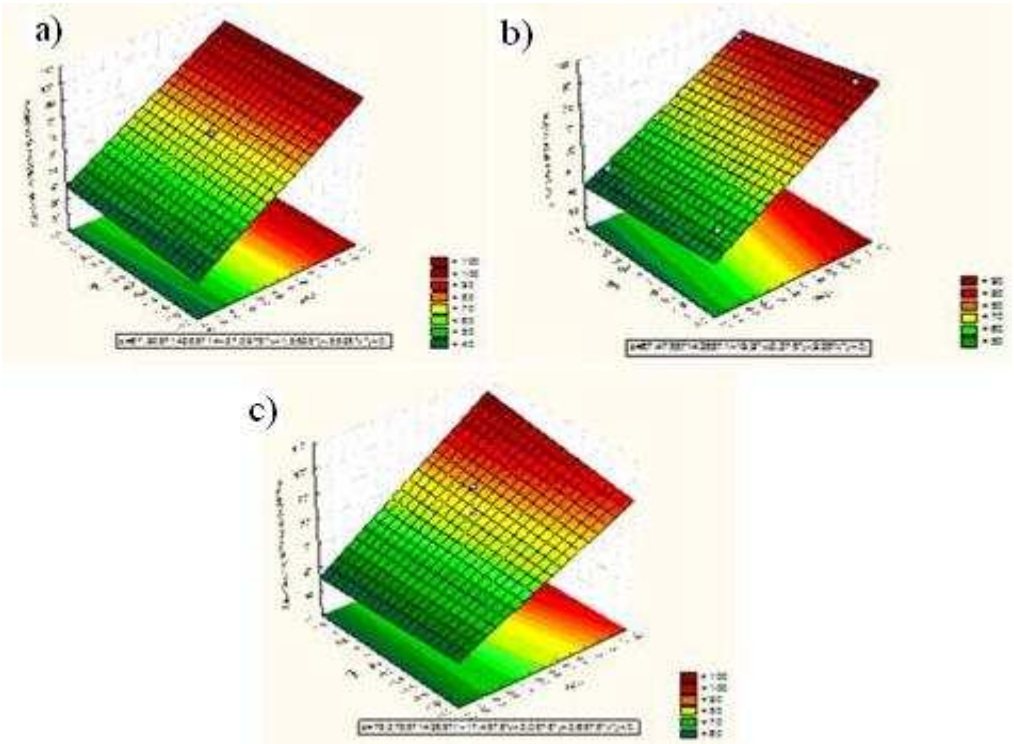

Figure 3: a) Response surface for natural smectite clay, b) chemically activated and c) thermally activated smectite clay.

In the Pareto charts, values that exceed a reference line, i.e., those that correspond to the confidence interval 95%, are significant[27].

The Pareto charts and response surface graphs show that the NaCl factor is statistically significant for natural and chemically activated clays. In the case of thermally activated clay, it was found that NaCl is not statistically significant. It was also found that other factors such as thermal activation may have been responsible for the higher efficiency in the adsorption process, resulting in greater statistical significance.

3.2 Adsorption kinetics

Conducting adsorption studies of dye Reactive Red 120 using adsorbents montmorillonite SWy-1, bentonite MX80 and Beidellite SBld-1,[26] obtained the following results for the maximum adsorption capacity: 1.19, 2.8, and 2.7 mg/g at concentrations of 5, 15, 25 mg L^{-1}, respectively, while this study obtained 4.91, 4.33 and 4.77 mg/g.

The adsorption kinetics for the three smectite clays are shown in Figures 4 and 5.

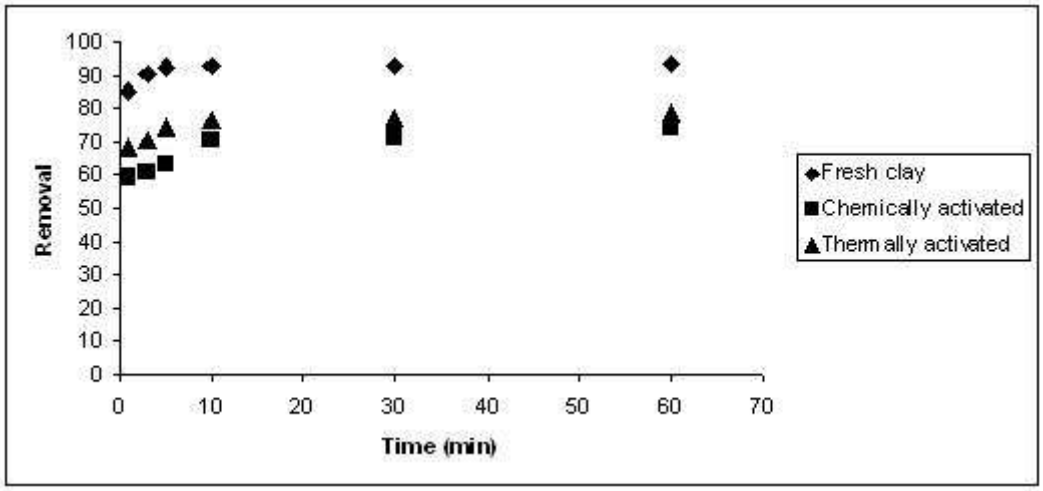

Figure 4: Removal percentage for the three clays

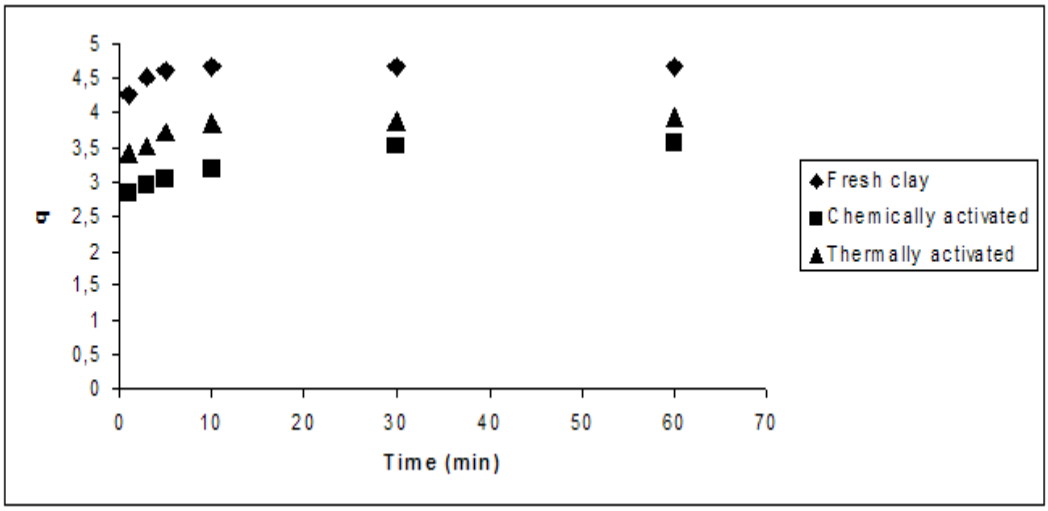

Figure 5: Maximum adsorption capacity for the three clays

The graphs show that the removal percentage and maximum adsorption capacity increase over time, reaching the adsorbent saturation condition from the time of 10 minutes.

There was a decrease in the final pH of the dye buffer solution. This reduction is due to the reaction of $C_6H_8O_7$ with a source of high-purity sodium (NaCl), producing $Na_3C_6H_5O_7$ and HCl, which is responsible for the decrease in pH, as shown in reaction (1):

$$C_6H_8O_7 + 3\ NaCl \rightarrow Na_3C_6H_5O_7 + 3\ HCl \quad (1)$$

The straight line $\log(q_e - q_t) \times t$ indicates the invalidity of the Lagergren equation for the current system and also explain that the process did not follow the pseudo-first-order kinetic model.

The best linearity was obtained for the pseudo-second-order model shown in Figure 6 for natural, chemically and thermally activated clays, respectively.

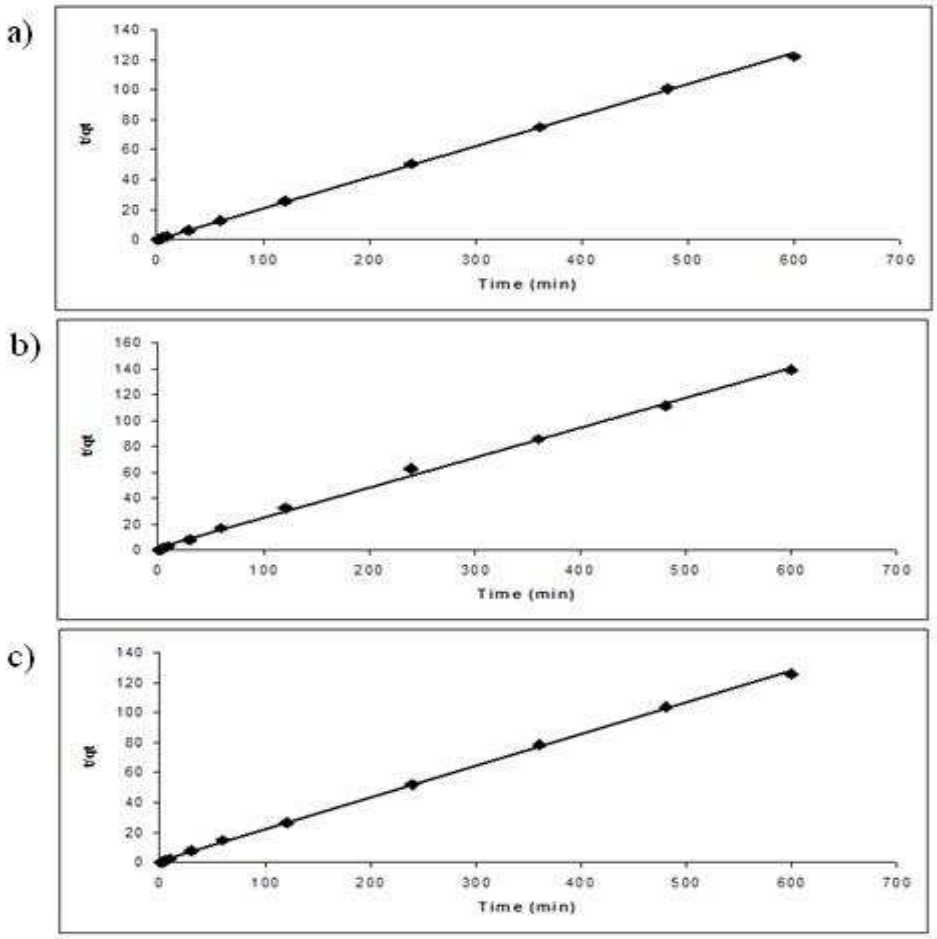

Figure 6: a) Pseudo-second-order model for natural smectite clay, b) Pseudo-second-order for chemically activated and c) Pseudo-second-order for thermally activated smectite clay.

Based on the graphs that represent the pseudo-second-order kinetics plotted for the three smectite clays studied, the kinetic parameters for the dye removal were calculated, as shown in Table 2.

Table 2: Parameters for the pseudo-second-order kinetics.

Clay	$q_{e,exp}$ (mg/g)	Pseudo-second-order		
		$q_{e,cal}$ (mg/g)	k_2 (mg/g.min)	R^2
In-natura	**137,28**	**136,98**	**0,1777**	**1**
Chemically activated	**136,43**	**136,98**	**0,01719**	**0,9999**
Thermally activated	**139,82**	**138,88**	**0,1705**	**1**

With R^2 values of 0.999, it was found that the pseudo-second-order model is the best for the adsorption process under study.

3.3 Adsorption isotherms

Previous studies using Langmuir isotherms came to unsatisfactory results. The profiles of adsorption isotherms of textile dye Reactive Yellow 4G-BF 200% have been described by the Freundlich model by means of Equation (9):

$$q_e = k_f C_e^{1/n} \tag{9}$$

where q_e is the amount of dye adsorbed at equilibrium per mass unit of smectite clay, C_e is the dye concentration in the aqueous phase at equilibrium and constants n and k_f are the Freundlich coefficients in the system. These constants indicate the adsorption capacity and intensity, respectively. Equation (9) can be linearized by taking the logarithmic form of Equation (10):

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{10}$$

The linear form of the Freundlich adsorption isotherm is shown in Figures 7 for the three smectite clays studied.

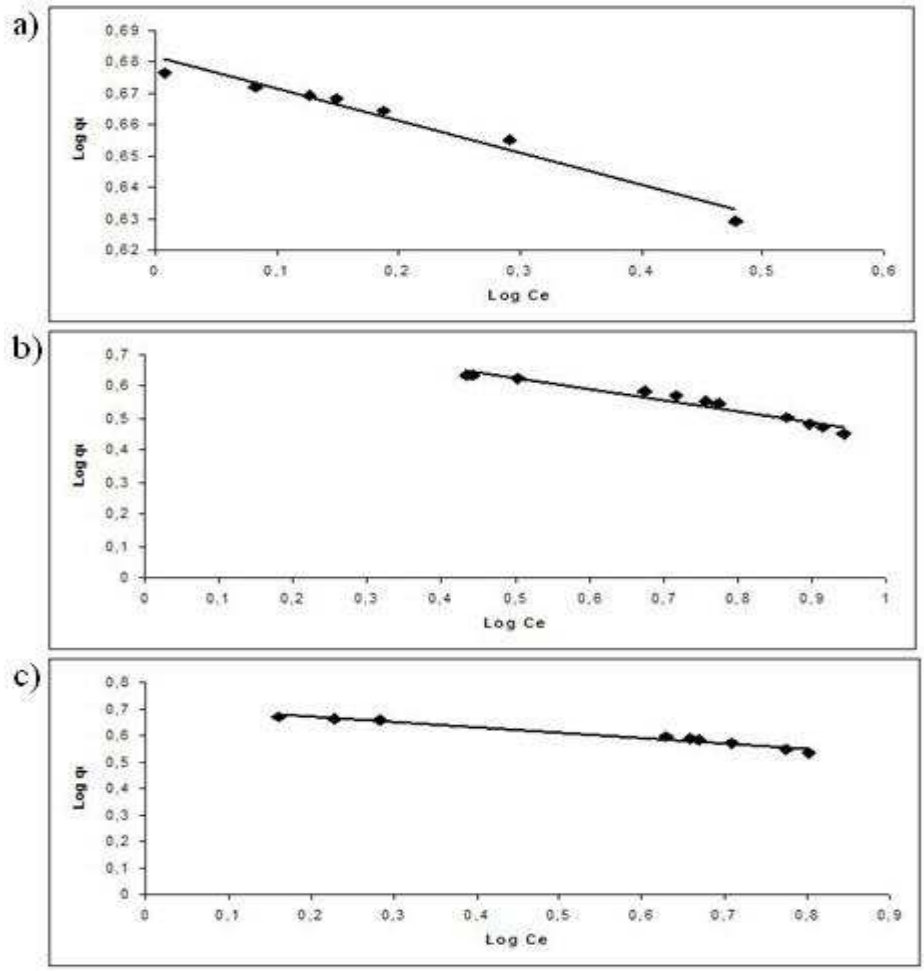

Figure 7: Adsorption isotherms for natural smectite clay, b) Pseudo-second-order for chemically activated and c) Pseudo-second-order for thermally activated smectite clay.

Based on these isotherms, the Freundlich coefficients for the dye adsorption were calculated, as shown in Table 3.

Table 4: Freudlich coefficients for the dye adsorption

Clay	Freundlich		
	k_f (dm^3g^{-1})	n	R^2
Fresh clay	**4,806**	**1,035**	**0,9655**
Chemically activated	**2,226**	**1,049**	**0,9531**
Thermally activated	**5,096**	**5,115**	**0,97**

The Freundlich adsorption model is the one that best suits studies conducted with the three clays, with R^2 values equal to 0.965, 0.854 and 0.970 for natural, chemically and thermally activated smectite clays, respectively, with n values equal to 1.035, 1.049 and 5.115 and $k_f\,(dm^3g^{-1})$ of 4.806, 2.226 and 5.096, for natural, chemically activated and thermally activated smectite clays, respectively.

According to[28, 29], the Freundlich equation is often used to demonstrate adsorption on solids with heterogeneous surface and is often better than the Langmuir equation for the adsorption of cations and anions by clays.

4. CONCLUSION

The results obtained in this work, based on the 2^2 factorial design adopted, lead to the conclusion that values of 96, 96.5 and 95.8% corresponding to the removal percentage of natural, chemically and thermally activated smectite clays, respectively, show that the activation processes used did not effectively increased the adsorption capacity of the smectite clay. Thus, the use of natural smectite clay provided an efficient adsorption without costs generated by activation.

The present study demonstrated that the smectite clay is an effective adsorbent for the removal of textile dyes in aqueous solutions.

It was found that the method used in this study produces satisfactory results when compared to those obtained by[30].

Statistical analyzes have shown that NaCl is the most statistically significant variable for natural, chemically and thermally activated smectite clays, confirming its role as agent that fixes the dye in the clay pores. Several studies on the colloidal properties of smectite clays in aqueous suspension have shown that the addition of electrolytes reduces the electrostatic repulsion between the residual charges present in the leaves due to the ionic strength effect. Thus, there is compression of layers, resulting in particles with lower swelling capacity and greater number of associated leaves, so that the particle size increases. Accordingly, the addition of an appropriate amount of NaCl (0.5-1.0 mol L^{-1}) to clay suspensions accelerates the process of particles association, with effects similar to those detected in clays for a long times in the absence of salt[31].

The kinetic data have fit well to the Freundlich isotherm and the kinetic model that best fitted to the results was the pseudo-second-order model.

5. ACKNOWLEDGMENTS

The authors thank CNPq and PROACAD-UFPE-Brazil for the financial support. They also thank TEXPAL for providing the chemical structure of the dye studied.

1. Kadirvelu K.; Kavipriya M.; Karthika C.; Radhika M.; Vennilamani N.; Pattabhi S. *Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions*, Bioresour. Technol. v. 87, n. 1, p. 129-132, 2003.
2. Teng M., Lin S. *Removal of basic dye fromwater onto pristine and HCl-activated montmorillonite in fixed beds*, Desalination, v. 194 p. 156–165, 2006.
3. Slokar Y.M.; Le Marechal A.M. *Methods of Decoloration of Textile Wastewaters*, Dyes Pigm, v. 37 p. 335–356, 1998.
4. Hutzinger O. (Ed.). *The Handbook of Environmental Chemistry, Anthropogenic Compounds*, Springer-Verlag, New York, p. 181–215, 1980.
5. Robinson T.; McMullan G.; Marchant R.; Nigam P. *Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative*, Bioresour. Technol, v. 77, p. 247–255, 2001.
6. Al-Futaisi A.; Jamrah A.; Al-Hanai R. Aspects *of cationic dye molecule adsorption to palygorskite*, Desalination, v. 214, p. 327–342, 2007.
7. Malik P.K. *Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of acid yellow 36*, Dyes Pigments, v. 56, p. 239–249, 2003.
8. Ramakrishna K.R.; Viraraghavan T. *Dye removal using low cost adsorbents*, Water Sci. Technol, V. 36, p. 189–196, 1997.
9. Eren E., Afsin B. Investigation of a basic dye adsorption from aqueous solution onto raw and pre-treated sepiolite surfaces, Dyes Pigments, v. 73 p. 162–167, 2007.
10. Ozcan A.; Oncu E.M.; Ozcan A.S. *Adsorption of Acid Blue 193 from aqueous solutions onto DEDMA-sepiolite*, J. Hazard. Mater, v. 129, p. 244–252, 2006.
11. Ozcan A.; Oncu E.M.; Ozcan A.S. *Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite*, Colloids Surf. A: Physicochem. Eng. Aspects, v. 277 p. 90–97, 2006.
12. Qiao Shizhang; Hu Qiuhong; Haghseresht Fouad; Hu Xijun; Qing (Max) Lu Gao. *An investigation on the adsorption of acid dyes on bentonite based composite adsorbent*, Separation and Purification Technology, v. 67, p. 218–225, 2009.
13. Ozcan A.; C¸. lu Omerog˘; Erdog˘an Y.; Ozcan A.S. *Modification of bentonite with a cationic surfactant: an adsorption study of textile dye Reactive Blue 19*, J. Hazard. Mater, v.140 n. (1–2), p. 173–179, 2007.
14. Wang S.; Li H.; Xu L. *Application of zeolite MCM-22 for basic dye removal from wastewater*, J. Colloid Interface Sci., v. 295 n. 1, p. 71–78, 2006.
15. .-C. Wang C; .-C. Juang L; .-C. Hsu T; .-K. Lee C; .-F. Lee J; -C. Huang F. *Adsorption of basic dyes onto montmorillonite*, J. Colloid Interface Sci., v. 273 n. 1, p. 80–86, 2004.
16. Wang L.; Wang A. *Adsorption characteristics of congo red onto the chitosan/montmorillonite nanocomposite*, J. Hazard. Mater., v. 147, p. 979–985, 2007.
17. Ozacar M.; Sengil I. A. *Adsorption ofmetalcomplex dyes fromaqueous solutions by pine sawdust*, Bioresour. Technol., v. 96, p. 791–795, 2005.
18. Mitchell M.; Ernst W.R.; Lightsey G.R.; *Adsorption of textile dyes by activated carbon produced from agricultural, municipal and industrial wastes, Bull*. Environ. Contam. Toxicol., v. 19, n. 1, p. 307 – 311, 1978.
19. Ozcan A.S.; Erdem B.; Ozcan A. *Adsorption of Acid Blue 193 from aqueous solutions onto BTMA-bentonite*, Colloids Surf. A: Physicochem. Eng. Aspects, v. 266, p. 73–81, 2005.
20. Sanghi R.; Bhattacharya B. *Review on decolorisation of aqueous dye solutions by low cost adsorbents*, Color. Technol., v. 118 p. 256–269, 2002.
21. Ardizzone S.; Gabrielli G.; Lazzari P. *Adsorption of Methylene Blue at solid/liquid and water/air interfaces*, Colloids Surf. A: Physicochem. Eng. Aspects, v. 76, p. 149–157, 1993.
22. Tsai W.T.; Chang C.Y.; Ing C.H.; Chang C.F, *Adsorption of acid dyes from aqueous solution on activated bleaching earth*, J. Colloid Interface Sci., v. 275, p. 72–78, 2004.
23. Gürses A.; Karaca S.; Doar Ç.; Bayrak R.; Açıkyıldız M.; Yalçın M. *Determination of adsorptive properties of clay/water system: methylene blue sorption*, J. Colloid Interface Sci. V. 269, p. 310–314, 2004.

24. Peker S.; Yapar S.; Besun N. *Adsorption behavior of a cationic surfactant on montmorillonite*, J. Colloid Interface Sci. A, v. 104, p. 249–257, 1995.
25. Mathialagan, T.; Viraraghavan, T. *Biosorption of pentachlorophenol by fungal biomass*, 2005.
26. Allen S.J.; Gan Q.; Matthews R.; Johnson P.A. *Kinetic modeling of the adsorption of basic dyes by kudzu*, J. Colloid Interface Sci., v. 286, p. 101–109, 2005.
27. SILVA, G. L, Reduction of dye in effluent of dyeing process of industrial laundries for adsorption in clay, PhD Thesis, School of Chemical Engineering, - UNICAMP, Campinas-SP, p.120, 2005.
28. Arias, M.; Pérez-Novo, C.; Osorio, F.; López, E.; Soto, B. *Adsorption and desorption of copper and zinc in the surface layer of acid soils.* Colloid and Interface Science, San Diego, v. 288, n.1, p.21-29, 2005.
29. Arias, M.; Pérez-Novo, C.; López, E.; Soto, B. *Competitive adsorption and desorption of copper and zinc in acid soils*. Geoderma, Amsterdam, v. 133, n. 3-4, p.151-159, 2006.
30. Errais, E.; Duplay, J.; Darragi, F.; M'Rabet, I.; Aubert, A.; Huber, F.; Morvan, G. ; *Eficient anionic dye adsorption on natural untreated clay: Kinetic study and thermodynamic parameters*, Desalination, v. 275, p. 74–81, 2011.
31. Neumann, M. G.; Gessner, F.; Ana P. P. C.;, Sartori, R.; Schmitt Cavalheiro, C. C., *Interações entre corantes e argilas em suspensão aquosa*, Química Nova, v. 23, p. 6, 2000.