Adsorption of Synthetic Orange Dye Wastewater in Organoclay

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The aim of this study is to evaluate adsorption kinetics and isotherms of synthetic orange dye onto organoclay prepared from commercial sodium bentonite (Fluidgel called) from aqueous solutions. The effects of pH, contact time, initial dye concentrations, dosage clay and temperature were investigated experimentally. Commercial sodium bentonite was modified by using quaternary ammonium cations (hexadecyltrimethylammonium bromide) as a modifying agent. The characterization of commercial Fluidgel and modified clay (organophifilic Fluidgel) was accomplished by using XRD, TGA, BET and SEM/EDX techniques. The optimum pH value for the adsorption experiments was found to be next of 6 (pH not adjusted) and all the experiments were carried out at this pH value. The pseudo-first-order kinetic model agrees very well with the experimental results. Equilibrium data were also fitted to the Freundlich isotherm model in the studied temperature range for low initial concentrations of synthetic orange. The results indicate that organoclay is a suitable adsorbent for the adsorption of dyes.

1. Introduction

The pollution of water resources with industrial effluents containing organic compounds and toxic substances is a matter of great concern. Environmental contamination has been pointed as one of the greatest problems of modern society, mainly due to the population explosion and the increased industrial activity (Zhang et al., 1998; Colpini et al., 2008). Generally, effluents from textile industries, paper printing and photography contain residues of dyes and chemicals. However, the textile industry stands out because it produces large amounts of effluents which can cause serious environmental problems since they contain colored compounds resulting from dyes unfixed to fibers during the dyeing process (Colpini et al., 2008). Synthetic dyes have increasingly been used in the textile and dyeing industries due to low-cost in synthesis, high stability to light and temperature, compared with natural dyes (Gök et al., 2010). Dye molecules have two major components: the chromophore groups, responsible for making the colour such as -C=C- and -N=N-, and the auxochrome groups, as for example: $-NH_2$, -OH, -COOH and $–SO_3H$, which render the solubility of the molecules and give affinity for the fibers (Colpini et al., 2008; Gök et al., 2010). Synthetic dyes in the water bodies, even at very low concentrations, can be highly toxic to living organisms, reducing the growth of bacteria and preventing the photosynthesis in aqueous flora (Hameed, 2008; Vimonses et al., 2009; Fiorentin et al, 2010). Due to the dyes having complex aromatic structures, they are usually biologically non-degradable and present high stability and toxicity and it is therefore necessary to eliminate organic pollutants by proper treatment techniques. Removal methods of dye molecules from water can be classified in many categories such as physical, chemical, biological, radiation and electrochemical processes. Among these methods, adsorption can be thought to be efficient process for the treatment of wastewater due to its low-cost and ease of operation as well as greater efficiency. Although activated carbon seems to be an efficient adsorbent, it has high operation costs. For this reason, many studies revealed that other alternative adsorbents such as clays, including bentonite (Özcan et al,

2007; Gök et al., 2010), montmorillonite (Wang and Wang, 2008), sepiolite (Santos and Bonaventura, 2008), raw red mud (Souza et al., 2011) and zeolite (Wang et al., 2006), are used as adsorbents which could effectively treat wastewaters. Bentonites or smectite clays have properties such as high cation exchange capacity, are readily available and offer a low cost alternative for organic compounds removal, and are reusable (Bertagnolli et al., 2011). Natural clays are hydrophilic and, therefore, inefficient for the adsorption of organic compounds in water. When subjected to chemical treatments, such as for example, with quaternary ammonium salts, surface properties of bentonite can be greatly changed presenting a hydrophobic and organophilic character, which exhibit a high affinity for organic compounds. These modified bentonites have been widely used in wastewater treatment process (Gök et al., 2010; Bertagnolli et al., 2011, Almeida Neto et al., 2012). In this work, the adsorption capacity of commercial sodium bentonite modified with quaternary ammonium salt for the removal of Orange II sodium salt, a synthetic dye, was examined. The effects of initial dye concentration, clay mass, pH and temperature for the adsorption were investigated. For data fitting kinetic models were used pseudo-first-order, pseudo-second-order and intraparticle diffusion. Langmuir and Freundlich models were adjusted to experimental data. Kinetic models will be evaluated in order to identify potential adsorption process mechanisms and to understand the possible physical-chemical interactions involved in the adsorption phenomenon of adsorption between the organoclay surface and dye molecules.

2. Materials and methods

The dye Orange II sodium salt was obtained from Fluka analytical, and used without further purification. The organoclay was prepared from commercial sodium bentonite, from the Northeastern region of Brazil (Boa Vista-PB), called Fluidgel and processed by Dolomil Ltda. The hexadecyltrimethylammonium bromide (HDTMA) selected as a modifying agent was provided by Sigma-Aldrich. Cation exchange capacity of commercial Fluidgel clay was determined by using the ammonium acetate method reported in the literature (Almeida Neto et al., 2012) and it was found to be 1.71 meq.g^{-1} of clay.

2.1 Preparation of organoclay
Commercial bentonite (100g) was dispersed in 1L of deionized water for 20min and them, organoclay prepared by adding HDTMA 1.0 times of the cation exchange capacity of bentonite and stirred for 2 h. After this treatment, the solid phase was separated by vacuum filtration; them washed with deionized water in abundance and, then dried at 60 ± 5 °C for 48 h. Finally, it was crushed and sieved in particles with average size of 0.855 mm for the adsorption tests.

2.2 Material characterization
The chemical analysis of both clays, commercial bentonite and organoclay, was performed by using an energy dispersive X-ray spectrometer (EDX-Oxford 7060) attached to a scanning electron microscope (SEM-LEO 440i). The BET surface areas of commercial and modified bentonite were determined from the N$_2$ adsorption isotherm with surface area analyser (Quantachrome Instruments, Nova 1200). The X-ray diffraction of both clays were obtained using a Shimadzu diffractometer, model XRD 7000. Thermal analysis (Shimadzu TGA-DTA 50 model) was carried out to observe the modification is accomplished or not. The thermal analyses for commercial bentonite and organoclay were recorded in the temperature range 25-1000°C at a heating rate of 10°Cmin^{-1}. A Hanna HI 2221 pH meter was used for all pH measurements, and all the absorbance measurements of reactive dye were made with a UV-vis spectrophotometer (Shimadzu-UV-1240) at the $\lambda_{máx}$ = 436 nm.

2.3 Batch adsorption studies
Adsorption experiments were carried out by using the batch technique. To determine the optimum pH value where the maximum adsorption was accomplished, dye solutions (100 mg.L^{-1}) were adjusted to pH 1.0, 4.0 using HNO$_3$ and pH 6 (not adjusted). The experiments were conducted in continuously stirred beakers, using a magnetic stirrer, containing 1500 mL of dye solutions and 1.5 g of organoclay at room temperature. After the optimum pH value was found, the effect of initial concentration of dye was investigated. The values of concentration analyzed were 50, 70, 100 and 200 mg.L^{-1}. Samples were withdrawn at predetermined intervals of time and were centrifuged at 4000 rpm for 7 min and the supernatant was analyzed by means of UV-vis spectrophotometer. For the adsorbent loading studies, 1500 mL of solution (100 mg.L^{-1}) of dye was added to continuously stirred beaker with different adsorbent amounts (1, 2 and 3 mg.L^{-1}) at room temperature ($\cong$ 25ºC). The concentration of the dye in the solution was determined using UV-vis spectrophotometer. Equilibrium experiments were carried out by contacting, in Erlenmeyer flask, 0.08 g of organoclay with 80 mL of dye solution in the different initial concentrations (1 to 200 mg.L^{-1}). The samples were shaken (200 rpm) at three temperatures (25, 35 and 45 ºC). The dye concentration in solution before and after adsorption was determined using UV-vis spectrophotometer.

3. Results and discussion

3.1 Characterization of the adsorbent

The diffractograms obtained by X-ray diffraction for commercial clay and for organoclay are not characterized by a highly crystalline structure. The difficulty in identifying peaks is explained by non-diffraction of X-ray, which had a deviation throughout the process what could characterize the formation of an inter-crystalline joint of clays (Vieira et al., 2010). The occurrence of a peak before $2\theta = 10$ ° is representative of the basal distance (d_{001}) for smectite clays. This peak tends to be intense, which enables their detection even in small quantities. The HDTMA addition promotes the modification of the clay structure changing the angle 2θ of 6.9 (Commercial Fluidgel) to 4.3 (organoclay) and, consequently, an increase in the interlayer basal distance of 13 Å to 21 Å after organophilization process. This significant increase in the basal distance of organoclay after treatment show effective intercalation of cations quaternary of ammonium in the interlamellar layers. These results indicate that commercial bentonite was successfully modified with HDTMA. Similar results were obtained for Bertagnolli et al., 2011. The specific surface areas of commercial clay and organoclay were determined as 60 and 6 $m^2.g^{-1}$, respectively. The decrease of the surface area was induced by incorporation of quaternary salt molecules between the silicate layers. This decrease can be attributed to the microstructure of organoclay, since the intercalation of the quaternary salt causes an expansion interlayer, as seen in the analysis of X-ray diffraction, such that the cations of the salt can block this space inhibiting the passage of molecules N_2. These results also indicate that commercial bentonite was successfully modified with HDTMA. The thermal analysis of commercial Fluidgel and organoclay was also performed to observe the modification of bentonite. The peak DTG at 270 °C for organoclay, attributed to the combustion of the organic part derived from quaternary ammonium salt, confirms modifications, whereas this peak is not observed in commercial clay. When DTG peaks are at around 100 °C, attributed to the loss of adsorbed water on the surface of the adsorbent and the water of hydration around the exchangeable cations, for organoclay compared to that of commercial clay, the intensity of the peak decreased due to increase in hydrophobicity as a result of modification. The morphology of the both samples analyzed by SEM is very similar, showing an aspect more porous, however not significant, after treatment with the HDTMA. The chemically treated clay has an aspect slightly expanded, which indicates delamination of the layers of the clay mineral due to the presence of cations of the salt. The molecular composition obtained from EDX analysis for both clays shown that all ions have an average composition within the expected (Almeida Neto et al., 2012). EDX is only a qualitative analysis and was used for understanding the chemical composition of clays and the corresponding values of percentage of compounds obtained, although an average of three measures should not be quantified. The chemical analysis by EDX determined qualitatively shows, for both samples, the presence of significant Si and Al elements that constitute the base of clays of group of smectites, from the structure of phyllosilicate. Besides the presence of Mg and Fe possible elements of isomorphous substitution is observed also the presence in small amounts, Ca, K and Ti. Accordingly to the chemical composition analysis, the sodium was the main cationic exchanger, since the analysis of modified clay showed no peaks associated its presence, confirming that most of the sodium cations have been exchanged by ammonium alkyl cations from the HDTMA.

3.2 Effects of pH and adsorbent dosage

In the present work the effect of pH in the adsorption of synthetic Orange dye onto organoclay were determined for values of 2.0, 4.0 e next of 6.0 (not adjusted) at room temperature ($\cong 25$ºC), initial dye concentration of 100 $mg.L^{-1}$ and clay dosage of 1.0 $g.L^{-1}$. It was observed that the equilibrium adsorption capacity is little pH dependent, in the range studied. The amount of dye adsorbed decreases slightly for lower pH (pH = 2). The amount of dye adsorbed at pH 2.0, 4.0 and 6.0 (not adjusted), in equilibrium was of 91.94 $mg.g^{-1}$, 96.23 $mg.g^{-1}$ and 96.34 $mg.g^{-1}$, respectively. Although the pH of the solution is an important variable in adsorption of ions, it seems to be not so important in the adsorption of synthetic orange, in the range studied. These results are in agreement with Brandão et al. (2010). Therefore, pH was not controlled and initial pH next of 6 was used for further experiments.

The removal of synthetic orange by modified Fluidgel at various adsorbent dosages (1.0, 2.0, 3.0 and 5.0 g) for the volume of 1000 mL at the initial dye concentration 100 $mg.L^{-1}$ was investigated and it was found out that uptake of orange dye is not dependent of amount of the adsorbent added, in the range studied. Although the equilibrium conditions was reached more rapidly with increased of adsorbent dosage. The maximum dye removal at adsorbent dosage 1.0, 2.0, 3.0 and 5.0 $g.L^{-1}$ was of 96.34, 98.08, 97.51 and 97.61 $mg.g^{-1}$, respectively. Therefore 1.0 g of adsorbent per 1000 mL of solution (1$g.L^{-1}$) was used for further experiments.

3.3 Effects of contact time and initial dye concentration

The adsorption capacity of organophilic Fluidgel versus the contact time is shown in Figure 1. The results revealed that the adsorption capacity increased with the contact time. In this study, the contact time necessary to reach the adsorption equilibrium was found to be dependent on initial dye concentration. For low initial dye concentration (50 and 70 mg.L^{-1}) the contact time necessary to reach the adsorption equilibrium was 60 min. For initial dye concentration of 100 mg.L^{-1} the contact time necessary to reach the adsorption equilibrium was 120 min whereas for initial dye concentration of 200 mg.L^{-1} the equilibrium time was 300min. These results indicate rapid adsorption for initial dye concentrations less than 100 mg.L^{-1}.

The effect of initial dye concentration on the adsorption was also studied at different concentrations of dye (50, 70, 100 and 200 mg.L^{-1}) at initial pH value next 6.0 and room temperature. The Figure 1 and Table 1 shows the effect of initial dye concentration on the amount of dye adsorbed. The amount adsorbed was greater for higher initial dye concentration. The amount of orange adsorbed, in equilibrium, increased from 46.33 to 190.31 mg.g^{-1} when the initial dye the initial dye concentration increased from 50 to 200 mg.L^{-1}, respectively. Indeed, at higher initial concentrations, the resistance to mass transfer between the solid and aqueous phase is more easily overcome due the driving forces, moreover the number of collisions between dye molecules and adsorbent is increases, increasing the adsorption (Aksu and Tezer, 2005).
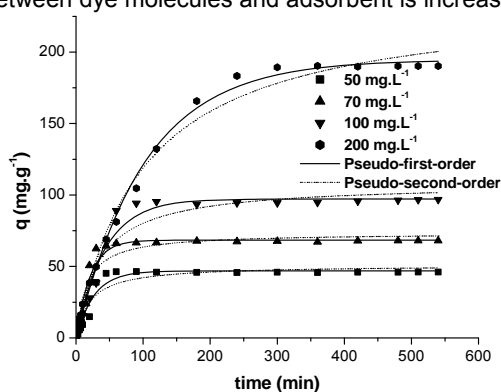

Figure 1: effect of contact time for the adsorption of dye onto organoclay at various initial concentrations
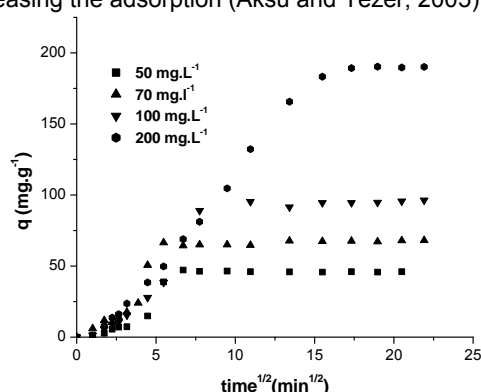
Figure 2: the intraparticle diffusion kinetic model fit for the adsorption of dye onto organoclay at various initial concentrations

Table 1: The pseudo first-order, pseudo second-order and intraparticle diffusion kinetic constants obtained from orange dye concentration effect.

Dye concentration (mg.L^{-1})	R (%)	qe$_{exp}$ (mg.g^{-1})	Pseudo 1st order			Pseudo 2nd order		
			qe$_{eq}$ (mg.g^{-1})	k$_1$ (L.mg^{-1})	R^2	qe$_{eq}$ (mg.g^{-1})	k$_2$ (L.mg^{-1})	R^2
50	95.5	46.33	46.89	0.0372	0.96	50.85	0.0484	0.93
70	97.5	66.49	68.39	0.0480	0.97	73.39	0.0646	0.94
100	98.5	96.34	97.17	0.0235	0.98	108.22	0.0286	0.96
200	99.5	190.31	194.60	0.0097	1.00	237.23	0.0101	0.99

Dye concentration (mg.L^{-1})	Intraparticle diffusion		
	k$_{in}$ (mg.g^{-1}.min$^{-1/2}$)	C (mg.g^{-1})	R^2
50	10.2249	-	0.99
70	18.4707	-	0.99
100	1	0	1.00
200	13.2901	-	1.00

The pseudo-first order, pseudo-second order and intraparticle diffusion models, described in detail in Vieira et al., (2010), was applied for the interpretation of experimental data. The kinetic parameters of adsorption of dye onto organoclay under different initial dye concentrations were calculated from these plots (Figure 1) and are given in Table 1. The calculated qe values agree with the experimental qe values, and the correlation coefficients for the pseudo-first-order kinetic plots were also found to be very high.

Although, the pseudo-second order model also fits well to the experimental data, especially for higher initial dye concentrations (100 and 200 mg.L^{-1}).

The plot of q *versus* t^{0,5} (Figure 2) gives a straight line that does not pass through origin, except for initial dye concentrations of 100 mg/L^{-1}, showing that adsorption of dye onto organoclay is not an exclusivity of intraparticle diffusion model. The K$_{in}$ values were calculated by using correlation analysis (Table 1). The values of intercept q (parameter C) give an idea about the boundary layer thickness; it means that larger is the intercept grater boundary layer effect will be (Kannan and Sundram, 2001). In this study the effect of the boundary layer was negligible. The Table 1 also shows the variation of percentage reduction (% R) with initial dye concentration. For the initial dye concentration of 50, 70, 100 and 200 mg.L^{-1} the percentage reduction was 95.5, 97.5, 98.5 and 99.5, respectively.

3.4 Adsorption isotherms

Adsorption isotherms play a very important role for understanding adsorption mechanism. The variation of the dye concentration with the same mass of the adsorbent is used to determine an adsorption mechanism. The Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) adsorption isotherm models were applied to describe the dye-organoclay system. The Figure 3 shows the adsorption isotherms at three different temperatures and initial dye concentrations of 1 to 200 mg.l^{-1}, while the Figure 4 shows the Langmuir and Freundlich adsorption isotherm models adjusted to the experimental data in the initial dye concentrations between 1 to 20 mg.L^{-1}. The calculated parameters of the Langmuir and Freundlich isotherms for the adsorption of dye onto organoclay are listed in Table 2, for low initial dye concentrations. As follows from these data that the adsorption of dye onto organoclay is better fitted to the Freundlich isotherm model than those of the Langmuir, as indicated by the R^2 values in Table 2. Although the experimental data do not fit well on none of the models studied, in the measured initial concentrations range (1 to 200 mg.L^{-1}). According to the results shown in Figure 3 the isotherms are not favorable. However, for low initial dye concentrations (1 to 20 mg.L^{-1}) of Freundlich model fit well to the experimental data, with a correlation coefficients values greater than 0.96. This indicates that the dye adsorption on the surface of organoclay takes place by heterogeneous sites, with a non-established mechanism. The 1/n Freundlich constant values reflects that dye have high affinity with the organoclay, because in all cases, 1/n < 1, what indicates favorable adsorption. It is possible to see that the maximum adsorbed capacity (q$_m$) increases as the process temperature rises. These results indicate that adsorption on organocly surface is favorable by increasing the energy, indicating this is an endothermic process. On the other hand, according to R$_L$ Langmuir kinetic parameter (Table 3), the isotherm can be considered favorable (0<R$_L$<1) to dye adsorption.
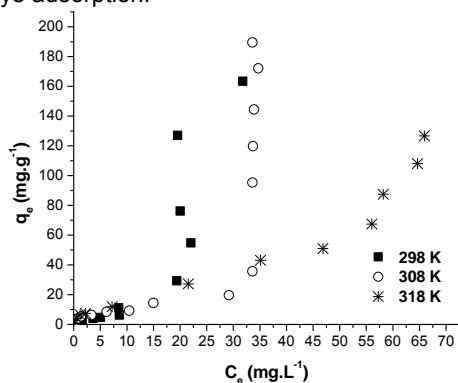

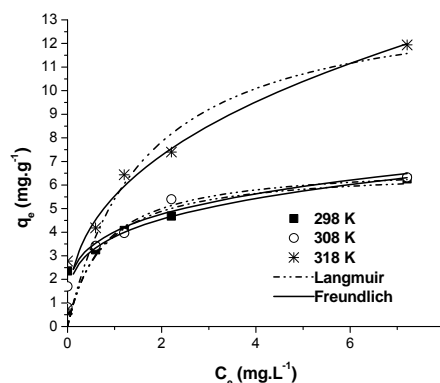Figure 3: adsorption isotherms of dye onto organoclay (1 to 200mg.L^{-1})

Figure 4: Langmuir and Freundlich isotherms fits for the adsorption of dye (1 to 20 mg.L^{-1})

Table 3: Langmuir and Freundlich isotherms models parameters (initial dye concentrations 1 to 20 mg.L^{-1}).

Temp. (K)	Langmuir					Freundlich		
	q$_{mexp}$ (mg.g^{-1})	q$_m$ (mg.g^{-1})	K$_L$ (L.mg^{-1})	R^2	*R$_L$	K$_F$	1/n	R^2
298	11.15	6.73	0.602	0.91	0.078	2.672	0.395	0.96
308	9.258	10.16	0.725	0.75	0.070	4.549	0.312	0.97
318	11.94	14.33	0.609	0.88	0.079	5.535	0.390	0.99

*R$_L$ = 1/(1 + bC$_0$), where C$_0$ is higher value of the initial concentration (mg.L^{-1})

4. Conclusions

The present work shows that organoclay is an effective adsorbent for the removal of Synthetic Orange dye from aqueous solutions. The modification of commercial bentonite was confirmed by using DRX, TG/DTG, BET and SEM/EDX analysis.The amount adsorbed varied with initial dye concentration, contact time and temperature. However, the amount of dye adsorbed is not dependent of amount of the adsorbent added and decreases slightly for lower pH (pH = 2), in the range studied. With the increase in the temperature, the amount adsorbed of dye increased, indicating that the adsorption of dye onto organoclay is an endothermic process. The best correlation was obtained using the pseudo-first-order-order kinetic model. Equilibrium data were also fitted well to the Freundlich isotherm model for low initial dye concentrations. The results indicated that organoclay is a promising technology adsorbent for the removal of waste dyes.

Acknowledgements

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