

Removal of Supranol Yellow 4GL by adsorption onto Cr-intercalated montmorillonite

Z. Boubarka^a, A. Khenifi^a, N. Benderdouche^b, Z. Derriche^{a,*}

^a *Laboratoire de Physico-Chimie des Matériaux, Département de Chimie, Faculté des Sciences, USTO-MB.BP 1505, Oran El Menouer 31000, Algeria*

^b *Faculté des Sciences et Sciences de l'Ingénieur, Université de Mostaganem, B.P. 188.27000 Mostaganem, Algeria*

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Abstract

Cr(III)-intercalated montmorillonite was utilized as an adsorbent for the removal of the organic pollutant, Supranol Yellow 4GL, a synthetic dye used for chemical fibres. The material was prepared by the reaction of Na montmorillonite with a base-hydrolyzed solution of Cr nitrate salt ($\text{OH}^-/\text{Cr}^{3+}$ molar ratios of 2). XRD data showed that the interlayer spacing (d_{001}) of montmorillonite was increased from 12.35 to 23.06 Å. The kinetics and mechanism of the adsorption of the acid dye, Supranol Yellow 4GL, on Cr(III)-intercalated montmorillonite was investigated. The equilibrium time was reached within 30 min. The process follows pseudo-second-order rate kinetics. The Langmuir isotherm described the adsorption data over the concentration range (20–160 mg/l). The separator factor R_L revealed the favourable nature of this adsorption process. Also, the thermodynamic parameters such as ΔS° , ΔH° , ΔG° were determined.

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1. Introduction

The textile industries effluents contain an important amount of colour, dissolved surfactant and a large amount of suspended solids and hence are an important pollution problem in developing countries. However, the main pollution source of textile wastewater comes from the dyeing and finishing processes.

The presence of colours will reduce aquatic diversity by blocking the passage of light through water. Most of the dyes used are toxic to aquatic organisms [1]. Colour removal is a major problem because some dyes are stable to biological degradation and conventional chemical treatment [2]. Wastewaters are released there without any treatment and so there is a need to use low cost adsorbents for dye removal. Activated carbon is the most widely material used for that purpose but it remains an expensive material. Cheaper substitutes such as fly ash [3], silica gel [4], wood [5], biogas slurry [6] and clay materials have been applied with varying success for colour removal [7–8]. Several references have outlined the applicability of inorganic

adsorbents for removing reactive dyes. Clay has shown a high adsorption capacity, furthermore, the adsorption capacity of this adsorbent may exceed that of activated carbon under the same conditions of temperature and pH [9].

Many studies have also reported the use of inorganic clays prepared by intercalation of metallic polycations such as aluminium Al_{13} for the adsorption of organic compounds [10].

Bouras et al. studied the removal of anionic dye by surfactant-modified Ti-pillared montmorillonite. The results of these studies led to the conclusion that modified clay tailored for specific adsorption purposes showed some promise [11]. The affinity of clay minerals for organic bases seems to increase with increasing polarizing power of the interlayer cations, increasing surface area and decreasing surface-charge density. Pillared clays and their uncalcined hydroxy-intercalated precursors possess most of these properties. Therefore, these modified clays are expected to show higher sorption capacities for organic compounds than common clay minerals. Al, Zr and Ti hydroxy-intercalated and pillared have been recently used to remove anionic organic compounds. Matthes and Kahr [12] has found that the maximum sorption capacities of atrazine on Zr-intercalated bentonite and activated carbon GAC in ultrapure water were nearly identical. Cr-intercalated clay exhibits higher surface area than above

* Corresponding author. Tel.: +213 41 53 04 63; fax: +213 41 53 04 63.
E-mail address: derriche.zoubir@yahoo.com (Z. Derriche).

materials. This paper is part of a broader study concerning the sorption behaviour of Cr-hydroxy-intercalated clay for organic compounds to develop novel applications for these materials. The prime objective of the present study is to investigate the potential of chromium-intercalated clay which can be used as adsorbent in wastewater treatment. The present investigation reports the sorption capacity and mechanism of azo dye Supranol Yellow 4GL by Cr-intercalated montmorillonite.

2. Experimental

2.1. Starting materials

The clay used in this study was supplied by ENOF (an Algerian manufacture specialized in the production of non-ferric products and useful substances). The main impurities are quartz, cristobalite and calcite. The material was purified in laboratory to remove carbonates, iron hydroxide and organic matter. The X-ray diffractogram is presented in Fig. 1. Its structural formula is $(\text{Si}_{7.41}\text{Al}_{0.59})^{\text{IV}}(\text{Al}_{2.82}\text{Fe}_{0.24}\text{Mg}_{0.48})^{\text{VI}}(\text{Ca}_{0.08}\text{Na}_{0.76}\text{K}_{0.1})\text{O}_{20}(\text{OH})_2$. A suspension in distilled water enabled us to obtain, a colloidal suspension after 12 h. After sedimentation, the clay fraction montmorillonite ($<2\ \mu\text{m}$) was recovered. The solid phase was then saturated with sodium ions by stirring in a 1 M sodium chloride solution. This was done in triplicate. The saturation was achieved and the solid was washed with distilled water to remove excess salt. The material obtained is called sodium-exchanged montmorillonite or BNa^+ , whose mineralogy was evaluated by X-ray diffraction. The cation exchange capacity (CEC) was 101.25 meq/100 g of clay and the surface area was $110\ \text{m}^2/\text{g}$ [13].

2.2. Preparation of hydroxy-intercalated montmorillonite

Intercalation of Cr-polyhydroxo cations was based on a study by Pinnavaia et al. [14]. The pillaring solution was prepared by adding dropwise an aqueous sodium carbonate (0.2 M) to an

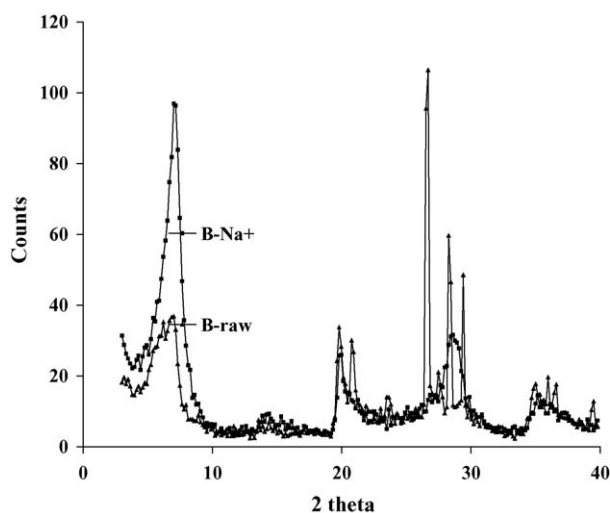


Fig. 1. X-ray diffraction pattern of precursor montmorillonite before and after purification.

aqueous solution of 0.1 M chromium(III) nitrate under vigorous stirring to obtain an OH/Cr ratio of 2. The solution was kept for 96 h at $95\ ^\circ\text{C}$. The pillaring solution was slowly added under vigorous stirring to a 1% (wt.%) montmorillonite solution to a ratio of 20 mmol Cr per gram of clay [14]. The resulting slurry was stirred for 2 h, maintained at room temperature for 24 h, washed by centrifugation until the supernatant was chloride-free as indicated by the AgNO_3 test. The product was dried at $35\ ^\circ\text{C}$ and gently ground in an agate mortar. The material obtained is called Cr-intercalated montmorillonite denoted B–Cr.

2.3. Sorbate

Supranol Yellow 4GL is one of the dyes used in the dyeing industry of the Tlemcen area (Algeria) for colouring silk. It was provided by the Ciba Society (Zurich, Switzerland) and was used as received. Synthetic test dye solution was prepared by dissolving accurately weight amount of dye (1 g/l) in distilled water and subsequently diluted to required concentrations [13].

2.4. Characterization methods

The surface area of all samples was measured by adsorption of nitrogen according to the BET-method on a Micrometrics 2000 apparatus. The samples were outgassed at $180\ ^\circ\text{C}$ during 5 h at vacuum of 10^{-4} Torr. The basal spacing of the samples was measured by X-ray diffraction using a Siemens D5000 instrument, using $\text{Cu K}\alpha$ radiation.

2.5. Equilibrium batch experiments

Adsorption of Supranol Yellow 4GL tests were carried out in a batch process by varying adsorbent dose, adsorbate concentration at a constant agitation speed (200 rpm) for specific period of contact time (range: 5–60 min) in a thermostatic shaker. Influence of pH on the dye adsorptive uptake was studied by adjusting the reaction mixture before shaking to different pH values (2–12) using dilute NaOH or HCl solutions. At equilibrium, the adsorbent and adsorbate were separated by filtration on a membrane filter and for the progress of adsorption, the concentration of the dye in the solution was analyzed spectrophotometrically using a double beam SAFAS spectrophotometer at $\lambda_{\text{max}} = 405\ \text{nm}$. The amount adsorbed (mg/g) was calculated using the following equation:

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

where C_i and C_e are the initial and final concentrations (mg/l) of dye, respectively, m the mass of adsorbent (g) and V is the solution volume (l). Blanks containing no dye were used for each series of experiments as controls. All experiments were performed in duplicate.

3. Results and discussion

As can be seen in Fig. 2, the d_{001} peak of the intercalated-chromium appears at 2θ angles smaller than the original clay (i.e., at $2\theta = 4^\circ$ for the intercalated sample compared to

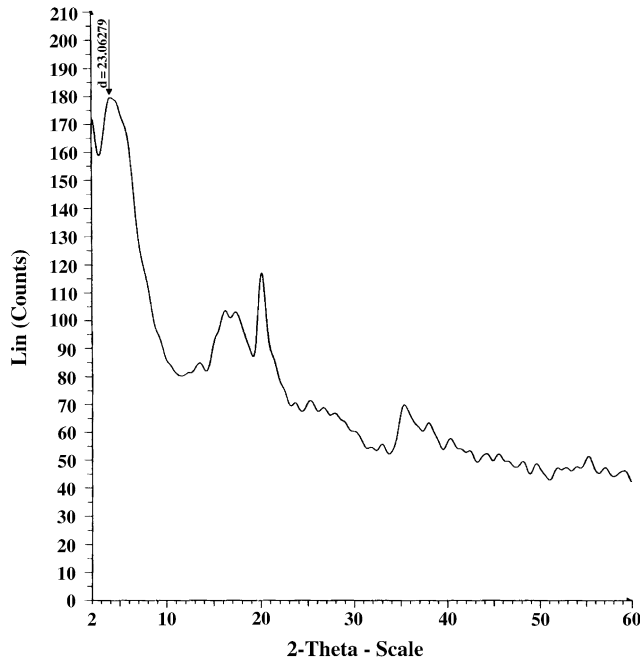


Fig. 2. X-ray diffraction pattern of Cr-intercalated montmorillonite.

$2\theta = 9.08^\circ$ of the original clay in Fig. 1). This result clearly indicates an expansion of interlamellar space from 12.35 to 23.06 Å which occurs in the presence of the metal polyoxocations intercalated montmorillonite; likewise, we observed an increase of the BET surface area from 110 to 317 m²/g (Table 1).

3.1. Effect of contact time

Figs. 3 and 4 show the amount of dye removal at various initial solute concentrations and adsorbent doses by chromium-intercalated montmorillonite. The plots show two distinct phases in which the major portion of adsorption was completed in the first 30 min and the equilibrium was reached. The sorption capacity at equilibrium increases from 3.52 to 44.40 mg/g with an increase in the initial dye concentration from 10 to 70 mg/l and an increase from about 28 to 90 mg/g in the equilibrium sorption capacity with a decrease of adsorbent dose from 1.4 to 0.3 g/l. The phenomenon takes relatively short contact time. The data for the amount of the dye adsorbed per unit mass of B–Cr for a fixed dose of the adsorbent with different concentrations of the dye solution are presented in Table 2 which indicated that an increase in initial dye concentration results in increase dye uptake. From Table 3, it was noted that the amount adsorbed considerable increased with contact time at lower B–Cr doses for a fixed dye concentration. In order to express the mechanism of the adsorption process onto this adsorbent, a simple kinetic

Table 1
Basal spacing and surface area for chromium-intercalated montmorillonite

Samples of clays	Basal spacing (Å)	S _{BET} (m ² /g)
BNa ⁺	11.88	110
Cr–B	23.06	317
Al–B [13]	20.06	229

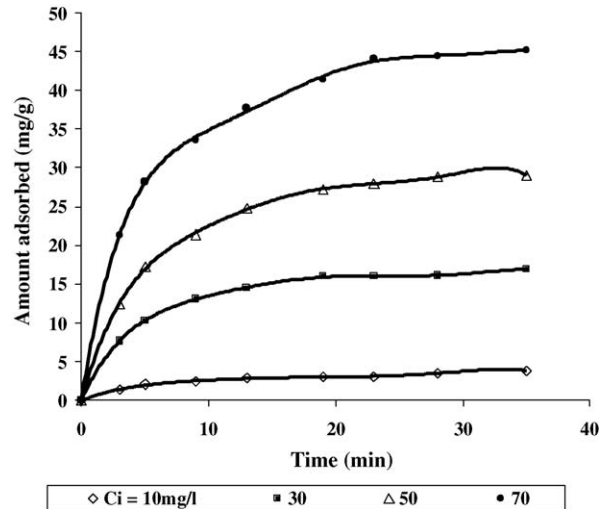


Fig. 3. Effect of contact time on the adsorption of Supranol Yellow 4GL onto Cr(III)-intercalated montmorillonite at various initial concentrations (adsorbent dose w/V = 1.4 g/l, pH 6.3 and T = 20 °C).

analysis of adsorption, which is the pseudo-first-order equation in the following form [15] can be used:

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

where K₁ is the rate constant of pseudo-first-order adsorption (min⁻¹) and q_e is the maximum amount of adsorbate that can be adsorbed in monolayer coverage (mg/g).

On the other hand, a pseudo-second-order equation based on adsorption capacity may be expressed in the following form [16]:

$$t/q_t = 1/K_2 q_{e2}^2 + 1/q_{e2} t \tag{3}$$

where K₂ is the rate constant of pseudo-second-order adsorption (g/(mg min)) and q_{e2} is the amount of dye adsorbed at equilibrium (mg/g).

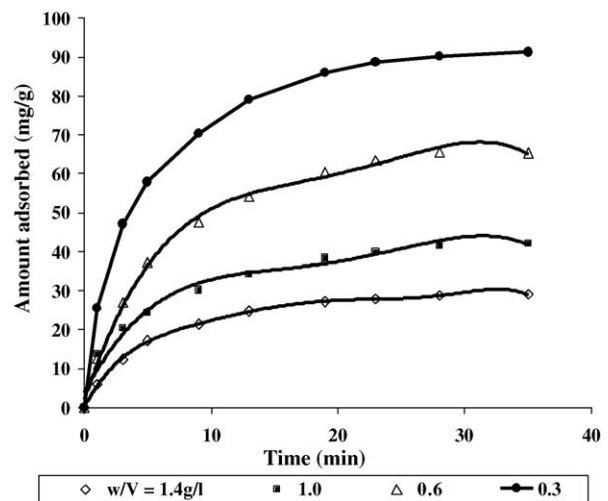


Fig. 4. Effect of contact time on the adsorption of Supranol Yellow 4GL onto Cr(III)-intercalated montmorillonite at various adsorbent doses (C₀ = 50 mg/l, pH 6.2 and T = 20 °C).

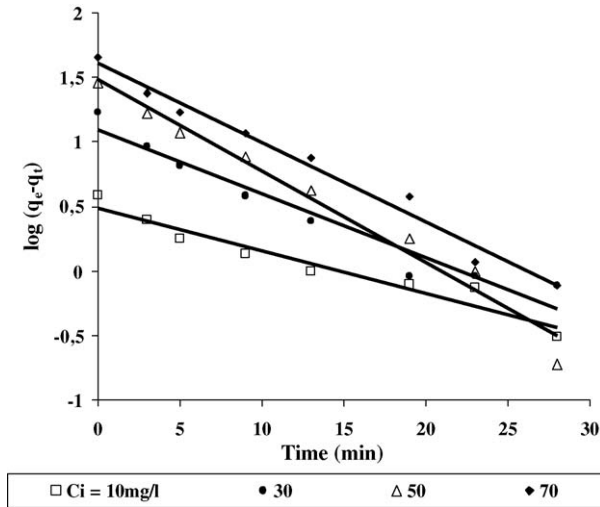


Fig. 5. Test of first-order equation for Supranol Yellow 4GL onto Cr(III)-intercalated montmorillonite at various initial concentrations (adsorbent dose $w/V = 1.4$ g/l, pH 6.3 and $T = 20^\circ\text{C}$).

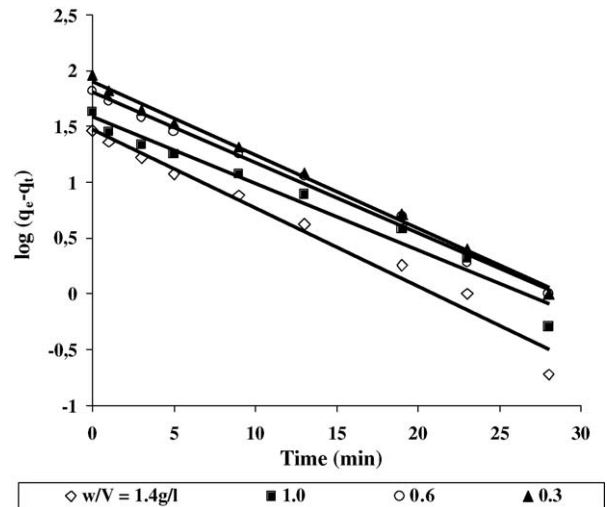


Fig. 6. Test of first-order equation for Supranol Yellow 4GL onto Cr(III)-intercalated montmorillonite at various adsorbent doses.

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. Figs. 5–8 illustrate the fitted results. The rate constants K_1 and K_2 obtained from the plots of Eqs. (2) and (3) are shown in Tables 2 and 3. Figs. 5 and 6 show the linearized form of the pseudo-first-order. It is clear that the plots have high correlation coefficient (R^2 : 0.93–0.98) but the straight line plots of $\log(q_e - q_t)$ against t do not elucidate that kinetics of sorption on B–Cr followed first-order model. The data show a good compliance with the pseudo-second-order equation and the regression coefficients for the linear plots were higher than 0.99 for all the systems in these studies. The sorption of Supranol Yellow 4GL on B–Cr may be described by the pseudo-second-order equation (Figs. 7–8), as the correlation coefficient for the first-order analysis was lower than that for the second-order model. Similar trends were observed for the adsorption of commercial basic blue dye (BB69) and direct red dye (DR227) on activated clay [17] and for the adsorption of Supranol Yellow 4GL and Eri-

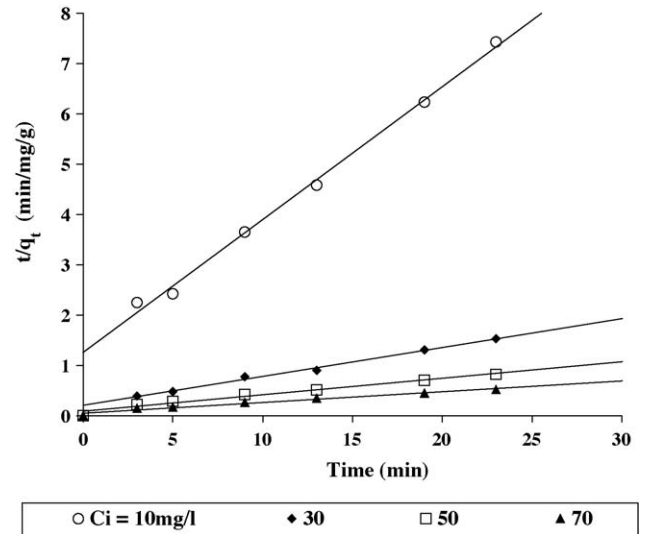


Fig. 7. Test of second-order equation for Supranol Yellow 4GL onto Cr(III)-intercalated montmorillonite at various initial concentrations (adsorbent dose $w/V = 1.4$ g/l, pH 6.3 and $T = 20^\circ\text{C}$).

Table 2
Kinetic parameters vs. initial concentration

C_0 (mg/l)	r_1^2	q_1 (mg/g)	K_1 (min^{-1})	r_2^2	q_2 (mg/g)	K_2 (g/(mg min))	K_i (mg/g/min ^{1/2})	r_3^2
10	0.941	3.07	0.075	0.984	3.792	0.032	0.727	0.968
30	0.946	12.33	0.113	0.998	17.513	0.013	3.751	0.974
50	0.979	30.57	0.163	0.999	30.487	0.006	6.401	0.981
70	0.982	40.77	0.141	0.999	46.948	0.004	9.582	0.963

Table 3
Kinetic parameters vs. adsorbent dose

w/V (g/l)	r_1^2	q_1 (mg/g)	K_1 (min^{-1})	r_2^2	q_2 (mg/g)	K_2 (g/(mg min))	K_i (mg/g/min ^{1/2})	r_3^2
1.4	0.973	30.57	0.163	0.999	33.44	0.0062	6.401	0.981
1	0.990	34.71	0.119	0.995	46.72	0.0053	8.554	0.971
0.6	0.988	62.82	0.142	0.998	76.33	0.0028	14.529	0.983
0.3	0.992	77.26	0.146	0.995	101.01	0.0025	20.017	0.965

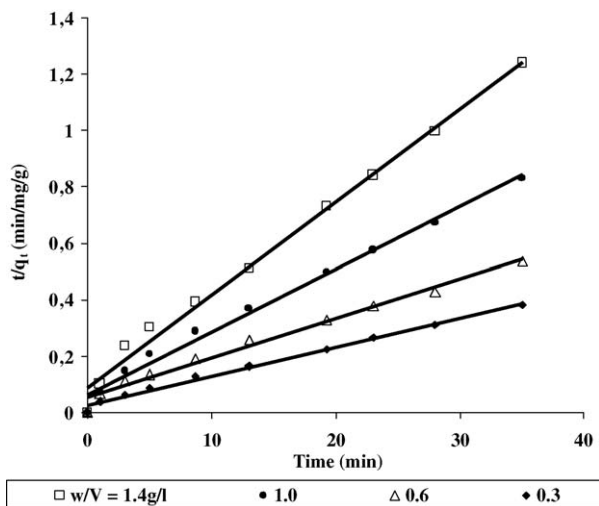


Fig. 8. Test of second-order equation for Supranol Yellow 4GL on Cr(III)-intercalated montmorillonite at various adsorbent doses.

onyl Red RS on polyaluminium hydroxide exchanged bentonite [18].

However, the values of the rate constants (K_2) were found to decrease from 3.2×10^{-2} to 4×10^{-3} g/(mg min) as the initial concentration increased from 10 to 70 mg/l, showing the process to be highly concentration dependent, which is consistent with studies reported by Ho et al. [19,20]. Also the values of K_2 increased from 2.5×10^{-3} to 6.2×10^{-3} g/(mg min) as the adsorbent dose increased from 0.3 to 1.4 g/l. With increasing adsorbent doses, both initial rate and rate constant K_2 increases. This implies that the number of active sites increase on the adsorbent surface as parallel to increasing adsorbent dose.

The relatively rapid process of the present experiments (30 min) is a first indication of a diffusion-controlled process. In order to examine the suitability of intraparticle diffusion in fitting our data, the rate constant for intraparticle diffusion is given by Weber and Morris [21]

$$q_t = K_i t^{1/2} \quad (4)$$

where q_t is the amount adsorbed (mg/g) at time t (min). Figs. 9 and 10 present the amount of colour adsorbed, q_t , versus the square root of time. All the plots have the same general features. The K_i values were obtained from the slope of linear portions of the curves for various dye concentrations and adsorbent dose (Tables 2–3). The results show that increasing initial solute concentration and decreasing dose of adsorbents increased the intraparticle diffusion rate constant. From these figures, it may be observed that the straight lines did not pass through the origin and this further indicates that the intraparticle diffusion is not the only rate controlling step. Poots et al. [22] proposed that during the early stages of adsorption, some boundary layer resistance was involved which decreases as the available external surface area also decreases.

The adsorption of dye Supranol Yellow 4GL on chromium-intercalated montmorillonite is not a first-order reaction. The correlation coefficients, R_2^2 , for the pseudo-second-order kinetic model are greater than the intraparticle diffusion coefficient,

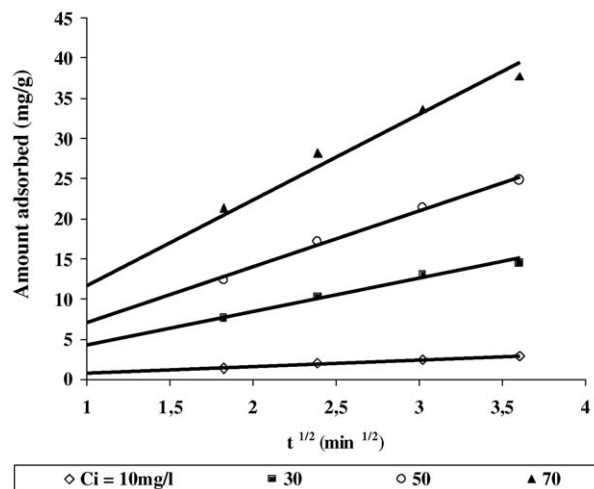


Fig. 9. Amount of dye adsorbed vs. $t^{1/2}$ for intraparticle transport of Supranol Yellow 4GL by Cr(III)-intercalated montmorillonite for various initial concentrations (adsorbent dose $w/V = 1.4$ g/l, pH 6.3 and $T = 20$ °C).

coefficients, suggesting that the rate-limiting step may be chemical sorption.

3.2. Effect of initial concentration

Equilibrium adsorption studies are performed to provide the capacity of the adsorbent. The adsorption equilibrium is established when the concentration of adsorbate in the bulk solution is in dynamic balance with that of the surface. The adsorption isotherm giving the amount adsorbed per gram of adsorbent q_e (mg/g) versus equilibrium concentration C_e (mg/l) show a Langmuir isotherm in Fig. 11. The Langmuir adsorption isotherm [23] has been successfully applied to many other real sorption processes. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. The plot indicates that adsorption increases initially with concentration but then reaches saturation. The monolayer formation for the present system was confirmed by the lin-

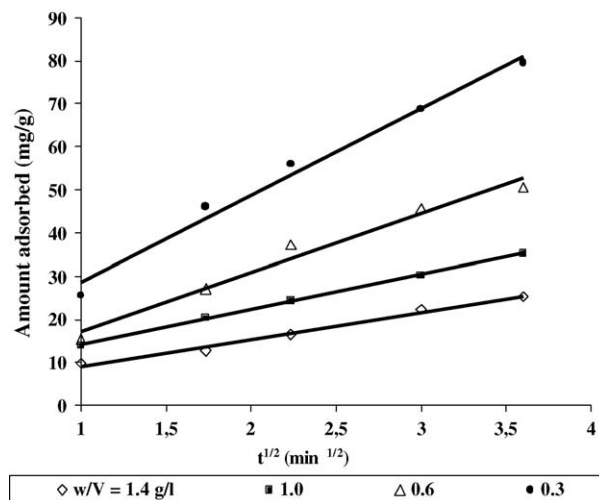


Fig. 10. Amount of dye adsorbed vs. $t^{1/2}$ for intraparticle transport of Supranol Yellow 4GL by Cr(III)-intercalated montmorillonite for various adsorbent doses.

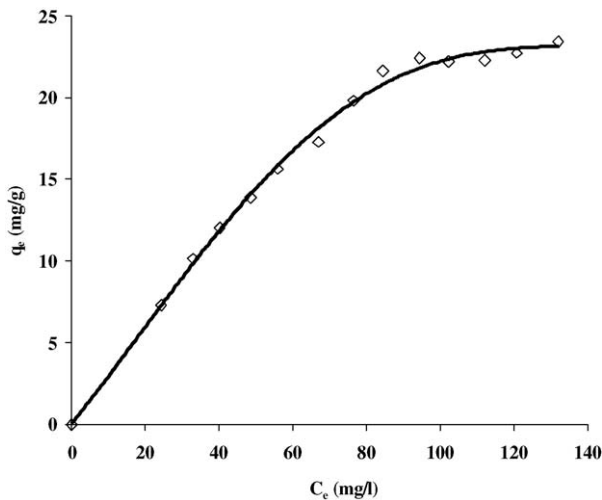


Fig. 11. Adsorption isotherm of Supranol Yellow 4GL onto Cr(III)-intercalated montmorillonite.

ear plot of $1/q_e$ versus $1/C_e$ (Fig. 12) according to the Langmuir isotherm:

$$1/q_e = 1/q_{\max} + 1/b q_{\max} C_e \quad (5)$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/l), q_{\max} (mg/g) and b (l/mg) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and slope of the linear plot of experimental data of $1/q_e$ versus $1/C_e$ (Eq. (5)). Fig. 12 shows the linear plot with a correlation coefficient of 0.9871. The maximum uptake of dye was obtained as $q_{\max} = 58.47$ mg/g and b as 6.220×10^{-3} l/mg. The main characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L which is defined by the following equation [24]:

$$R_L = \frac{1}{1 + b q_{\max} C_0} \quad (6)$$

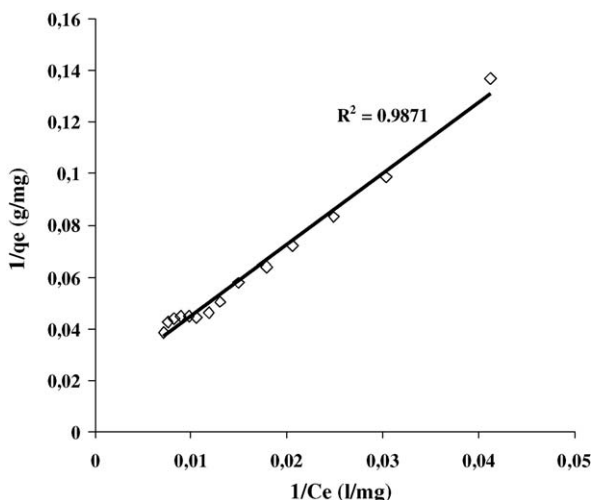


Fig. 12. Langmuir isotherm for Supranol Yellow 4GL adsorption onto Cr(III)-intercalated montmorillonite.

where C_0 is the highest initial dye concentration (mg/l) and b is the same as above. The value of R_L indicates the nature of the adsorption process to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

In this study, the low value of R_L ($R_L = 0.0224$) indicates a favourable adsorption. Hence the q_{\max} , b and R_L values indicate that this material exhibits a good potential for the adsorption of Supranol Yellow 4 GL.

3.3. Effect of initial pH

The removal of dye from aqueous solution by adsorption is related to the pH of the solution which affects the surface charge and the degree of ionization and species of adsorbate. The clay exchanged with sodium (BNa) does not induce a significant removal except for low pH [13]. The removal of dye should therefore require a previous protonation followed by cation exchange. The dye exists in anionic form, so no adsorption takes place on BNa both have negative charge (electrostatic repulsion).

The effect of pH on the adsorption was studied by varying the initial solution pH under constant process parameters. The results are shown in Fig. 13. The extent of sorption decreased from 98.04 to 3.74 mg/g when the pH of the system was varied from 2.8 to 12.1 at 100 mg/l initial dye concentration. The dye uptake was higher in acidic pH range. However, within the range of pH 6–8 it almost remained constant. When BNa^+ were treated with intercalation solution (Cr–OH), the exchangeable Na^+ was replaced by Cr–OH species. The Cr–OH solution contained trimeric species, $\text{Cr}_3(\text{OH})_4^{5+}$, as the principal ones, followed by tetra- $\text{Cr}_4(\text{OH})_6^{6+}$, mono- $\text{Cr}(\text{H}_2\text{O})^{3+}$ and dimer- $\text{Cr}_2(\text{OH})_2^{4+}$ species [25]. On increasing the concentration of the hydrogen ion in the dye solution, the surface OH⁻ ions would get neutralized by protonation which facilitates the diffusion of dye molecules in the vicinity of the adsorbent. On the other hand, a diminished adsorption at higher pH may be due to the abundance of OH⁻ ions and consequently ionic repulsion between the negatively charged surface and the anionic dye

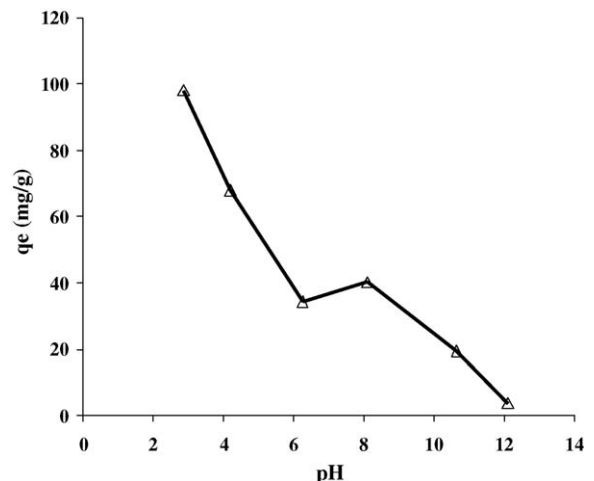


Fig. 13. Effect of pH on the adsorption of Supranol Yellow 4GL onto Cr(III)-intercalated montmorillonite.

molecules [26]. At a low pH range, the positive charge density increases resulting an enhancement of the adsorption of the anionic dye Supranol Yellow 4GL. Similar descriptions have been reported by our previous work, for the sorption of Supranol Yellow 4GL on aluminium-pillared clay. As suggested, the uptake dye is overcoming the clay exchange capacity [13]. The dye is adsorbed by outer surface of pillars and the interlayer exchange cations. Chromium-intercalated montmorillonite sorbed higher quantities of dye than the aluminium-pillared montmorillonite and their precursors at the same pH and temperature.

3.4. Effect of temperature

The temperature range used in this study varied from 283 to 313 K at 100 mg/l dye solution concentration having a pH 6.38. The sorption capacity decreased from 46.30 to 11.34 mg/g indicating that the temperature unfavours the adsorption of dye.

The thermodynamic parameters of the adsorption were determined using the following equations [27]:

$$\log k_d = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (8)$$

$$K_d = \frac{q_e}{C_e} \quad (9)$$

where K_d is the distribution coefficient and is equal to the ratio of the amount adsorbed (q_e in mg/g) to the equilibrium concentration (C_e in mg/l). R is the gas constant.

The values of ΔH° and ΔS° were obtained from the slope and intercept of the linear plot of $\log K$ versus $1/T$ (Fig. 14). The negative values of ΔG° (Table 4) indicate that the adsorption of Supranol Yellow 4GL on chromium-intercalated montmorillonite is spontaneous. The negative value of ΔH° confirmed the exothermic nature of the process. The positive value of ΔS° shows increased randomness at the solid–solution interface during the adsorption of dye onto chromium-intercalated montmorillonite.

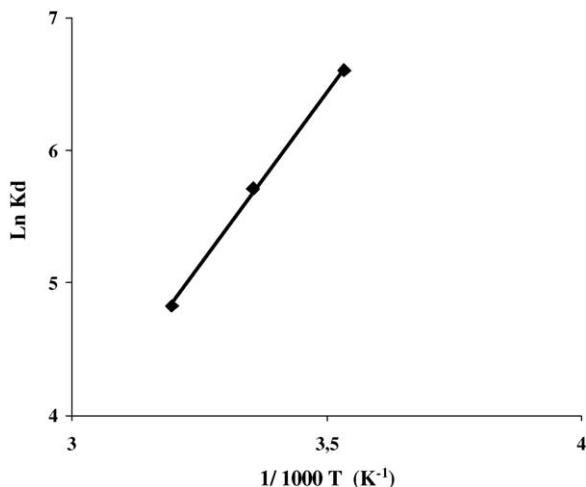


Fig. 14. Effect of temperature on the adsorption of Supranol Yellow 4GL onto Cr(III)-intercalated montmorillonite.

Table 4
Thermodynamic parameters

Temperature (K)	K_d (cm ³ /g)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
283	735.622	-14.43	-	-
298	302.444	-13.275	-43.560	98.891
313	124.721	-12.30	-	-

4. Conclusion

This study shows that Cr(III)-intercalated montmorillonite is efficient for removing acid Supranol Yellow 4GL from synthetic aqueous solutions. The equilibrium adsorption is practically achieved in 30 min. The adsorption process is found to be second-order with intraparticle diffusion. The latter is not the only rate limiting step. Almost total removal was observed at pH 2.8. Langmuir adsorption model fitted well the isothermal data. The sorption capacity variation with temperature revealed an exothermic process of dye on Cr(III)-intercalated montmorillonite.

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