

Sorption study of an acid dye from an aqueous solutions using modified clays

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Abstract

The removal of the pollutant Supranol Yellow 4GL (S.Y.4GL) was studied by using different clays: clay exchanged with sodium (BNa⁺) and hydroxyaluminic polycation pillared clays in the presence or absence of non-ionic surfactant. While decomposing the surfactant at 500 °C, the surface of the clay changed significantly. The study of the behaviour of the three clays with respect to coloring solutions, allowed to determine the equilibrium time and the rate-determining step of the dye S.Y.4GL adsorption. Two simplified kinetic models, were tested to investigate the adsorption mechanisms in terms of pseudo-first order and pseudo-second order equations. Besides, the adsorption capacity data were fitted to Langmuir and Freundlich equations as well. A better fixation was obtained with an acidic pH. The effect of temperature on the adsorption of dye has been also studied and the thermodynamic parameters ΔG° , ΔH° and ΔS° were determined.

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1. Introduction

Bentonite is a clay mainly composed of montmorillonite known as a 2/1 type aluminosilicate. Its crystalline structure presents an alumina octahedral between two tetrahedral layers of silica. The isomorphous substitution of Al³⁺ for Si⁴⁺ in the tetrahedral layer and Mg²⁺ for Al³⁺ in the octahedral layer results in a net negative surface charge on the clay. This charge imbalance is offset by exchangeable cations, denominated exchange cations (typically Na⁺ and Ca²⁺) to compensate the negative charges at the surface. The parallel layers in these structures are held together by weak electrostatic forces and can expand by penetration of polar species between the clay layers [1]. Among of the important clay

derivatives, are the pillared clays obtained from the insertion and grafting of metal oxidic species to the clay surface. The pores opening of the interlayers of pillared clays depend on the nature, size and shape of intercalated species and are generally much larger than typical zeolites cages. Many different pillaring polyoxocations (Al, Ni, Zr, Fe, Cr, Mg, Si, Bi, Be, B, Nb, Ta, Mo, Ti and Cu) have been used and reported in the literature [2–6]. However, only the Al-polyoxocation, i.e., [Al₁₃O₄(OH)₂₄(H₂O)₁₂] or Al₁₃ has been well defined for its chemical composition, structure and charge [7]. Having a high surface area and porosity, these microporous materials are commonly used as catalysts [8] and selective adsorbents [9].

Recent research works have shown that chemically modified clay minerals represent an innovative and promising class of sorbent materials [10–14]. In replacing the natural inorganic exchange cations by surfactants, clay surfaces change from hydrophilic to hydrophobic. Organoclays

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have applications as sorbents for a great variety of organic pollutants, such as phenol [15].

The combination of these two kinds of materials to form a new type of adsorbent may produce somewhat optimal properties. The key element is the incorporation of surfactant as templates. Some authors tried to modify the adsorptive properties by intercalating organo-inorganic moieties [16] in inter-layer space montmorillonite. The resulting materials exhibit improved adsorption capacities towards hydrophobic organics. In addition, the presence of surfactant in the pillaring solution seems to yield pillared products with more regular pillar distribution. Removal of the templates produces new matrices characterised by high specific surface area, textural mesoporosity, high chemical stability and catalytic cracking activity greater than the conventional alumina pillared clay [17].

Adsorption techniques for color removal are becoming popular and many adsorbents have recently been tested such as silica [18], hardwood sawdust [19], fly ash [20], chrome sludge [21], waste red mud [22] and biogas waste slurry [23]. The use of bentonite in the treatment of effluents containing dyes has been investigated by many research workers in the field showing the interest of organophilic clays as an alternative [24]. Clays in the presence of aluminum polymers removed 72–88% of industrial dyes [25].

The present work compares three different types of clays; clay exchanged with sodium (BNa^+) and hydroxyaluminic polycations pillared in the presence or absence of non-ionic surfactant as template for treating effluents containing acid dye Supranol Yellow 4GL. This latter is an industrial dye used in the tint of chemical fibres.

2. Experimental

2.1. Starting materials

The bentonite used in this study was supplied by ENOF (an Algerian manufacture specialised in the production of non-ferric products and useful substances). It has been received without any treatment. The bentonite was purified in laboratory to remove carbonates, iron hydroxide and organic matter. The bentonite was dispersed in distilled water and the clay fraction ($<2\ \mu\text{m}$) was recovered by sedimentation. The solid phase was then saturated with sodium ions by stirring in a 1 M sodium chloride solution, three times. The saturation was achieved and the solid was washed with distilled water to remove excess salt. The material obtained is called sodium-exchanged bentonite or BNa^+ . Its structural formula is $(\text{Si}_{7.41}\text{Al}_{0.59})^{\text{IV}}(\text{Al}_{2.82}\text{Fe}_{0.24}\text{Mg}_{0.48})^{\text{VI}}(\text{Ca}_{0.08}\text{Na}_{0.76}\text{K}_{0.1})\text{O}_{20}(\text{OH})_2$. The physical properties are given in Table 1.

The non-ionic surfactant agent used is an alkylated polyethylene oxide surfactant $\text{C}_{9-11}-\text{H}_{19-23}\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$. It is a non-ionic surfactant provided by ENAD (an Algerian detergent manufacture).

2.2. Preparation of hydroxyaluminic polycation pillared clays

Al-pillared clay was prepared by intercalating the sodium clay with hydroxy-aluminum oligomeric cations. The pillaring solution was prepared by adding slowly 0.2 M NaOH solution to 0.1 M AlCl_3 solution under vigorous stirring, until the OH/Al ratio reaches the value 2. To accelerate the formation of Al_{13} , the solution was kept for 7 days at room temperature. The pillaring solution was slowly added under vigorous stirring to a 1% weight bentonite solution to a ratio of 5 mmol Al/g bentonite [26]. The mixture was allowed to react at room temperature for 48 h before washed by centrifugation, until chloride-free as indicated by the AgNO_3 test. The product was dried at room temperature and gently ground in an agate mortar and calcined at $500\ ^\circ\text{C}$. This material obtained is called Al-pillared bentonite denoted BP.

The surfactant-hydroxy-aluminum modified clay was prepared in similar way, by first adding know quantity of surfactant (Empilan) to aluminum pillaring solution. The ratio surfactant/clay was fixed at 0.36 g of surfactant per gram of clay. The reaction mixture was maintained at room temperature for 48 h and the product was separated by centrifugation, washed and dried at room temperature. The final material was then calcined at $500\ ^\circ\text{C}$. The corresponding sample is surfactant-Al-modified bentonite denoted BPS. Table 1 presents the characteristics of BP and BPS obtained by XRD, BET specific surface area (S_{BET}) and CEC measurements.

2.3. Sorbate

Supranol Yellow 4GL 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.

2.4. Characterization methods

The cation exchange capacity of bentonite was determined with methylene-blue and conductimetric methods. The adsorption of methylene blue dye on bentonite in solution, is used to determine either their cation-exchange capacities (CEC) or their total surface area (S_{total}). 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 colorimetrically

Table 1
Basal spacing and surface area for sorbents used

Samples of clays	Basal spacing (\AA)	S_{BET} (m^2/g)
BNa^+	11.88	110.07
BP	18.592	220.67
BPS	18.43	348.23

at $\lambda_{\max} = 665$ nm. The amounts of adsorbed solution at flocculation point, were referred to 100 g of clay. These values allowed the determination of both CEC and surface area.

The conductometric method was based on changed 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 [27,28].

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 250 °C during 5 h at vacuum of 10^{-4} Torr. The basal spacing of the samples was measured by X-ray diffraction (XRD) by means Siemens D5000 instrument, using Cu $K\alpha$ radiation.

2.5. Adsorption studies

Adsorption on all three sorbents prepared, was determined using the batch method. A fixed amount of the sorbent 0.1 g was added to 100 ml of dye solution of required concentration 100 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 analyzed colorimetrically using a spectrophotometer (SAFAS UV mc^2) by measuring absorbance at $\lambda_{\max} = 405$ nm.

Isothermal studies were conducted by adding 0.1 g of the clay to 100 ml of dye solution of varying concentration. Effect of sorbent dosage was studied by sorbent weight from 0.1 to 0.5 g at fixed dye concentration. The pH of all solutions in contact with clays, was adjusted at pH 4 by adding of 0.1 N hydrochloric acid.

The percentage removal ($P\%$) of dye and amount adsorbed (q_e) were calculated using the following relationships:

$$P\% = 100(C_i - C_e)/C_i \quad (1)$$

$$q_e = (C_i - C_e)V/m \quad (2)$$

where C_i is the initial concentration of the dye solution (mg/l), C_e the concentration of the dye solution at the adsorption equilibrium (mg/l), V the volume of the dye solution (ml) and m the weight of the clay (mg).

3. Results and discussion

Table 1 summarizes the d_{001} reflexion and surface area data for all the samples analyzed. From Table 1, it is clear that the increase of basal spacing and surface area occur in the presence of the metal polyoxocations-surfactant modi-

fied bentonites. These results are similar to those previously reported for pillared hydroxy-Al-montmorillonite [26]. The pillared clays have similar basal spacing BP ($d_{001} = 18.59 \text{ \AA}$) and BPS ($d_{001} = 18.43 \text{ \AA}$), indicating that non-ionic surfactant does not cause significant change in the basal spacing. Nitrogen adsorption measurements carried out on calcined samples revealed a surface area for BPS ($S = 384.23 \text{ m}^2/\text{g}$), higher than that for BP ($S = 220 \text{ m}^2/\text{g}$).

The initial surface (S_{total}) of bentonite evaluated by methylene blue method was $792 \text{ m}^2/\text{g}$ with a cation exchange capacity ($\text{CEC} = 101.25 \text{ meq}/100 \text{ g}$ of clay). Whilst the conductimetric method gives a $\text{CEC} = 99 \text{ meq}/100 \text{ g}$ of clay. The incorporation of a non-ionic surfactant during the pillaring process increased significantly the surface area. Pinnaivaia et al. [29] find that the pillar population density inside the galleries is not significantly affected by the co-adsorption of the non-ionic surfactant. However, the removal of the surfactant by calcination at 500 °C improve the formation of mesopores by substantial delamination of the clay [29].

3.1. Effect of contact time

The adsorption data of Supranol Yellow 4GI versus contact time is presented in Fig. 1. The sorbate concentrations in solution were determined at different times from initial solutions of 100 mg/l and a sorbent dosage of (1 g/l). All the experiments conducted here were at pH 4. The plots representing adsorption of dye on BNa^+ and BP, visualise three distinct phases: the first phase indicates the instantaneous sorption of the dye within 10 min of contact time, the second one shows a gradual equilibrium and the third one indicates the final equilibrium. The uptake of dye on BNa^+ reaches equilibrium

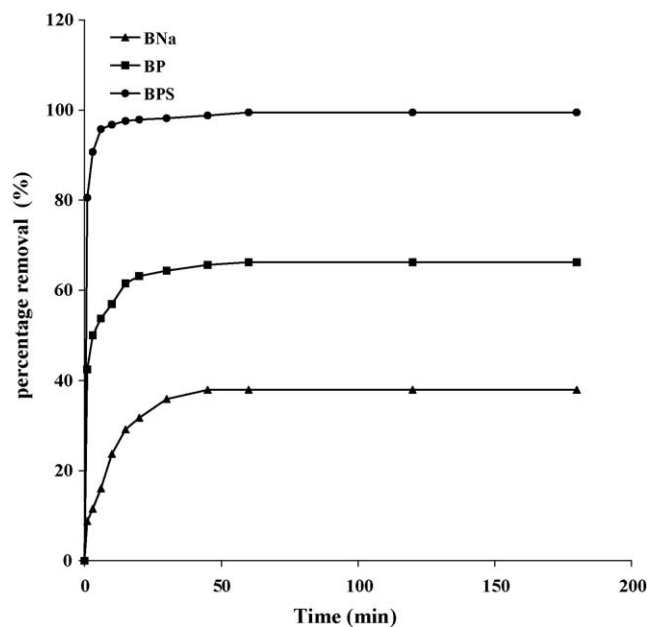


Fig. 1. Effect of contact time on dye uptake ($C_0 = 100 \text{ mg/l}$, sorbent dosage 1 g/l, $T = 293 \text{ K}$ and pH 4).

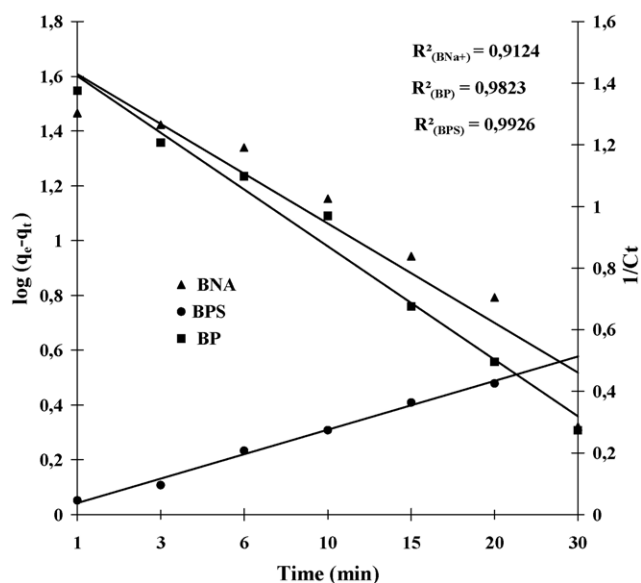


Fig. 2. Pseudo-first order and pseudo-second order plots for dye adsorption.

in 45 min with 37% of dye removal, while on BP, it reaches equilibrium in 30 min with 60% of dye removal. In the case of BPS, the uptake was very rapid and it attained equilibrium at 15 min with 99% removal.

In order to study the rate-determining step for the adsorption of Supranol Yellow 4GL on BNa^+ , BP and BPS, two kinetic models were tested to fit experimental data obtained from bath dye removal experiments: the pseudo-first order kinetic model proposed by Lagergreen [30] and used successfully by Trivedi and Patel [31]. The pseudo-second order kinetic model described by Ho and McKay [32] and tested by Kacha et al. [33]

The pseudo-first order model assumes that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and the amount of solid uptake with time

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \quad (3)$$

where q_e and q_t are the amounts of dye adsorbed per unit mass of the adsorbent (mg/g) at equilibrium and time t , respectively and k_1 is the rate constant of adsorption (min^{-1}).

The pseudo-second order model is based on adsorption equilibrium capacity

$$1/C_t = 1/C_i + k_2t \quad (4)$$

where C_i is the initial concentration (mg/l), C_t the concentration at time t (mg/l) and k_2 in the rate constant of the pseudo-second order equation ($\text{g mg}^{-1} \text{min}^{-1}$).

Both $\log(q_e - q_t)$ and $1/C_t$ values were calculated from the kinetic data of Fig. 1 and plotted against time as Fig. 2. The straight line plots indicate that the adsorption process of Supranol Yellow 4GL on BNa^+ and BP is a first kinetic order. The values of rate constant were calculated from the slope of the plots, as 0.078 and 0.079 min^{-1} for BNa^+ and BP

respectively. The higher rate indicate the higher affinity for this dye, consistent with its higher adsorption. Similar trends were observed in the adsorption of direct red 12 [34].

In case of BPS, the kinetic data do not fit the first order equation. Good correlation coefficients were obtained by fitting the experimental data to Eq. (4), indicating that the adsorption process on BPS is pseudo-second order as shown in Fig. 2. This difference of the efficiency removal is a probable consequence of different surface properties and dye structure. The adsorption of Supranol Yellow 4GL may take place by cation exchange [25], discussed later on under pH effect. Similar behaviours have been observed by other workers in the field [34,35]. The sorption of Supranol Yellow 4GL on BP proceeds also by cations exchange mechanisms in residual sites of the clay and furthermore in aluminum pillars. In this process, the color diffuses easily into the porous structure of the adsorbent. The presence of pillars imparts ion-exchange properties. The highest removal of dye by BPS indicates that this latter is more hydrophobic in nature than BNa^+ and BP and the instantaneous adsorption is probably due to the involvement of mesoporosity structure leading to a better diffusion of dye molecule. This process takes place in two phase: firstly, the dye molecules should orientated themselves to find a suitable position in the interlamellar space of adsorbent and secondly the polymerization of color is provided by hydrophobic interaction [36]. The sorption of the dye in excess of BPS is may be attributed to cation exchange and to the aggregation of dye of molecules onto the intercalated at the interlamellar space. Thus this reaction may be due to complexation between dye and the Al-pillars on one hand and to dye–dye interactions on the other hand.

3.2. Effect of sorbent dosage

The effect of sorbent dosage on the percentage of dye adsorbed was studied and presented in Table 2. The results indicate the adsorption percentage decrease with increasing amount of BNa^+ . This suggest that dye do not show evident interaction of excess BNa^+ in suspension. In this manner, the interaction of protonated color on the suspension of BNa^+ presents a complex behaviour, due to hydrophilic sorbents and aggregation of dye molecules. A maximum removal of 34% is obtained at a dosage of 1 g/l. The increasing percentage removal of Supranol Yellow 4GL (see Table 2) is found to be negligible after dosage 3 g/l for pillared sorbents (BP and BPS). A dosage 1 g/l is then used for all further studies.

Table 2
Effect of sorbent dosage on dye adsorption

Sorbent dosage (g/l)	BNa^+ (%)	BP (%)	BPS (%)
1	37.8	69.3	98.5
2	31.7	69.9	99.7
3	25.4	71.8	100
4	12.9	71.86	100
5	12.9	71.86	100

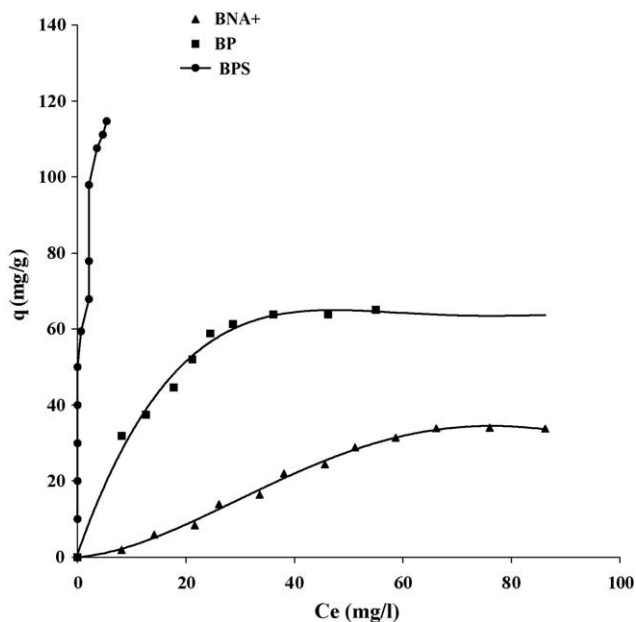


Fig. 3. Adsorption isotherms of dye removal on different sorbents used at 293 K and pH 4.

3.3. Effect of initial concentration

In order to appreciate the interaction between the sorbate and sorbents, we present the isotherm q_e versus C_e and the linear fittings to Freundlich and Langmuir equations given respectively by linear forms

$$\log q_e = \log k_f + n \log C_e \quad (5)$$

$$C_e/q_e = 1/(q_o b) + (1/q_o)C_e \quad (6)$$

where q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/g); C_e the equilibrium concentration of dye (mg/l); k_f the Freundlich constant which measures the adsorption capacity; n is an indicator of adsorption effectiveness; q_o and b are the Langmuir constants which are the measurements of monolayer (maximum) adsorption capacity and energy of adsorption, respectively [37].

In Fig. 3, the sorption isotherm shows that the minimum amount of Supranol Yellow 4GL is sorbed by BNa^+ . Greater quantities of dye are sorbed by BP and BPS, respectively. In the concentration range 10–100 mg/l, BP and BPS remove 66 and 99%, respectively. Indeed, BPS has not yet reached its saturation. This may be assumed to a monolayer formation in the active sites on the surface, and furthermore adsorption on sorbed dye as primary monolayer, are supposed to be new adsorption sites. The degree of isotherm linearity can be assessed from the slopes of the isotherm plots in Fig. 4, and the corresponding Freundlich n values are given in Table 3. The sorption of dye on BNa^+ is linear, while those of BP and BPS are non-linear. The adsorption capacity of BNa^+ is less than that of BP because of three reasons: (a) their different hydrophobicities, (b) the surface of natural clay is not high and (c) the adsorption on BP occurs essentially on the inter-

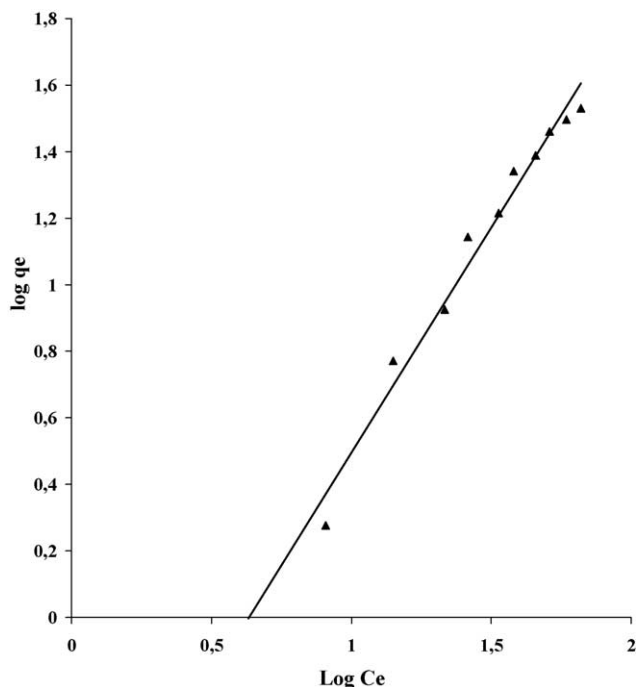


Fig. 4. Freundlich isotherm for BNa^+ .

lamellar pillars. The non-linear isotherm and high sorption capacity of BP and BPS depend mainly on the micropore structure and the surface area.

There are clear differences between the sorption of dye on pillared clays because they present difference textures. The regression coefficients are high, indicating that the Langmuir model is able to describe the experimental isotherms (Figs. 5 and 6), and that the adsorption occurs in the inter-layer pores. The adsorption behaviour of dye is reflected by Langmuir constant and the monolayer capacity values. BPS has a high affinity for removal dye. The non-linear on BNa^+ however, do not produce good fit to the experimental data and results are therefore not given.

3.4. Effect of initial pH

The experimental results show that the adsorption of acidic dye increases with the decrease in pH values (Fig. 7). The pK_a value 6.4 is estimated on the basis of pH data for diluted dye solutions. The extent of solution decreased from 25.44 to 7.59 mg/g for BNa^+ ; 51.44 to 12.38 mg/g for BP and 98.50 to 20 mg/g for BPS.

For $\text{pH} \geq 6$, BNa^+ does not induce a significant removal. The dye exists in anionic form, so no adsorption takes place

Table 3
Langmuir and Freundlich parameters

Samples	K_f	n	R^2	q_e (mg/g)	b (mg^{-1})	R^2
BNa^+	0.14	1.34	0.97	–	–	–
BP	14.26	0.40	0.90	63.93	0.2	0.96
BPS	66.05	0.32	0.79	111.11	3.9	0.99

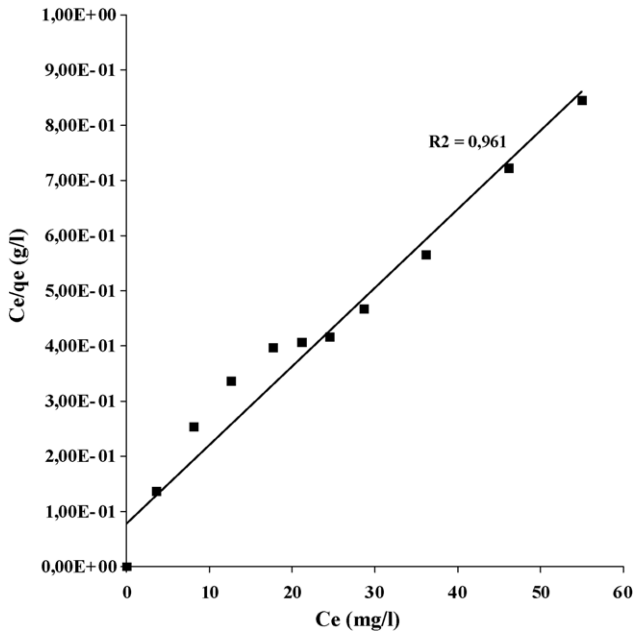


Fig. 5. Langmuir isotherm for BP.

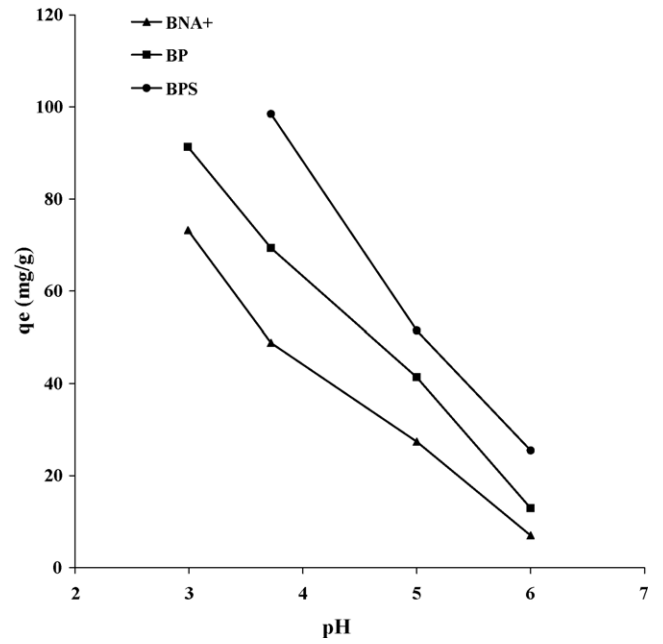


Fig. 7. Effect of pH on dye removal.

on BNa^+ , as both have negative charge (electrostatic repulsion). At pH 4, the sorption on BNa^+ is slightly enhanced by protonation of dye or the positively charged surface at lower pH [38]. In acidic pH, both the dye and surface dissociate [35]. In this case, the mechanism may be assumed by ionic exchange [33].

On BP and BPS, the dye is adsorbed by the outer surface of pillars and the interlayer exchange cations, as the higher amounts adsorbed on BPS and BP overcoming the clay exchange capacity. The dye adsorbed on the BPS material with

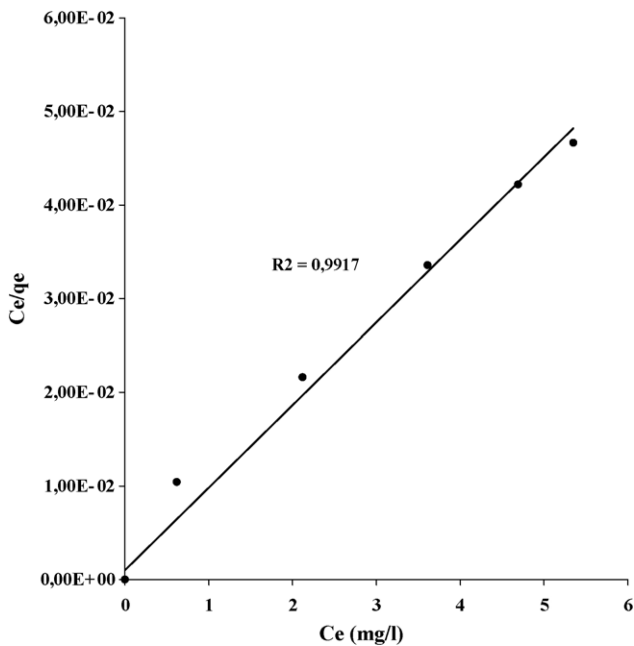


Fig. 6. Langmuir isotherm fitting for BPS.

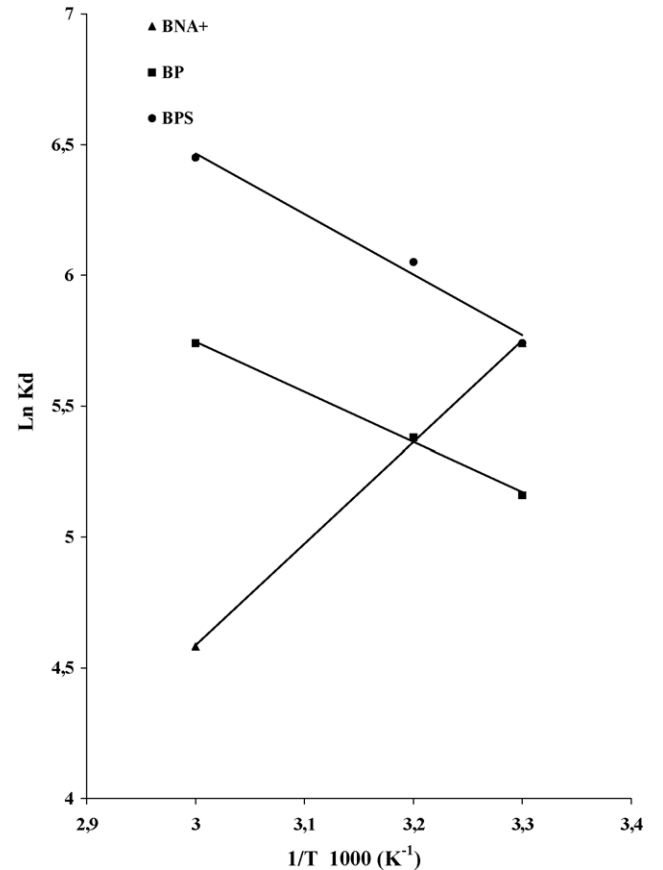


Fig. 8. Thermodynamic parameters of dye removal ($C_0 = 100$ mg/l, sorbent dosage 1 g/l, and pH 4).

Table 4
Thermodynamic parameters of dye removal

	ΔG° (kJ/mol)				
	ΔH° (kJ/mol)	ΔS° (J/mol)	303 K	313 K	323 K
BNa	-32.32	-5.88	-14.47	-14.01	-12.30
BP	+15.92	+9.55	-13.00	-14.01	-14.42
BPS	+19.25	+11.15	-14.47	-14.75	-17.33

a high affinity, in the pH range used. The charge developed by the new matrix becomes an exchange site for this anionic dye whatever its kind in solution (anion, cation or molecule). The surface of pillars varies as function of H^+ or OH^- , since the molecule dye depend upon the degree of ionisation. As a result, the incoming like 4GL coordinates to the forming sites.

3.5. Effect of temperature

The temperature range used in this study is 30–50 °C. The adsorption capacity of Supranol Yellow 4GL on BP and BPS increase with increasing temperature, but that on BNa decreases. Such discrepancies may be due to different adsorbents. Thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) are determined using the following equations [39]:

$$K_d = q_e / C_e \quad (7)$$

$$\Delta G = -RT \ln K_d \quad (8)$$

$$\ln K_d = (\Delta S^\circ / R) - (\Delta H^\circ / R) / T \quad (9)$$

The results presented in Fig. 8 and Table 4 show that the values of ΔG° are negative, indicating that the adsorption process is spontaneous for the dye with a high affinity on BPS. The standard enthalpy change (ΔH°) for the adsorption on BP and BPS is positive indicating that the process is endothermic in nature. The positive values of ΔS° show increased disorders at the solid–solution interface during the adsorption of dye [39].

4. Conclusion

Polymeric Al species with non-ionic surfactant (Emplan) have been used as pillaring species to modify the montmorillonite for water treatment. The study results demonstrate that the increase in basal spacing and surface area occur in the presence of the metalpolymer and surfactant montmorillonite. Al-pillared and Al modified clays display a high anionic dye Supranol Yellow 4GL adsorption capacity with respect to the starting montmorillonite BNa^+ . Thus the adsorption capacity of the modified clay materials could be investigated for other contaminants (organic matter and pesticides).

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