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Adsorption study of an industrial dye by an organic clay

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Abstract In this study, the adsorption of an industrial dye Supranol Yellow 4GL onto Cetyltrimethylammonium-bentonite (CTAB-bentonite) is investigated. The organobentonite is synthesised by exchanging cetyltrimethylammonium cations (CTAB) with inorganic ions on the surface of bentonite. The adsorption of Supranol Yellow 4GL onto organobentonite is found to be maximum when the concentration of CTAB exchanged is 100% according to the cation exchange capacity of the clay (CEC). The modification of organobentonite is examined using XRD and FTIR techniques.

The effect of the process parameters such as: contact time, adsorbate concentration, adsorbent dose, pH and temperature are reported. Nearly 1200 seconds of contact time are found to be sufficient for the adsorption to reach equilibrium. The pseudo second order model is used to describe the kinetic data, and the rate constant is therefore evaluated. The dye adsorption to organobentonite is characterized by monolayer isotherm and caused by adsorption with relatively strong uptake. The Langmuir and Freundlich models adsorption are applied to describe the isotherm equilibrium and to determine its constants. The Langmuir and Freundlich models agree well with the experimental data with a adsorption capacity of 0.5 g of dye per g of organobentonite. A better fixation was obtained at acidic pH. The effect of temperature on the adsorption of dye has been also studied and the thermodynamic parameters ΔH, ΔS, ΔG, were determined. Organobentonite is found to be effective for removing Supranol Yellow 4GL dye from wastewater.

Keywords Adsorption · Supranol Yellow 4GL · Bentonite · CTAB · Langmuir

Abbreviations

C_i	the initial concentration of dye, g/L
C_e	the concentration of dye in solution after equilibrium, g/L
V	the total volume of the solution, L
m	the mass of the adsorbent, g
q_e	the amounts of dye adsorbed at equilibrium time, g/g
q	the amounts of dye adsorbed at time t, g/g
K_1	the pseudo-first order rate constant, sec^{-1}
K_2	the pseudo-second order rate constant, sec^{-1}
q_m	the amount of solute adsorbed per weight of adsorbent in forming a complete monolayer on the surface, g/g
b	Langmuir constant related to the energy, L/g
R_L	dimensionless separation factor
k and n	Freundlich constants
k_d	the partition coefficient, L/g

1 Introduction

One of the major problems concerning textile wastewaters is coloured effluents. Though not particularly toxic, dyes have an adverse aesthetic effect because they are visible pollutants. The presence of colour reduces aquatic diversity by blocking the passage of light through water. The main pollution source of textile wastewater comes from dyeing processes, with the degree of colouration being dependent

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on the colour/shade dyed and the type of dye used (Degs et al. 2000). Moreover, some dyes might be toxic to various organisms (Khattri and Singh 1999).

Dyes can be classified in two main categories: those soluble in water and those insoluble in water. Soluble dyes are the most difficult to remove. Most of the commercially used dyes are resistant to biodegradation (Mahlok et al. 1975; Horning 1977), photo degradation (Gardiner and Borne 1978) and oxidizing agents (Poots et al. 1976). While both biological and physical/chemical methods have been employed for dye removal, the former have not been very successful, due to the essential non-biodegradable nature of most of the dyes (Mahlok et al. 1975; Horning 1977; Brower and Reed 1987). The physical/chemical methods that have been proven to be successful are adsorption, coagulation/flocculation, membrane filtration, chemical oxidation and electrochemical treatment (Konduru et al. 1997). Currently the adsorption technique is proved to be an effective and attractive process for the treatment of these dye-bearing wastewaters (El Guendi 1995; Mc Kay and Allen 1980). The use of activated carbon as an adsorbent is still very popular because of its extended surface area, micro porous structure, high adsorption capacity and high degree of surface reactivity. However, regeneration or reuse of carbon results in a steep reduction in performance, and efficiency becomes unpredictable or dependent on massive carbon dosages (Raghavacharya 1997). Hence low cost adsorbents are being investigated. Materials that have been used in their natural state to adsorb dyes from solution include pine bark (Al-Asheh and Duvniajak 1997), lignite (Allen and Brown 1995), linseed cake (Liversidge et al. 1997), sunflower stalks (Sun and Xu 1997), banana peel (Namasivayam et al. 1998), orange peel (Arami et al. 2005), chitosan (Chung et al. 2005), and eucalyptus bark (Morais et al. 1999).

The use of bentonite in wastewater treatment has received increasing attention and currently offers a very attractive method for pollution remediation. Besides it is plentiful, inexpensive and available in many countries. Bentonite is a smectite, which is a 2:1 layered silicate that swells when contacted by water. The inner layer is composed of an octahedral sheet, which is situated between two tetrahedral sheets. The substitutions of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} or Zn^{2+} for Al^{3+} in the octahedral layer result in a net negative surface charge ion the clay. The charge imbalance is offset by exchangeable cations such as H^+, Na^+, or Ca^{2+} on layer surfaces (Raghavacharya 1997). Because of the repulsion interactions between the negatively charged surface of clays and anionic dyes, only few studies on the adsorption of acid dyes have been carried out using bentonite as an adsorbent. Bentonite in which the inorganic exchangeable cation is replaced with an organic cation modified the clay's surface properties from organophobic to strongly organophilic and therefore the adsorption capacity increases (Smith et al. 1991). As a result, organobentonites are powerful adsorbents for organic pollutants relative to natural bentonite and other clays (Boyd et al. 1988). Organobentonites have been investigated for a wide variety of environmental applications. Harper and Purnell (1990) have studied the use of organobentonite for sampling airborne organic contaminants. Jordan (1949) has prepared a series of organobentonites complexes called bentones. Barrer and Macleod (1955) have made the early studies in describing the reaction and the effects of loading and chemical character on the adsorption. Lizhong et al. (1998) have studied the use of cetyltrimethylammonium bromide-bentonite to remove organic contaminants of varying polar character from water.

The present work is aimed to study the adsorption capacity and mechanism of removal of anionic dye Supranol Yellow 4GL by organobentonite. The goal of this study was to demonstrate the potential of cetyltrimethylammonium exchanged bentonite for removing anionic dye Supranol Yellow 4GL from aqueous solutions. Batch kinetic experiments were performed to provide appropriate equilibrium time; the experimental data were evaluated by applying the pseudo-second adsorption kinetic model. The effect of process parameters such as: adsorbate concentration, adsorbent dose, pH and temperature was investigated.

2 Materials and method

2.1 Preparation of organo-bentonite (adsorbent)

The start clay used in this study is supplied by ENOF (an Algerian manufacture specialized in the production of non ferric products and useful substances) at the rough state. This clay has undergone a purification protocol composed of several stages: disintegration to disperse the layers of clay and recovery of the fraction of clay lower than 2 µm. The recovered suspension was treated by an acid solution (0.05 N) to eliminate carbonates, and then saturated by sodium chloride (0.1 N) three times. Thus the recovered clay known as sodium bentonite was washed several times and was dried at ambient temperature.

The surfactant used to modify the bentonite is a cationic surfactant, Cetyltrimethyl-ammonium bromide (99%), of chemical formula $C_{19}H_{42}NBr$ provided by ACROS ORGANICS.

Organobentonite was prepared by insertion of a quaternary ammonium salt, the cetyltrimethylammonium bromide, between the layers of the bentonite by a simple cationic exchange. The samples of the organophilic bentonite were obtained by dispersing quantities of 0.5 g of sodium bentonite in 100 mL of CTAB solution.

Different concentrations of CTAB were obtained by adding 5–150% of the CEC to clay. All the samples were maintained under constant agitation during 24 h, and washed several time with distilled water to eliminate the excess of the surfactant. Organobentonites were recovered by centrifugation and dried at 60 °C (Lizhong et al. 1998).

2.2 Characterization methods

The cation exchange capacity (CEC) was determined with methylene blue and conductimetric methods. The adsorption of methylene blue dye on bentonite in solution, is used to determine either cation- exchange capacities (CEC) or their total surface area. In a series of 100 mL glass bottles, we place successively 20 mL of sorbent dosage (2 g/L) and a variable volume of methylene blue at initial concentration 0.5 g/L. The mixtures were kept at room temperature during 1 h under stirring. After centrifugation, the supernatant was dosed calorimetrically at $\lambda_{\max} = 665$ nm. The amount of adsorbed solution at flocculation point, were referred to 100 g of clay. These values allowed the determination of both CEC and surface area. Conductimetric method was based on exchanged species. Ion exchanges between Mg–Ba occur by titrating the barium saturated montmorillonite suspension 1 g/100 ml with 0.02 M $MgSO_4$ solution. The plot of specific conductance against the titrant volume shows two phases. The first curve obtained with little change in conductance owing to the formation of insoluble $BaSO_4$ and the second curve, the conductance increased owing to the presence of excess magnesium ion and sulfate ion in the solution. The equivalent point is taken at the intersection of the two linear portions corresponding to the CEC (Bouberka et al. 2005; Kahr and Madsen 1995; Chiu et al. 1990).

The basal spacing of the samples was measured by X-ray diffraction using a Siemens D5000 instrument, using Cu Kα radiation. The surface area of starting material was measured by adsorption of nitrogen according to the BET-method on a Micrometrics 2000 apparatus. Spectra of infrared absorption (IR) were determined between 4000 and 400 cm^{-1} by a PHILIPS PU 9714 spectrophotometer. Samples were analysed by preparing KBr discs. The sample was finely ground to avoid effects of diffusion. 99×10^{-3} g of pure potassium bromide and 1×10^{-3} g of sample were compressed under vacuum at room temperature. The transparent disc was fixed on a support.

2.3 Adsorbate

The selected dye is an industrial colouring substance used in synthesis for dyeing the chemical textiles. It is synthesized and marketed under a code and commercial name Yellow Supranol 4GL (Kacha et al. 1997) and used without further purification. Its maximum wavelength of adsorption at 410 nm is determined by a UV-Visible spectrophotometer SAFAS.

2.4 Adsorption experiments

The effect of CTAB concentration used to modify the bentonite on the removal rate of Supranol Yellow 4GL from water was carried out by using 100 mL of a 0.1 g/L dye solutions with 0.5 g of organobentonite. The dye solutions were stirred using a magnetic stirrer in 200 mL Erlenmeyer. The optimum concentration of CTAB used to modify bentonite is determined as 100% CEC and used as adsorbent throughout all adsorption experiment.

The kinetic study was carried out by introducing quantities of 0.2 g of organobentonite into 100 mL of solutions of dye at 0.1 g/L, the mixtures are put under constant agitation for variable times (from 180 to 3600 sec). The adsorption isotherm was carried out for alternatives concentrations of dye varying between 0.1 and 1.4 g/L, a constant organobentonite mass of 0.2 g, a solution of 100 mL and an agitation time of 3600 seconds. The influence of the organobentonite mass on the adsorption of the Yellow Supranol dye is studied for masses varying between 0.05 and 0.2 g, a concentration of dye of 0.1 g/L, and agitation of 3600 seconds. The effect of pH on the adsorption of the dye on organic clay is carried out for a fixed concentration of dye, 0.6 g/L, an organobentonite mass of 0.2 g and a total solution volume of 100 mL. The pH of the solution is adjusted by solutions of HCl or NaOH (0.1 M) according to desired values. The effect of temperature is studied for concentration ranging between 0.1 and 1.4 g/L, an organobentonite mass of 0.2 g and a total solution volume of 100 mL. The control of temperature is carried out by thermostatic baths regulated at temperatures from 5 to 50 °C. For all the experiments, after agitation, the material was separated from the liquid phase by centrifugation at a speed of 5000 rpm. The concentration of the supernatant is measured by a colorimeter at $\lambda_{\max} = 410$ nm. The quantity of dye adsorbed by the clay is calculated using the following formula:

$$q_e = (C_i - C_e)\frac{V}{m}. \tag{1}$$

C_i (g/L) is the initial concentration of dye; C_e (g/L) is the concentration of dye in solution after equilibrium; V (L) is the total volume of the solution and m (g) is the mass of the adsorbent.

3 Results and discussion

3.1 Characterization of bentonite

X-ray spectra of rough clay and sodium bentonite are presented on Fig. 1. They show a reduction in the intensity

Fig. 1 XRD spectra of natural bentonite and sodium exchanged bentonite

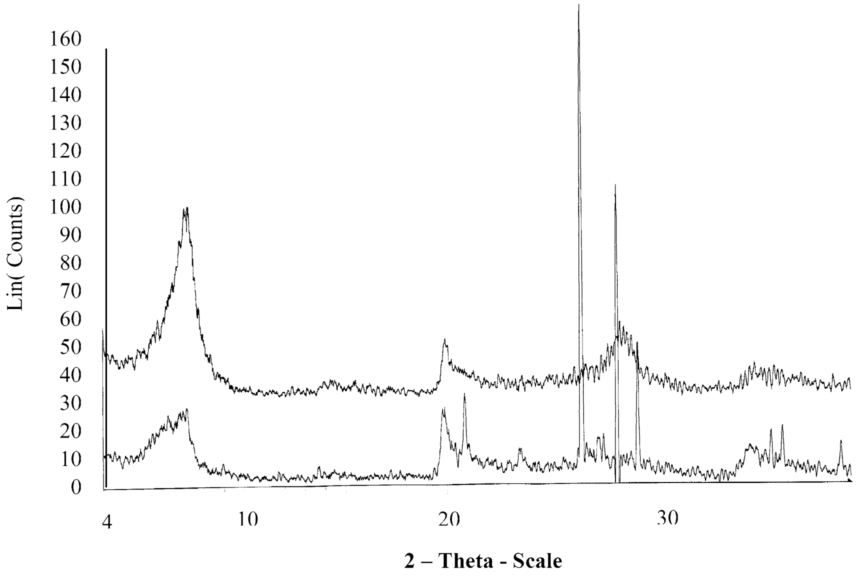
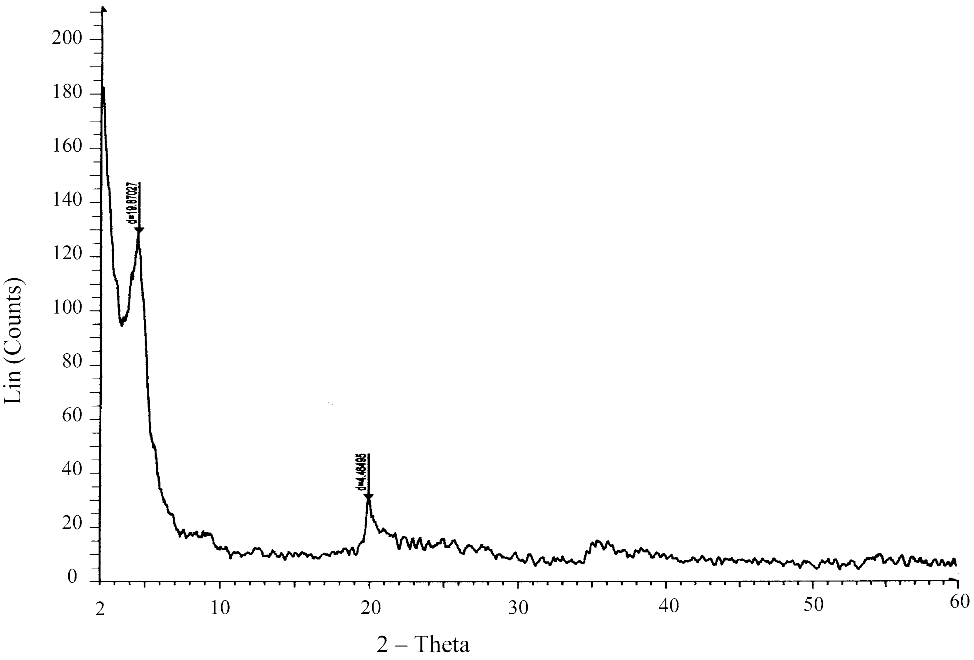


Fig. 2 XRD spectrum of the organo-bentonite



of the picks relative to impurities and increase in those of montmorillonite which proves the effectiveness of the treatment of the purification. The characterization of the sodium bentonite reveals the following results: An inter reticular distance d_{001} of 12.35 Å, a cation exchange capacity (CEC) of 103 meq/ 100 g and a surface area of 126 m^2/g.

Bentonite modified by large alkyl cations such as CTAB gives organophilic clay. The interlayer spacing increased with the amount of cationic surfactant used in synthesis. The X-ray diffraction patterns of organobentonite (Fig. 2) exhibit an interlayer spacing at 19.87 Å. This basal spacing corresponds to a bilayer of organic cations between the silicate layers, giving a thickness about 7 Å. The orientation of alkylammonium ions between silicated layers is variable. Alkylammonium ions form a monolayer (13.7 Å), a double layer (17.7 Å), a pseudo-trimolecular layer (21.7 Å) or a parafinic complex (>22 Å) (Jaynes and Boyd 1991).

The IR spectrum of organobentonite was shown in Fig. 3. The band at 3618 cm^{-1} correspond to stretching vibrations of hydroxyl groups attached to octahedral layer. The massif between 3390 and 3420 cm^{-1} demonstrates the presence of a water monocouche (Shu et al. 1997). The band at 1635 cm^{-1} corresponds to the OH deformation of wa-

Fig. 3 FTIR spectrum of the organo-bentonite

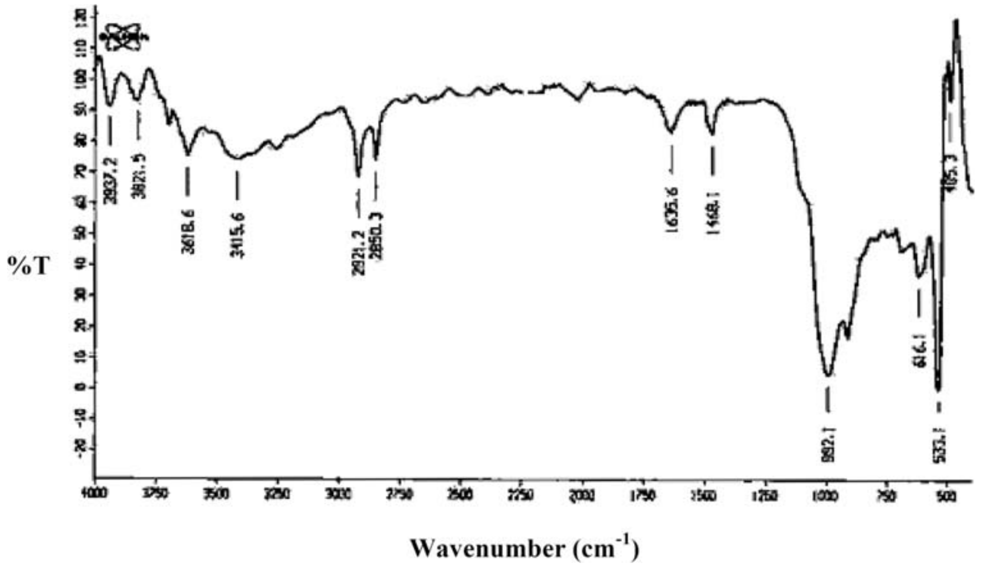
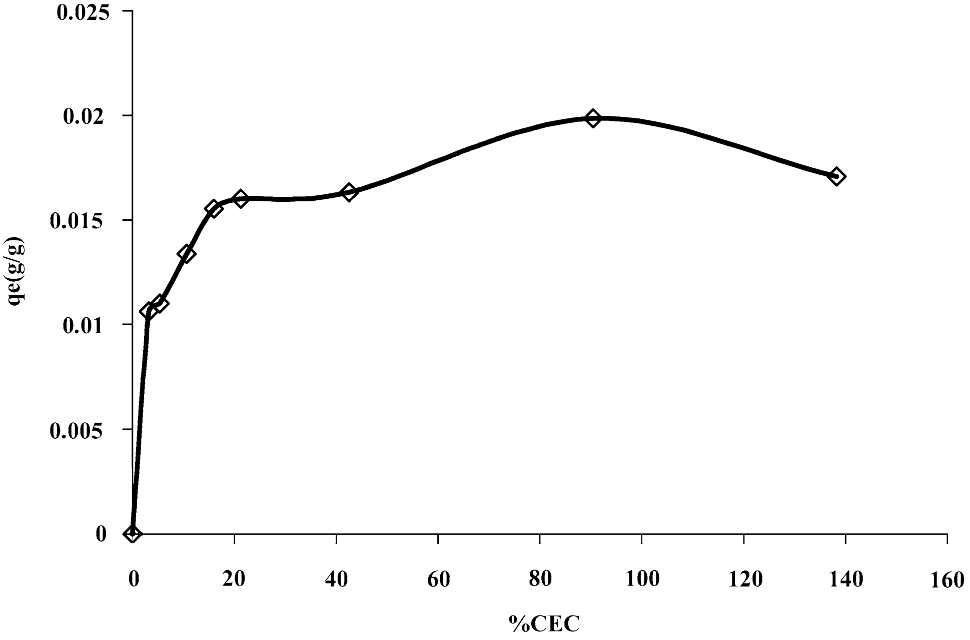


Fig. 4 Variation of the quantity of dye adsorbed with the percentage of CTAB exchanged in the clay



ter, because the OH stretching band at 3390 cm^{-1} suggests the presence of some interlamellar water. Besides, the wavelengths bands at 2921 cm^{-1} and 2850 cm^{-1} correspond to the symmetric and asymmetric stretching vibrations of the methylene and methyl group CH_2, CH_3 of the aliphatic chain of the surfactant.

3.2 Effects of CTAB concentrations on adsorption properties of organo-bentonite

The effect of CTAB concentration used in modifying the bentonite on the removal rates of Supranol Yellow 4GL from water is investigated. Figure 4 presents in abscissa a clay materials prepared by exchanging the sodium of bentonite with different concentration of CTAB, this latter was converted to a percentage according to the CEC (5–150%) of the initial bentonite and in ordinate the quantity of dye removed per g of adsorbent. It indicates that the uptake of Yellow Supranol 4GL from water by organobentonite increased with increasing CTAB concentrations for modifying the bentonite. This finding agrees with previous results found by Lizhong et al. (1998) for the adsorption of different organic contaminants on organic clay. When the CTAB concentration is over 100% of CEC, the removal rates of Supranol Yellow 4GL become constant. Since a better adsorption of dye on organophilic bentonite is obtained for a

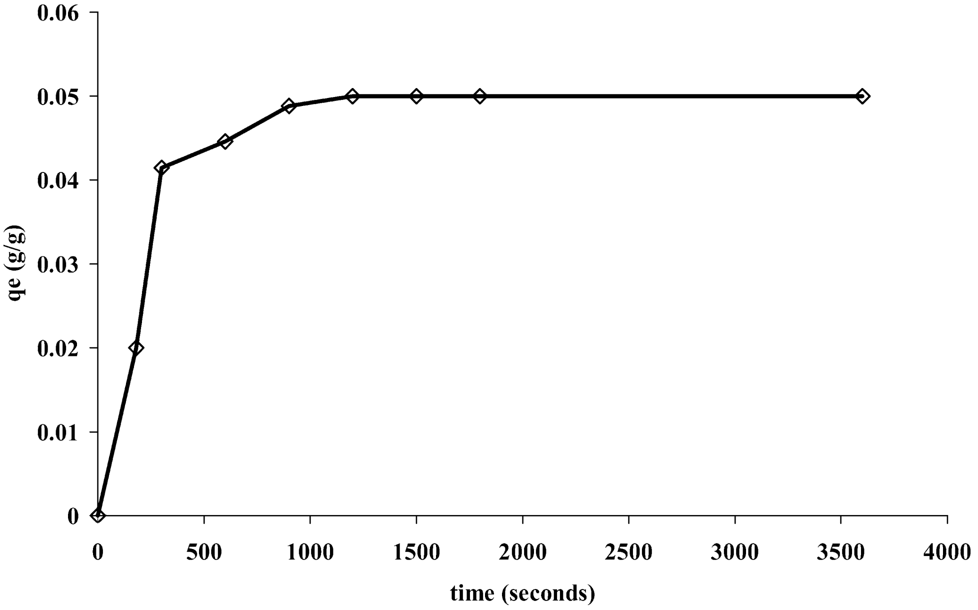


Fig. 5 Adsorption kinetic of Supranol Yellow 4GL onto organobentonite

concentration of exchanged CTAB corresponding to 100% of CEC, this material is used as adsorbent in all experiments. The bentonite exchanged with CTAB may be defined as organobentonite.

3.3 Effect of contact time

The thermodynamic equilibrium between the adsorbate in liquid phase and that fixed on the solid is reached with a speed which depends not only on diffusion of the components in the adsorbent but also on the interaction adsorbent/adsorbate.

The adsorption study of the dye, Supranol Yellow 4GL on organobentonite enables to examine the influence of contact time up on its retention, at adsorbate concentration of 0.1 g/L, adsorbent dose of 0.2 g and without modifying pH (medium pH = 6). Figure 5 clearly illustrates this behaviour. The first phase corresponds to a fast adsorption, whereas, the second one starts after 900 sec. At this stage, the adsorption of the pollutant becomes maximal (0.05 g of dye per g of organobentonite). It can be observed that the concentration of the remaining dye in solution decreases with time and reaches a constant value beyond which nothing can be removed from solution. At this phase, the amount of dye adsorbed onto the organobentonite is in a dynamic equilibrium with that desorbed from the adsorbent. The time required to attain this equilibrium is termed as the equilibrium time, and the amount of dye adsorbed reflects the maximum dye adsorption capacity of the particular adsorbent under particular operating conditions.

The equilibrium time was reached within 1200 seconds. Gupta and Shukla (1996) reported that the contact time for the adsorption of acid dye onto different adsorbents (Coal, Fly ash, China clay and wollastonite) required for attaining equilibrium were 3600, 4800, 6000 and 6000 seconds respectively.

The dynamic study of the present system may be analysed by Lagergreen (1898) equation:

$$\log(q_e - q) = \log(q_e) - \frac{(K_1 \times t)}{2.303} \tag{2}$$

where q_e and q (both in g/g) are respectively the amounts of dye adsorbed at equilibrium and time t; K_1 is the pseudo-first order rate constant (sec^{-1}).

The pseudo-second-order kinetic model described by Ho and Mc Kay (1998) is expressed as:

$$\frac{t}{q} = \left(\frac{1}{K_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) t \tag{3}$$

where q_e is the maximum adsorption capacity (g/g) for the pseudo-second-order adsorption, K_2 is the equilibrium rate constant of pseudo-second-order adsorption (sec^{-1}). The validity of the two models can be checked by the linearized plots of $\log(q_e - q_t)$ versus t for the former equation, and (t/q_t) versus t for the latter. The rate constants K_1 and K_2 obtained from the plots of (2) and (3) are shown in Table 1. The straight line plot of $\log(q_e - q_t)$ against t does not elucidate that kinetic of sorption on organobentonite followed first-order model. The data show a good compliance with the pseudo second-order equation and the regression coefficient for the linear plot was higher than 0.99 for the systems in these studies. The sorption of Supranol Yellow 4 GL on organobentonite can be described by the pseudo-second-order equation, as the correlation coefficient for the first-order analysis was lower than that for the second-order model. Similar trends were observed for the

Table 1 Comparison of the first and second-order reaction rate constants for the adsorption of 4GL onto organobentonite

First-order kinetic model			Second-order kinetic model		
K_1 (sec^{-1})	q_e (g/g)	R^2	K_2 (g/g sec)	q_e (g/g)	R^2
0.0039	0.05	0.966	0.016	0.05	0.995

Table 2 Effect of the adsorbent mass on the adsorption of Supranol Yellow 4GL

Dose of organobentonite (g)	0	0.012	0.025	0.05	0.1	0.15	0.2
Discolored percentage (%)	0	25.32	52.35	97.26	100	100	100

adsorption of commercial basic blue dye (BB69) and direct red dye (DR227) on activated clay (Wu et al. 2001) and for the adsorption of Supranol Yellow 4GL and Erionyl Red RS on polyaluminium hydroxide exchanged bentonite (Kacha et al. 2003).

3.4 Effect of adsorbent dose

The effect of adsorbent dose on the amount of dye adsorbed at initial concentration of adsorbate 0.1 g/L and pH = 6 is shown in Table 3. The percentage removal of Supranol Yellow 4GL increases with the increase in dose of adsorbent. This may be due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent (Nagarethinam and Mariappan 2001). The increase in the extent of removal of Supranol Yellow 4GL is found to be insignificant after a 0.05 g dose for organobentonite. Namasivayam and Yamuna (1995) obtained a maximum removal (90%) of direct red 12 by biogas residual slurry at a dose of 0.25 g.

3.5 Effect of the initial concentration of dye

The adsorption isotherm for Supranol Yellow 4GL at pH 6 and 25 °C is shown in Fig. 6. The isotherms have been classified according to Giles' classification (Giles et al. 1960). Giles has classified adsorption isotherms into four main groups: L, S, H, and C. According to the above classification, organobentonite shows L-type isotherm (Fig. 6), corresponding to the formation of a mono layer of dye on the surface of the adsorbent with adsorption capacity of 0.5 g of dye per gr of organobentonite. The equilibrium between the adsorbent and the adsorbate can be distinctly descried by Langmuir and Freundlich isotherms (Koumanova et al. 2002). The Langmuir isotherm equation initially derived from kinetic studies is based on the assumption that on the adsorbent surface there is a definite and energetically equivalent number of adsorption sites, at each of which one molecule of a perfect molecule may be adsorbed.

The linear form of the Langmuir isotherm equation may be presented:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{1}{q_m} C_e \tag{4}$$

where q_e is the amount of solute adsorbed per links of adsorbent (g/g); C_e is the concentration of solute remaining in solution at equilibrium (g/L); q_m (g/g) is the amount of solute adsorbed per weight of adsorbent in forming a complete monolayer on the surface; b is a constant related to the energy. The plot of (C_e/q_e) vs. C_e for the adsorption of 4GL onto organobentonite gives a straight line having the slope $1/bq_m$ and the intercept $1/q_m$. The linearized form of Langmuir equation confirms the application of the model of Langmuir in a broad area of concentration (0.1–1.4 g/L) with an empirical correlation coefficient very satisfactory. The value of the adsorption capacity of organobentonite calculated from Langmuir model has been found nearly equal to the experimental one as $q_m = 0.5$ g/g of organobentonite. Chiou and Chuang (2006) studied the adsorption of an acid (Metanil yellow) and reactive (reactive blue 15) dyes onto cross-linked chitosan beads, they have noted that the best results were obtained at acidic pH (4) with adsorption capacity of 1.334 and 0.722 g/g for acid dye and reactive blue respectively. Bouberka et al. (2005) for the adsorption of Supranol Yellow 4GL (the dye used in our study) by three materials: sodium bentonite and hydroxyaluminium polycation pillared clays in the presence or absence of non ionic surfactant noted a best fixation at pH (4) with adsorption capacity of 0.05, 0.06 and 0.12 g per g of adsorbent for the three materials respectively. Ozcan et al. (2006) have found for the adsorption of acid dye blue 193 onto sepiolite an adsorption capacity of 0.119 mmol/g which increased to 0.257 mmol/g when the adsorbent (sepiolite) was modified by DEDMA surfactant.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor R_L.

$$R_L = \frac{1}{1 + bC_i}. \tag{5}$$

The value of R_L indicates the shape of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The value of the factor of separation R_L indicates the nature of the favourability adsorption process and its feasibility.

The Freundlich isotherm model is an empirical equation to describe heterogeneous systems. The linearized Freundlich isotherm equation is expressed by:

$$q_e = kC_e^{1/n} \tag{6}$$

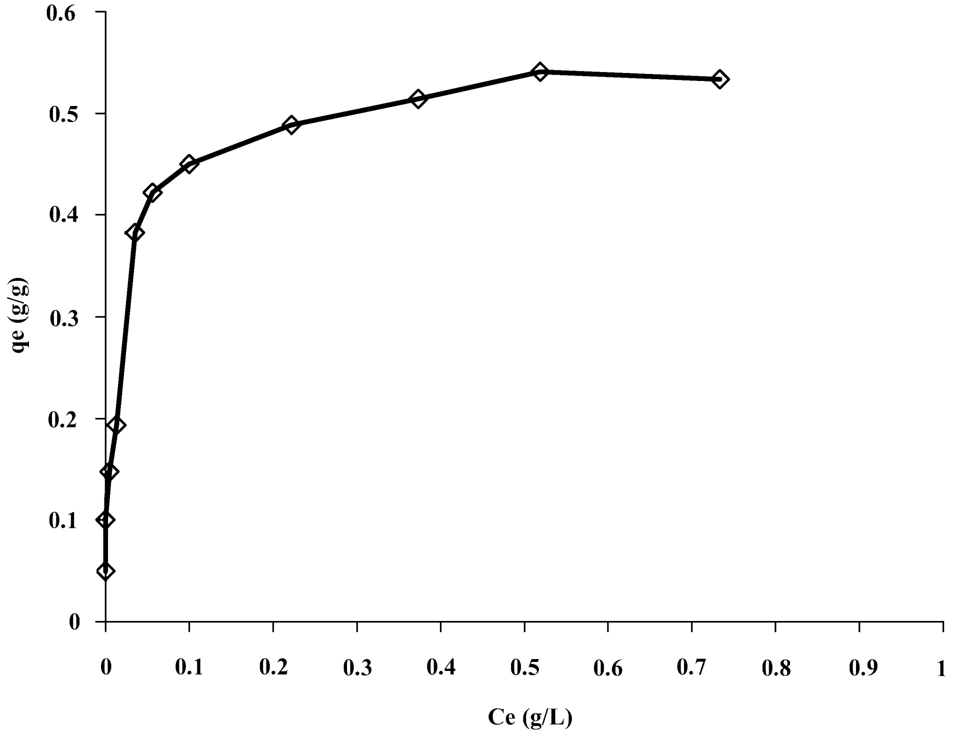


Fig. 6 Adsorption isotherm for Supranol Yellow 4GL onto organobentonite

Table 3 Isotherm constants for adsorption of Supranol Yellow 4GL on CTAB-bentoite

Langmuir model				Freundlich model		
q_e (g/g)	b (L/g)	R_L	r^2	K_f (g/ g)	$1/n$	r^2
0.54	74.07	0.01	0.99	0.09	3.60	0.91

Table 4 Effect of the pH on the adsorption of Supranol Yellow 4GL onto organobentonite

pH	3.5	6.5	9
q_e (g/g)	0.30	0.25	0.2

where q_e is the amount of solute adsorbed per links of adsorbent (g/g); C_e is the concentration of solute remaining in solution at equilibrium (g/L); k and n are Freundlich constants. One of the Freundlich constants k indicates the adsorption capacity of the adsorbent. The other Freundlich constant n is a measure of the deviation from linearity of the adsorption. The Freundlich isotherm fit very well the experimental data.

The value of the constant $1/n$ in Freundlich equation being smaller than 1, implies that the fixing process of the dye on organobentonite is favourable and it seem to suggest that physical, which is referred the adsorption bond becomes weak and conducted with van der walls forces, rather than chemical adsorption is dominant when it is used for adsorbing supranol yellow 4GL. The values of Freundlich and Langmuir constants are summarized in Table 2.

3.6 Effect of the pH

The pH exploits an important part on the quantity of the dye fixed. The choice of the pH values is carried out in order to examine the evolution of the adsorption of the dye associated with the various chemical forms present. The influence of initial pH solution on the adsorption of the Supranol Yellow 4GL is carried out for a fixed concentration of dye 0.6 g/L, a clay mass of 0.2 g and a contact time of 1200 seconds. The results are presented in Table 4. The adsorption of the Supranol Yellow 4GL on organobentonite shows that the best adsorption may be obtained at acidic pH. As the affinity of dye to organobentonite increased with decreasing pH. Since charge on the quaternized surfactant used to modified clay is pH-independent, and sorption onto the unmodified clay is negligible, the effect of pH would appear to lie in its alteration of sorbate speciation (Dentel et al. 1995). In acidic pH both the dye and surface dissociate (Bouberka et al. 2005; Paudit and Basu 2002). In this case the mechanism may be assumed by the charge developed by the organobentonite which becomes an exchange site for this anionic dye whatever its kind in solution (anion, cation or molecule). As result, the incoming like supranol yellow 4GL coordinates to the forming sites.

3.7 Effect of temperature

The study of the temperature effect on the adsorption of the dye Supranol Yellow 4GL on organobentonite is evaluated

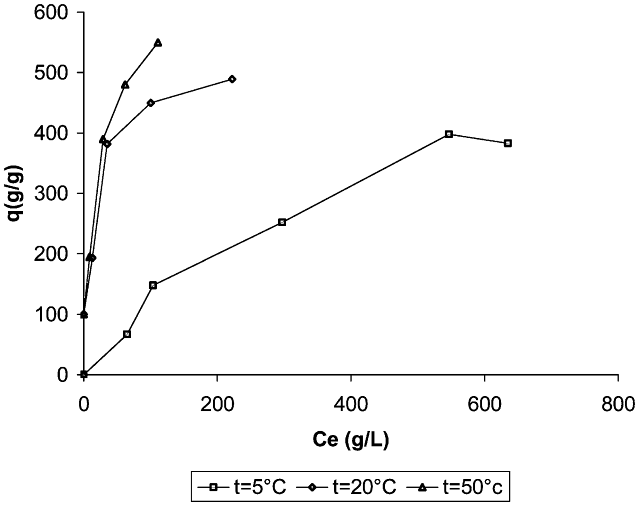


Fig. 7 Adsorption isotherm for surpranol yellow onto organobentonite at different temperatures

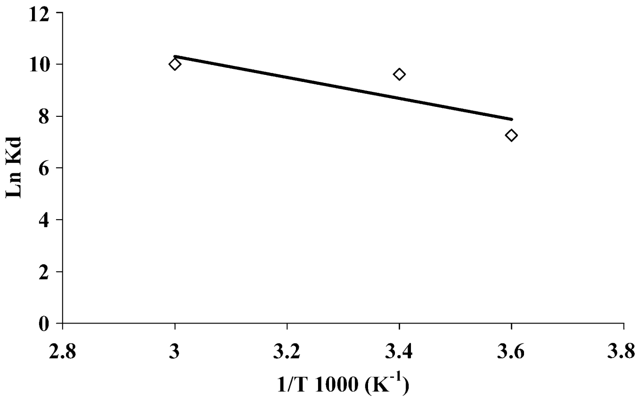


Fig. 8 Plot of $\ln K_d$ vs. $1/T$ for the estimation of thermodynamic parameters

using the following operating conditions a dye concentration ranging from 0.1 to 1.4 g/L, an organobentonite mass of 0.2 g and a solution volume of 100 mL at 5–50 °C . The variation of the quantity of the dye Supranol Yellow 4GL fixed on organic clay shows the positive effect of temperature on the adsorption. The results are presented in Fig. 7.

The partition coefficient is determined by the relation (Krishna and Bhattacheryya 2002):

$$k_d = \frac{q_e}{C_e}. \tag{7}$$

The thermodynamic parameters are deduced from the equations

$$\ln k_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{8}$$

$$\Delta G = \Delta H - T\Delta S. \tag{9}$$

The plot of $\ln k_d$ versus $1/T$ is presented in Fig. 8. From this latter, the following values are obtained: $\Delta H = 33.68$ kJ/mol, $\Delta S = 0.19$ kJ/mol, $\Delta G(278\,°\text{K}) = -19.14$ kJ/mol, $\Delta G(293\,°\text{K}) = -21.99$ kJ/mol, $\Delta G(323\,°\text{K}) = -27.69$ kJ/mol. The positive value of the enthalpy shows that the adsorption process of the Supranol Yellow 4GL on clay exchanged with the CTAB is endothermic. However, the negative value of ΔG decreased with an increase in temperature, indicating that the spontaneous nature of adsorption of dye is inversely proportional to the temperature.

4 Conclusion

Having an excess of negative charge on their surfaces, bentonite clays have a greater capacity to adsorb basic dyes compared to acid dyes. The preliminary tests show that the sodium bentonite doesn't possess a good ability for adsorption of anionic dye Supranol Yellow 4GL. Organobentonite is synthesised by exchanging cetyltrimethylammonium cations with inorganic ions on the surface of bentonite.

Yellow dye 4GL is found to adsorb better on the surface of organobentonite for a concentration of CTAB corresponding at 100% of CEC. The adsorption equilibrium is practically achieved in 1200 seconds. This behaviour is described by a monolayer Langmuir type isotherm. The adsorption process is found to be a second order kinetics. The dye uptake is very sensitive to pH and temperature changes in the adsorption system. The maximum dye uptake is observed at pH acid and high temperature. From this preliminary study, we may conclude that the organobentonite could be employed as adsorbent for Supranol Yellow 4GL.

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