Adsorption of Supranol Yellow 4 GL from aqueous solution by surfactant-treated aluminum/chromium-intercalated bentonite

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ABSTRACT

The aim of this paper is to study the adsorption of the acid dye Supranol Yellow 4 GL (S.Y. 4 GL) from aqueous solution on an inorgano–organo clay. Bentonite is naturally occurring clay with good exchanging ability. By exchanging its interlamellar cations with cetyltrimethylammonium bromide (CTAB) and hydroxya-luminic or chromium polycations, the properties of natural bentonite can be greatly improved. Batch adsorption tests of Supranol Yellow 4 GL were carried out at 20 °C and constant pH 6.5. To investigate the adsorption mechanisms, the simplified kinetic models, such as pseudo-first-order, pseudo-second-order, Elovich equation and intraparticle diffusion are tested. The results show that adsorption follows second-order rate kinetic. The correlation coefficients obtained for second-order kinetics model are greater than 0.998 indicating a better fitting of this equation. The experimental data are analysed by Langmuir, Fre-undlich and Elovich isotherms. The equilibrium adsorption capacity of anionic dye is determined from the Langmuir equation and found to be 142, 85 and 128, 20 mg/g (standard deviation; Δq (%) = 3.52 and 18.51) for CTAB-Cr-B and CTAB-Al-B, respectively.

1. Introduction

Clays have small particle size and unusual intercalation properties which afford them high surface area. They are alumino-silicates with a unique structure that allows modifications which should provide useful catalysts. They comprise layered sheets of octahedral sites between sheets of tetrahedral sites, where the distance between the layers can be adjusted by swelling. The interest of smectites among the clay minerals is the combination of cation exchange, intercalation, and the adjustable distance between layers.

In past decades, pillared interlayer clays (PILCs) and organoclays have attracted extensive attention because of their important applications in variety fields [1–3].

PILCs are prepared in various ways, generally by incorporation of metallic polycations replacing the exchangeable cations in the interlayer space of clay minerals [4]. They are widely used as catalyst carriers and catalysts while organoclays focused on intercalation of long-chain quaternary ammonium cations in the interlayer space. They are used to prepare clay-based nanocomposites as adsorbents to remove organic pollutants [5]. Both of PILCs and organoclays are prepared by replacing the exchangeable interlayer cations with metal hydrolysates and surfactants, respectively [4,5]. In the case of PILCs, the specific surface area and pore volume are greatly improved [4], and are important when they are used as catalysts and adsorbents. Owing to the hydrophilic surfaces of PILCs, they show poor affinity towards organic pollutants. However, after being modified with surfactants, the resultant organoclays show high efficiency in removing organic pollutants from water [6–8].

Zeilke and Pinnavaia [9] showed that these pillared clays might be applied as recyclable adsorbents for organic pollutants, but their affinity is low, in comparison with activated carbon. However, if the Al-pillared products are brought into contact with solutions containing long-chain quaternary alkyl ammonium ions, these latter are adsorbed on the clay surface and the pillars. Thus, the adsorptive capacity of these new materials towards organic molecules can be increased [10]. Zielke and Pinnavaia [9] studied modified clays for the adsorption of environmental toxicants and suggested the pillared, delaminated, and hydroxyl interlayer smectites can bind easily with chlorophenol. Srinivasan and Fogler [11] used inorgano–organo clays in the removal of benzo-pyrene and chlorophenols from industrial wastewaters.

In this paper, we study the adsorption of an acidic dye Supranol Yellow 4 GL, widely used in the tint of chemical fibres. The adsorption of this dye is achieved on two synthesised surfactant modified bentonite, intercalated initially by aluminum or chromium polycations and modified by co-adsorption with cetyltrimethylammonium bromide (CTAB). This assumption is

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made on the grounds that pillaring clays with metal hydrolysates results in a significant improvement of clay interlayer space, specific surface area and pore volume. Modifying bentonite with surfactants leads to the transformation of hydrophilic bentonite surfaces to hydrophobic ones.

2. Experimental

2.1. Starting materials

The Algerian bentonite supplied by ENOF was used. The structural formula of Na^+-bentonite is $((Si_{7.41} Al_{0.59})^{IV} (Al_{2.82} Fe_{0.24} Mg_{0.48})^{VI} (Ca_{0.08} Na_{0.76} K_{0.1})O_{20}(OH)_2)$. Its physical properties are listed in Table 1. A detailed characterisation of Na^+-bentonite was described in a previous work [12]. Al, Cr, Al/Cr-cetyltrimethylammonium bromide intercalated bentonite (referred to as Al-B, Cr-B; CTAB-Al-B and CTAB-Cr-B, respectively) were used as adsorbents. Cetyltrimethylammonium bromide (99%) provided by ACROS ORGANICS, was chosen as cationic surfactant.

2.2. Surfactant-treated aluminum-intercalated bentonite

The conventional pillaring solution of aluminum was prepared by adding slowly 0.4 M NaOH solution to 0.2 M AlCl₃ solution under vigorous stirring, until the OH/Al ratio reaches the value 2. To accelerate the formation of Al₁₃, the solution was kept for 7 days at room temperature. The surfactant-treated aluminum-intercalated clay was prepared by adding known quantity of surfactant (CTAB) to aluminum pillaring solution. The surfactant/clay ratio was fixed at 1.02 mmol of surfactant per gram of clay. This amount of CTAB is required to saturate the cation exchange capacity (CEC) of clay. The surfactant-pillaring solution was slowly added under vigorous stirring to a 1% weight bentonite solution to a ratio of 5 mmol of Al per gram of clay [13]. The mixture was allowed to react at room temperature for 48 h before separated by centrifugation, the solid phase was collected and washed with deionised water for several times until chloride-free as indicated by the AgNO₃ test. This material so obtained is denoted CTAB-Al-B.

2.3. Surfactant-treated chromium-intercalated bentonite

Hydroxychromium solution containing chromium-pillaring species was prepared on the basis of study by Pinnavaia et al. [14]. The pillaring solution was prepared by adding drop wise of an aqueous sodium carbonate solution (0.2 M) to an aqueous of a chromium (III) nitrate solution (0.1 M) under vigorous stirring to obtain an OH/Cr ratio of 2. The solution was kept for 96 h at 95 °C. The surfactant-treated chromium-intercalated clay was prepared by adding 1.02 mmol of surfactant (CTAB) per gram of clay to chromium-pillaring solution. The Na^+-bentonite clay was treated drop by drop with the surfactant-pillaring solution in order to obtain a ratio equal to 20 mmol of Cr (III) per gram of clay [14]. The resulting slurry was stirred for 2 h, and maintained at room temperature for 24 h. After the mixtures were separated by centrifugation,

the solid phase was collected and washed with deionised water until the supernatant was chloride-free as indicated by the AgNO₃ test. The product was dried at 35 °C and gently grounded in an agate mortar. The material so obtained is called CTAB-Cr-B. Table 1 presents the characteristics of CTAB-Al-B and CTAB-Cr-B obtained by X-ray diffraction (XRD), BET specific surface area (S_{BET}) and CEC measurements.

2.4. Adsorbate

Supranol Yellow 4 GL was provided by the Ciba society (Zurich, Switzerland) and was used as received. Synthetic test dye solution was prepared by dissolving an accurately weighed amount of dye (1 g/L) in distilled water and subsequently diluted to required concentrations. Supranol Yellow 4 GL is an industrial dye used for chemical fibres. Its formula and complete structure diagram are not available.

2.5. Characterisation methods

The CEC was determined with conductimetric method and quoted as 100 meq./100 g of bentonite. This method was based on charged species. In effect, ion exchange between Mg^{2+} and Ba^{2+} occurred by titrating a 1 g/100 mL barium saturated bentonite suspension with 0.02 M MgSO₄ solution. This latter was added drop wise to the Ba^{2+}-saturated bentonite while the pH was being maintained at a value of 6.5 by adding 0.1 M HCl. The conductivity of the suspension was continuously monitored with a conductimeter previously calibrated with 0.01 M KCl. At the beginning, a slight change in the conductivity was observed owing to the formation of insoluble BaSO₄ and then was increased after completing the addition. Changes in conductivity during the second phase could be not only due to the ion exchange reaction but also due to the formation of excess magnesium and sulphate ions in the solution. The plot of the specific conductivity against MgSO₄ added volume shows two linear portions. Their intersection gives the equivalent point corresponding to the CEC [15,16].

The surface area of all samples was measured by adsorption of nitrogen according to the BET-method on a Micrometrics 2000 apparatus. The basal spacing of the samples was measured by XRD by means of a Siemens D5000 instrument, using Cu Kα radiation. The infrared spectra (FTIR) of the samples were obtained with a PerkinElmer spectrometer.

2.6. Adsorption studies

Adsorption on the adsorbents was determined using the batch method. A fixed amount of the adsorbent (0.05 g) was added to 100 mL of dye solution of required concentration (50 mg/L) and the mixture was agitated for a predetermined time under constant temperature. At different time intervals of 5, 10, 15, 20, 30, 45, 50, 60, 75 and 120 min, the concentration of the dye in the solution was analysed colorimetrically using a spectrophotometer (SAFAS UV mc²) by measuring absorbance at $\lambda_{max} = 405$ nm. Isothermal studies were conducted by adding 0.05 g of the clay to 100 mL of dye solution of varying concentrations. The amounts of dye adsorbed (q_e) were calculated using the following relationship:

$$q_e = \frac{C_i - C_e}{m} \times V \tag{1}$$

where C_i is the initial concentration of the dye solution (mg/L), C_e is the concentration of the dye solution at the adsorption equilibrium (mg/L), V is the volume of the dye solution (mL) and m is the mass of the clay (mg).
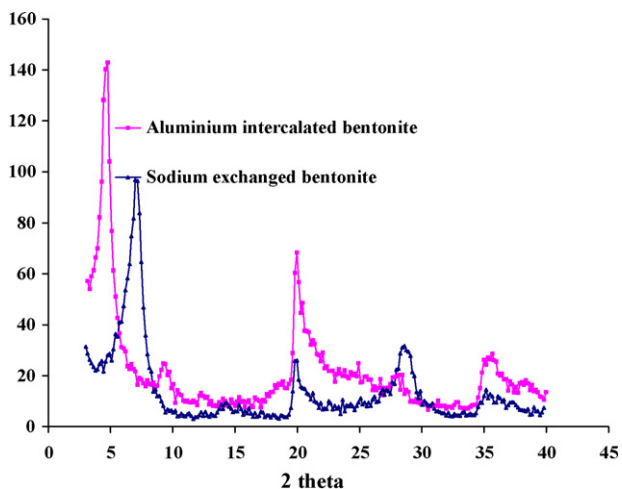
Table 1
Basal spacing, exchange capacity and surface area for Na^+-bentonite, aluminum-intercalated, chromium-intercalated and surfactant-treated-intercalated bentonites

Samples of clays	Basal spacing (Å)	S_{BET} (m²/g)	CEC (meq./100 g)
B–Na⁺	11.88	110	10125
Al-B	20.20	229	3116
Cr-B	23.06	317	59.3
CTAB-Al-B	19.67	25	–
CTAB-Cr-B	18.80	–	–

Fig. 1. X-ray diffraction patterns of sodium exchanged bentonite (Na$^+$-B) and aluminum-intercalated bentonite (Al-B).

3. Results and discussion

3.1. Characterisation of adsorbents

Table 1 summarizes the d_{001} reflexion and surface area data for all the samples analysed.

The thickness of the natural montmorillonite layer is 9.6 Å [17–19]. Depending on the kind of hydroxycation used as a pillar, the pillaring process leads more or less to an increase in the interlayer spacing. In the case of aluminum-intercalated clay, this increase is about 9.4 Å at 25 °C, which corresponds to the size of the Keggin cation. Fig. 1 shows the XRD patterns of aluminum-intercalated montmorillonite. The d_{001} peaks are quite sharp, indicating a relatively homogeneous pillaring process. However, the presence of a second peak at about $2\theta = 9°$ seems to indicate the existence of a fraction of materials not pillared [20].

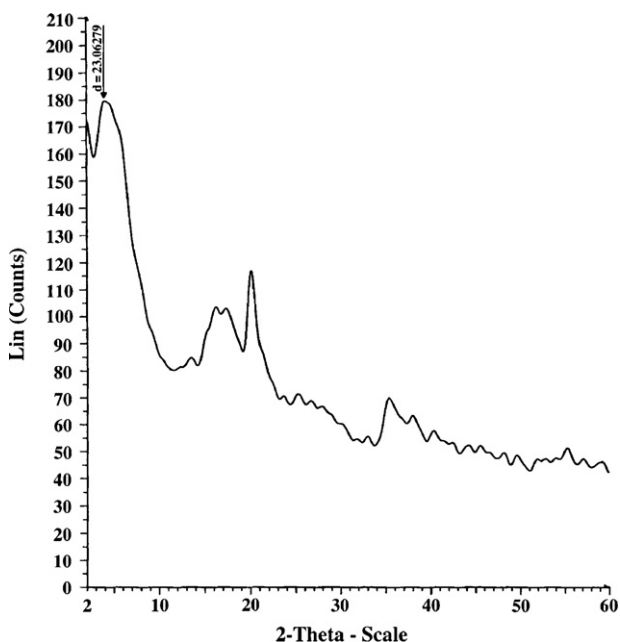In the case of chromium-intercalated montmorillonite, Fig. 2 shows the XDR patterns of Cr-B. As can be seen, the d_{001} peak of the intercalated-chromium appears at 2θ angles smaller than the original clay (i.e., at $2\theta \sim 4°$ for the intercalated sample compared to $2\theta \sim 9°$ of the original clay). This result indicates clearly an expansion of interlamellar space as a consequence of the pillaring process. However, in the presence of surfactants, polycations are protected from hydrolysis, resulting in the larger spacing being retained [21]. The incorporation of surfactant in pillaring solution, affected the basal spacing from 20.20 to 19.67 Å for Al polyoxocations and 23.06 to 18.8 Å for Cr species (Table 1).

An FTIR spectrum of CTAB-Al-B is shown in Fig. 3. The characteristic band of montmorillonite at 3618 cm^{-1} corresponds to stretching (γOH) vibrations of OH groups of the octahedral layer located in the inner blocks of new matrix. The band at 1639 cm^{-1} corresponds to the OH deformation of water, while the bands centred at 988 and 885 cm^{-1} are attributed to the deformation of vibrations of the hydroxyl groups related to tetrahedral aluminum. The appearance of characteristic bands of surfactant confirms the change of the clay surface properties. The intense band between 2859 and 2921 cm^{-1} can be assigned to the vibrations of CH$_2$ and CH$_3$ groups and their bending vibrations between 1380 and 1470 cm^{-1} confirming the intercalation of quaternary ammonium molecules between the silica layers.

The CEC can be used as a key factor for the synthesis procedure optimisation in order to obtain pillared clays with a desired population of pillars and controlled pore size distribution. On the other hand, the CEC of clays is only partially compensated by the charge of oligomers because a part of its exchangeable cations remains unchanged. Besides, the intercalation agents are usually prepared by partial hydrolysis of solutions of the cations, and their size and polymerisation degrees are not always well established. The residual CEC provides an approximate estimation of the clay layer charges, which are not compensated by positively charged oligomers species. A residual CEC is found for Cr-B sample and Al-B, which can indicate that this sample has lower amounts of intercalated pillars (Table 1).

The N$_2$ adsorption–desorption isotherms of intercalated clays have similar shapes. The isotherm shapes correspond to H3 type (figure not shown). This type is a hysteresis loop with a vertical adsorption branch at a relative pressure very close to 1 and a desorption branch close to medium pressure. Such a hysteresis loop
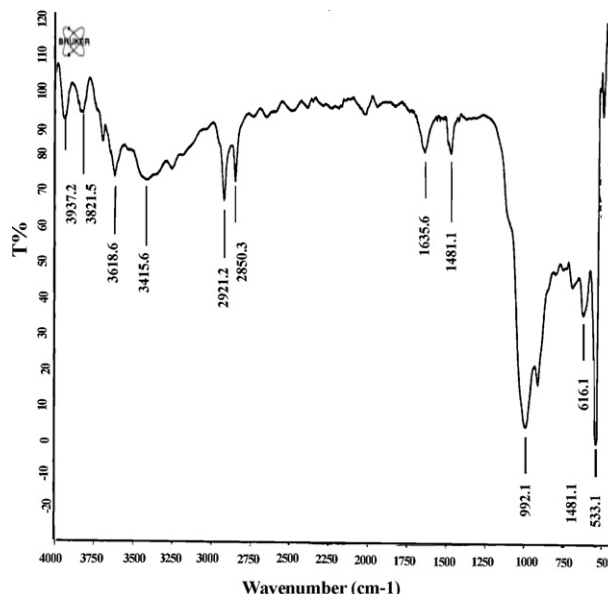

Fig. 2. X-ray diffraction patterns of Cr-intercalated montmorillonite.

Fig. 3. FTIR spectra of modified bentonite (CTAB-Al-B).

can be formed by very wide pores having narrow, short opening or pores formed by parallel plates at the same distance from each other (slit-shaped pores) [20]. The initial surface (S_{total}) of clay evaluated by methylene blue method is about 792 m^2/g with a CEC of 101.25 meq./100 g of clay, in good agreement with the conductimetric method (CEC = 99 meq./100 g of clay). The incorporation of surfactant into the pillaring solution significantly decreases the surface area. This can be explained in terms of filling the micropores by surfactant molecules. This phenomenon was reported previously by Michot and Pinnavaia [7], Wu et al. [8], Srinivasan and Fogler [11] and Bouras et al. [22].

3.2. Effect of contact time

The influence of contact time on removal of S.Y. 4 GL by CTAB-Al-B and CTAB-Cr-B at pH 6.3 and 20 °C is shown in Fig. 4. It is evident that both materials are efficient to adsorb dye with different efficiencies. The dye adsorption of the CTAB-Cr-B sample is faster than that of CTAB-Al-B sample. Moreover, the maximum amount of adsorbed dye (q_e) is higher for the CTAB-Cr-B sample (44.57 mg/g) than for the CTAB-Al-B sample (38.40 mg/g). To reach equilibrium, it takes 40 and 50 min for CTAB-Cr-B and CTAB-Al-B, respectively. The adsorption capacity of adsorbents with respect to equilibrium time is in concordance with the order of the structure heterogeneity (CTAB-Cr-B > CTAB-Al-B) and perhaps the surface area (CTAB-Cr-B > CTAB-Al-B). Thence, the removal of the dye from aqueous solution by adsorption is related to surface charge and the degree of ionisation and species of adsorbate. The extent of adsorption increases with increasing of structure heterogeneity. In effect, when B-Na$^+$ is treated with intercalation solution (Cr-OH), the exchangeable Na$^+$ is replaced by Cr-OH species. The Cr-OH solution containing trimeric species, $Cr_3(OH)_4^{5+}$, as the principal ones, follows by tetra-, $Cr_4(OH)_6^{6+}$, mono-, $Cr(H_2O)^{3+}$, and dimer-$Cr_2(OH)_2^{4+}$ species [23]. As it has been reported in our previous work [24], the same dye was adsorbed by the new charge developed in the chromium-intercalated montmorillonite. In this case, the dye is adsorbed by the outer surface of pillared clay and the interlayer exchange site.

Kinetics of the interaction between the surfactant-treated-intercalated bentonite and S.Y. 4 GL is studied by applying the following equations and models. Firstly, Lagergren equation [25,26] is applied, assuming pseudo-first-order kinetics, where the number of dye ions is greater than the number of adsorption sites on clay surfaces. The expression for the first-order rate constant, k_1, may be expressed as:
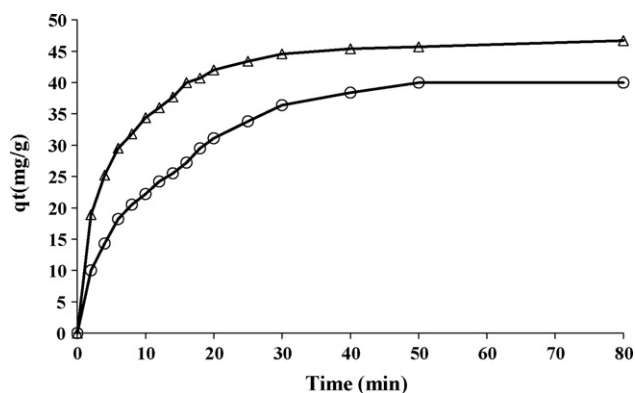
$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

The values of k_1 can be obtained from the slop of the plot of log ln($q_e - q_t$) vs. time. The validity of the first-order kinetics and hence the Lagergren equation can be tested by comparing theoretical q_e values obtained from the intercepts with the experimental ones. If the validity is less, the kinetics can be tested again for the following second-order mechanism using the linear form of the equations written by Ho et al. [27] as:

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} \left(\frac{1}{q_e} \right) t \tag{3}$$

The plot of t/q_t vs. t gives a linear relationship, allowing for computation of q_e and k_2. The validity of the model can also be tested by comparing obtained values of q_e to the experiment values. When the adsorbate ions and the surface sites interact chemically through a second-order mechanism, the application of the Elovich equation [28] may be more appropriate i.e.:

$$\frac{dq_t}{q_t} = \alpha \exp\left(-\beta q_t \right) \tag{4}$$

The Elovich coefficients α and β are known to represent the initial adsorption rate (g mg^{-1} min^{-2}) and the desorption constant (mg g^{-1} min^{-1}), respectively. Their values may be computed graphically from the plots of q_t vs. ln t, of the integrated form of Eq. (4).

For a porous substrate, the diffusion of adsorbate species into the pores is the rate determining process. Thence, the intraparticle diffusion rate constant, k_i, may be given by Weber and Morris's equation [29]:

$$q_t = k_i t^{0.5} \tag{5}$$

The plots of q_t vs. $t^{0.5}$ yield straight lines passing through the origin and the rate constant, k_i, can therefore be obtained from the slope. The mechanism of the interactions may also be governed by the slow transport of the adsorbate ions from the liquid phase up to the adsorbent surface.

The pseudo-first-order plots of ln($q_e - q_t$) vs. t of Lagergren equation are given in Fig. 5a. The plots present good linearity and yield the first-order rate constants 13.3×10^{-2} min^{-1} for CTAB-Cr-B and 8.7×10^{-2} min^{-1} for CTAB-Al-B (Table 2). In testing the validity of the pseudo-first-order kinetics, it turns out that q_e values obtained from the Lagergren plots compare poorly with the experimental q_e values (Table 3) yielding negative deviations (-15.16% for CTAB-Cr-B sample and -1.48% for CTAB-Al-B). Thus, despite the linearity of the Lagergren plots, the interactions do not appear to follow pseudo-first-order kinetics. Whereas, the second-order plots of t/q_e vs. t (Fig. 5b) are linear (R: 0.99) and the rate constant k_2 is 5.31×10^{-3} g mg^{-1} min^{-1} for CTAB-Cr-B and 2.35×10^{-3} g mg^{-1} min^{-1} for CTAB-Al-B (Table 2).

Fig. 4. Supranol Yellow 4 GL adsorption kinetics on surfactant-treated modified bentonite (△: CTAB-Cr-B, ○: CTAB-Al-B, clay 0.5 g/L, initial dye concentration 50 mg/L, pH 6.3 and T = 20 °C).

Table 2

First-order rate constant, second-order rate constant, Elovich coefficients and intraparticle diffusion rate constant for adsorption of Supranol Yellow 4 GL at 20 °C (clay 0.5 g/L, initial dye concentration 50 mg/L and pH 6.3)

Parameter		CTAB-Cr-B	CTAB-Al-B
Pseudo-first-order	$k_1 \times 10^2$ (min^{-1})	13.30	8.70
	R^2	0.969	0.987
Pseudo-second-order	$k_1 \times 10^3$ (g mg^{-1} min^{-1})	5.31	2.35
	R^2	0.999	0.995
Elovich	α (g mg^{-1} min^{-2})	52.88	11.45
	$\beta \times 10^3$ (g mg^{-1} min^{-1})	122	105
	R^2	0.950	0.972
Intraparticle diffusion	k_1 (g mg^{-1} min$^{-0.5}$)	5.78	7.04
	Intercepts	+15.45	−0.57
	R^2	0.978	0.978

Table 3
Experimental and computed q_e values from pseudo-first-order and pseudo-second-order plots for adsorption of dye at 20 °C (clay 0.5 g/L, initial dye concentration 50 mg/L and pH 6.3) onto CTAB-Cr-B and CTAB-Al-B.

Adsorbents		CTAB-Cr-B	CTAB-Al-B
q_e (mg/g)	Experiment	44.57	38.40
	Pseudo-first-order	37.81	37.83
	Pseudo-second-order	49.26	45.66
Deviation (%)	Pseudo-first-order	−15.16	−1.48
	Pseudo-second-order	+10.52	+18.90

From the consideration of the adsorbent–dye interactions, the pseudo-second-order rate constants may follow the sequence: CTAB-Cr-B > CTAB-Al-B. The comparison between experimental and theoretical values of q_e is given in Table 3 and the two sets of data show much better agreement. CTAB-Al-B gives the least deviation 10.52%, while CTAB-Cr-Al shows 18.90 %. The deviations still existing might be due to the uncertainty inherent in obtaining the experimental q_e values.

Interactions of S.Y. 4 GL with CTAB-Cr-B and CTAB-Al-B also yields good agreement with linear Elovich plots q_t vs. $\ln t$ (Fig. 5c) with correlation coefficients lying on the interval range 0.95–0.97 (Table 2). The Elovich equation describes predominantly chemical adsorption on highly heterogeneous adsorbents, but the equation does not propose any definite mechanism for adsorbate–adsorbent interaction [28]. The coefficients depend significantly on the amount of adsorbent. As a matter of fact, CTAB-Cr-B had a much higher initial rate of uptake (α = 52.88 g mg^{-1} min^{-2}) than CTAB-Al-B (α = 11.45 g mg^{-1} min^{-2}). This might result from very high surface area and CEC of CTAB-Cr-B compared to those of CTAB-Al-B.

The adsorption process is mainly controlled by diffusion from the solid–liquid interface towards the solid particles. This type of intraparticle diffusion may be tested by plotting q_t vs. $t^{0.5}$ (Fig. 5d). The plots are linear with regression coefficient of 0.978 for both CTAB-Cr-B and CTAB-Al-B samples (Table 2). The intraparticle diffusion rate for CTAB-Al-B is higher than that of CTAB-Cr-CTAB, which explains that the pseudo-second-order rate constant for CTAB-Al-B is much less than for CTAB-Cr-B. During the adsorption of dye onto CTAB-Al-B, some boundary layer resistance is decreased (intercept = −0.57) as the available external surface area decreases. Nevertheless, the plot of CTAB-Cr-B gives a large intercept (+15.44), suggesting that the process is dependant upon the surface adsorption. In conclusion, the intraparticle diffusion is not likely to be the controlling factor determining the kinetics of the processes. In the present case, the second-order model gives the best possible fit to the experimental data and consequently the adsorption of acidic dye on surfactant-treated metallic polycations intercalated bentonite follows a pseudo-second-order kinetic mechanism.

3.3. Adsorption isotherms

To gain further understanding of the behaviour and mechanism of CTAB-Cr-B and CTAB-Al-B with S.Y. 4 GL, the isotherms of these modified bentonites are studied as indicated in Fig. 6. The plots represent the form of dye adsorbed per unit mass of adsorbents, q_e, against the concentration of dye remaining in solution, C_e. In order to make clear the improvement of adsorption caused by CTAB, we include in Fig. 6, the adsorption of S.Y. 4 GL on Cr-intercalated bentonite and Al-intercalated bentonite at pH 6.5. For example, the dye adsorption on CTAB-Cr-B and Cr-B are respectively 138 and
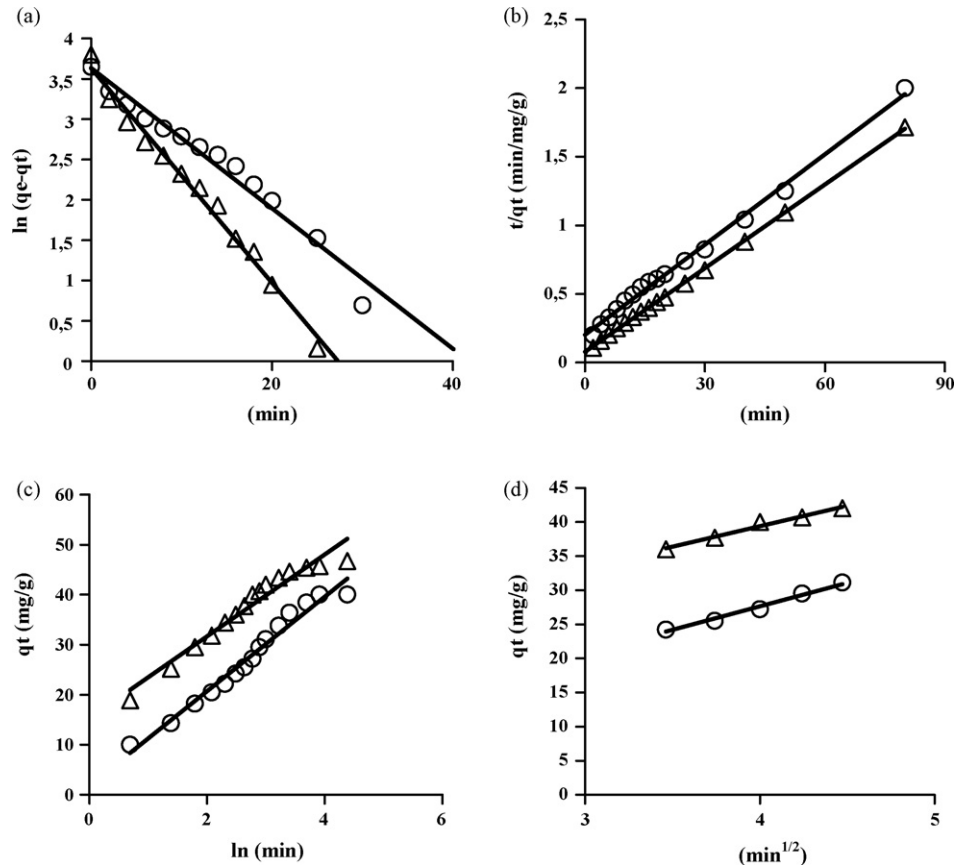

Fig. 5. Tests of first-order equation (a), of second-order equation (b) of Elovich equation (c) and intraparticle diffusion (d) for Supranol Yellow 4 GL onto surfactant-treated metallic polycations ($\triangle$: CTAB-Cr-B, $\bigcirc$: CTAB-Al-B, clay 0.5 g/L, initial dye concentration 50 mg/L, pH 6.3 and T = 20 °C).
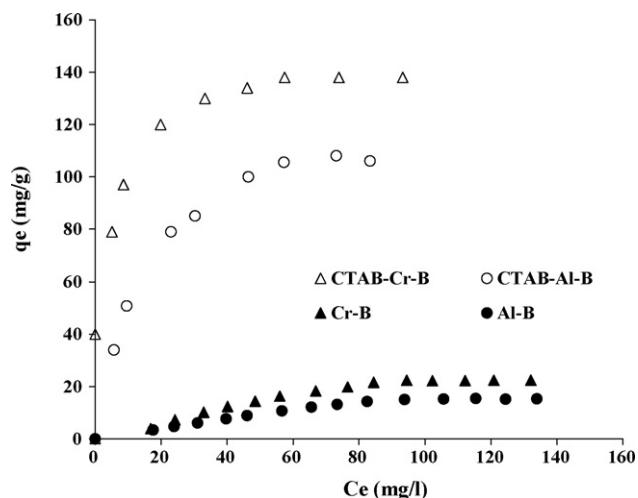
Fig. 6. Supranol Yellow 4 GL adsorption isotherms for Al-B, Cr-B, CTAB-Al-B and CTAB-Cr-B.

16.3 mg/g at an equilibrium concentration of less than 60 mg/L, which indicates that the hydrophobic effect is a key role in the process. All isotherms show the L-shape according to the classification of Giles et al. [30]. The L-shaped isotherm means that there is no strong competition between the solvent and adsorbate to occupy the adsorbent surface sites. In this case, the longitudinal axes of the adsorbed molecules are parallel to the adsorbent surface.

The sodium exchanged bentonite (Na^+-B) does not induce a significant removal. The dye exists in anionic form, so no adsorption takes place on Na^+-B, as both have negative charge (electrostatic repulsion). The affinity of clay minerals for organic compounds seems to increase with increasing surface area. Bentonite intercalated with polymeric Cr possesses larger S_{BET} than the Al-intercalated clay and Fe-intercalated clay. The S_{BET} values of Cr-B, Al-B and Fe-B are respectively 317, 229 and 165 m^2/g [31]. While, their d_{001} values are 23.06, 20 and 15.3 Å following the same order.

The loading by co-adsorption of CTAB species on modified bentonite, increases the affinity of the adsorbent. The surface properties of CTAB-Cr-B and CTAB-Al-B change from hydrophilic to hydrophobic character and lead to an increasing adsorption capacity towards acidic dyes.

Three linearized models are tested to describe the adsorption experimental results, namely the Langmuir, the Freundlich and the Elovich equations. The Langmuir adsorption isotherm [32], is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbate surface with a constant energy. There is no transmigration of adsorbate in the plane of adsorbate surface, while the Freundlich is naturally empirical [33]. Its satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous sorption. The Elovich model is of kinetic nature [34], and has a relation which differs from that of Langmuir by the evolution of the adsorption phenomenon. This latter can differ, in this case, in multiple layers by way of chemisorptions.

The Langmuir, Freundlich, and Elovich equations are expressed respectively,

$$\frac{C_e}{q_e} = \frac{1}{b\,q_{max}} + \frac{1}{q_{max}}\,C_e \tag{6}$$

$$\ln q_e = \frac{1}{n}\ln C_e + \ln k_f \tag{7}$$

$$\ln \frac{q_e}{C_e} = \ln(K_E q_{max}) - \frac{1}{q_{max}}q_e \tag{8}$$

where C_e (mg/L) is the equilibrium concentration of solute, q_e (mg/g) is the adsorbed quantity, q_m (mg/g) is the monolayer maximal adsorption capacity, b (L/mg) is a constant related to adsorption energy, k_f is an indicative constant of the relative adsorption capacity of the adsorbent ($mg^{1-(1/n)}\,L^{1/n}\,g^{-1}$) and $1/n$ is an indicative constant of the adsorption intensity and K_E is the Elovich equilibrium constant (L/mg).

In order to determine the validity of these models, the standard deviation Δq (%) is calculated, i.e.

$$\Delta q = \sqrt{\frac{\sum \left[(q_{t,\exp}q_{t,cal})/q_{t,\exp}\right]^2}{n-1}} \times 100 \tag{9}$$

Values of the Langmuir constants are presented (in Table 4) for the adsorption of S.Y. 4 GL onto CTAB-Al-B and CTAB-Cr-B. The values of the correlation coefficients obtained from Langmuir expression make in evidence that the adsorption of S.Y. 4 GL on CTAB-Cr-B and CTAB-Al-B follows the Langmuir isotherm. From Table 4, it can be seen that the values of maximum adsorption capacity obtained with the Langmuir expression are higher than the experimental data, corresponding to the adsorption isotherm plateaus. It seems that the isotherm obtained from Langmuir expression for adsorption of S.Y. 4 GL onto CTAB-Cr-B provides a better fit to the experimental data because of the higher correlation coefficients and relatively low values of the average percentage error ($\Delta q < 4\%$ (Table 4).

The favourable nature of adsorption can be expressed in terms of dimensionless equilibrium parameter of Hall et al. [35], i.e. $R_L = 1/(1+bC_0)$, where b is the Langmuir constant and C_0 is the initial concentration of the adsorbate in solution. The values of R_L indicate the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). The dimensionless separation factors calculated for S.Y. 4 GL onto CTAB-Cr-B and CTAB-Al-B are 0.0323 and 0.108, respectively. The R_L values are found to be less than 1 and greater than zero, indicating favourable adsorption.

The calculated Freundlich isotherm constants and the corresponding correlation coefficient values are grouped in Table 4. The correlation coefficients are high (≥ 0.910) showing a good linearity. The values of maximum adsorption capacity obtained using Freundlich equation are equal to those calculated using Langmuir model. It is clear, from average percentage error values (Table 4), that there is good agreement between the experimental and pre-

Table 4
Parameters of the Langmuir, Freundlich, and Elovich isotherms for the adsorption of S.Y. 4 GL onto CTAB-Al-B and CTAB-Cr-B

	CTAB-Al-B	CTAB-Cr-B
Freundlich		
$1/n$	0.421	0.189
k_f ($mg^{1-(1/n)}\,L^{1/n}\,g^{-1}$)	18.69	63.13
R^2	0.916	0.947
q_{max} (mg/g)*	113.86	142.37
Δq (%)	5.42	3.16
Langmuir		
b (L/mg)	0.068	0.445
q_{max} (mg/g)	128.20	142.85
R^2	0.996	0.998
Δq (%)	18.51	3.52
Elovich		
q_{max}	51.02	27.62
$K_E \times 10^{+4}$	14.450	1.070
R^2	0.966	0.911
Δq (%)	51.40	79.98

q_{max} (mg/g)* can be expressed in terms of $k_f \times C_0^{1/n}$ according to Halsey [37].

dicted values, suggesting that the Freundlich model is valid for the experimental equilibrium data. As shown in Table 4, for adsorption S.Y. GL onto CTAB-Al-B, Freundlich isotherm is more suitable for the experimental results than is the Langmuir model because of the lower average percentage error values ($\Delta q < 6\%$). The Freundlich parameter $1/n$ for the adsorption of Supranol Yellow 4 GL on both modified clays, ranging between 0 and 1, indicates the relative energy distribution on the adsorbent surface. It is evident from this data that the surface of modified clays is made up of heterogeneous adsorption [36]. Whereas considering a value of $1/n > 1$ indicates cooperative adsorption.

When considering the surfactant-treated modified bentonite, the Elovich isotherm constants, K_E and q_m, as well as the correlation coefficient, R^2, for the S.Y. 4 GL adsorption systems, are obtained using the non-linear form of the equation (Table 4). In all cases, the Elovich isotherm exhibits higher correlation coefficients, but lower than those obtained from Langmuir and Freundlich equations. In spite of the good correlation coefficients, the values of maximum adsorption capacity determined by using the non-linear transformation of the Elovich equation (Table 4) are much lower than the experimental adsorbed amounts at equilibrium. They correspond, as a result, to the plateaus of the adsorption isotherms. This means that the adsorption site that implies multilayer adsorption does not agree with the experiment, in the concentration range studied. Therefore, the Elovich model is unable to describe the adsorption isotherms of acidic dye onto surfactant-treated modified bentonite. In spite of the extremely higher coefficients of correlation, this model does not describe the equilibrium data because of the higher values of the average percentage error.

4. Conclusion

The results of this investigation show that modification of bentonite by inorganic polycations is a potential procedure for the preparation of adsorbents of anionic dye S.Y. 4 GL. By the modification of these materials by the cationic surfactant CTAB, the adsorption properties are considerably improved.

A comparative study of adsorption of S.Y. 4 GL on aluminum-intercalated bentonite (Al-B), chromium-intercalated bentonite (Cr-B), CTAB-treated aluminum-intercalated bentonite (CTAB-Al-B) and CTAB-treated chromium-intercalated bentonite (CTAB-Cr-B) evidences the high adsorption capacity of dye on the inorgano–organo bentonite obtained from adsorption isotherms (i.e. CTAB-Cr-B > CTAB-Al-B), which are modelled using different isotherm models. The Langmuir equation described well the experimental results but less accurate than Freundlich model. Whereas, the Elovich representation does not lead to a correct determination of the maximum adsorption capacity. The comparison between adsorption isotherms of the acid dye on both modified clays is significant. In effect, the chromium-intercalated bentonite in the presence of CTAB appears to be a better adsorbent than aluminum-intercalated bentonite in the presence of this surfactant. So, it is interesting to emphasize that modified adsorbents are found to conveniently decolor the dye solutions. The potential application of CTAB-treated chromium-intercalated clays for adsorption removal of acid dye from aqueous solutions is highly.

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