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Adsorption of Direct Red 2 on bentonite modified by cetyltrimethylammonium bromide

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Abstract

One kind of adsorbents with high adsorption capacity of direct dye was prepared by exchanging the organic cations as quaternary ammonium for sodium (Na^+) on the layer surface of clay. In this study, the adsorption of Benzopurpurin 4B (Direct Red 2) by cetyltrimethylammonium bromide–bentonite (CTAB–bentonite) has been examined in order to measure the ability of this mineral to remove colored textile dyes from wastewater. XRD data showed that the interlayer spacing (d_{001}) of bentonite was increased from 12 to 19 Å. The surface modification of CTAB–bentonite was examined using the FTIR technique.

The batch sorption model, based on the assumption of a pseudo-second order mechanism, has been developed to predict the rate constant of sorption and the equilibrium capacity with the effect of initial dye concentration, and temperature. The equilibrium time was reached within 40 min. The rates of sorption were found to conform to pseudo-second order kinetics with good correlation with regard to intra-particle diffusion rate. The adsorption capacity increased largely with increasing initial dye concentration and temperature. The related apparent activation energy was also evaluated and discussed. The adsorption capacity has been increased from 109.89 to 153.84 mg/g with increasing temperature from 20 to 60 °C.

Keywords: Isotherm; Kinetics; Benzopurpurin 4B; Organophilic clay; Pseudo-second order sorption kinetics; Thermodynamic

1. Introduction

Decolourising of textile and dye-manufacturing wastewater is currently a major problem for environmental managers. The coloured dye effluents are considered to be highly toxic to the aquatic biota and affect the symbiotic process by disturbing the natural equilibrium through reducing photosynthetic activity and primary production due to the colouration of the water in streams. Rao et al. [1] observed that the toxic nature of dye effluents cause death of soil microorganisms which may effect agriculture productivity. Azo group of dyes (monoazo, diazo, triazo and polyazo) are considered to be the largest chemical groups of dyes presently in existence (around 26,000 dyes). Various experiments conducted on animals revealed the potential of azo compounds to cause cancer and reported to be carcinogens for human being also [2,3]. Direct azo dyes, in particular, cause environmental concern due to their widespread use, their degradation products, such as toxic aromatic amines, and their low removal rate during aerobic waste treatment. Adsorption by solids is of great significant in connection with environmental and human health safety [4]. The most widely used adsorbent for industrial applications is activated carbon [5–7]. However, activated carbon is expensive and the higher the quality the greater the cost. Therefore, there is a need to carry out to produce relatively cheap adsorbents that can be applied to water pollution control. A wide variety of low cost materials, such as clay minerals [8], bagasse fly ash [9], wood [10], maize cob [11] and peat [12] are being evaluated as viable substitutes for activated carbon to remove dyes from coloured effluents. However, as the adsorption capacities of the above adsorbents are not large, new adsorbents are still under development. Adsorption and desorption of organic molecules in the clays is primarily controlled by the chemical properties of the molecules and surface properties of the clay. The 2:1 layer silicates are important constituents of soil to prepare organoclays for dyes sorption. Bentonite is substituted in the octahedral sheet results in a net negative charge on the clay surfaces. The charge imbalance is offset by the exchangeable cations [13]. In aqueous phase, water molecules are intercalated into the interlamellar space of bentonite, leading

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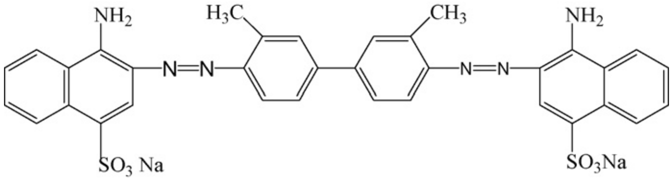

Scheme 1. A planar view of the chemical structure of Benzopurpurin 4B.

to an expansion of the clays. The dissolved organic compound can thus diffuse into the interlamellar space of bentonite and intercalated. However, by intercalation of long chain cationic surfactants, such as quaternary ammonium salts, into the interlayer space, the natural clay surface properties can undergo conversion of hydrophilic to hydrophobic characteristics, resulting in modified clays having high adsorptive capacities. Such organophilic clays have various applications [14], and also act as adsorbents for a great variety of organic pollutants [15–17]. There is little report on the adsorption of dyes onto organophilic clays. To assess the potential of the selected adsorbent potential, Direct Red 2, belonging to direct application class and diazo chemical class was employed as a model substrate in the present work. The use of direct dyes has been continuously increased in the textile industry and finishing processes since the discovery of synthetic fibers. The direct dyes which are chemically related to fibers deposit without the assistance of other chemicals products. They are water soluble and show the functional groups which can form a covalent interaction with the functional groups of the fibers. These dyes can be applied to most synthetic fibers using simple exhaustion techniques. The fibers of wool and silk are particularly well thus adapted for direct dyes, in addition to being used industrially for the coloration of a variety of substrates, have been used to define the pore structure and accessible surface of cotton fibers and microcrystalline products for many years [18–22]. Benzopurpurin 4B (Direct Red 2) is an azo dye, which contains two nitrogen double bonded groups (N=N) and a sulfonic group (NaO_3S). This sulfonic group makes it soluble in the aqueous medium. A planar view of the chemical structure of Benzopurpurin 4B is given in Scheme 1. The influence of initial dye concentration, temperature and initial solution pH on the adsorption of dye onto organophilic clay was investigated. The amounts of adsorbed at equilibrium were measured. The Langmuir and Freundlich isotherm models were tested for their applicability. The batch contact time method was used to measure the adsorption rate. The experimental data were analyzed using the pseudo-second order adsorption kinetic models, and kinetic constants were evaluated.

2. Materials and methods

2.1. Starting material

The bentonite investigated was a smectite with a mineralogical composition of 80% montmorillonite, 10% quartz, 3% cristobalite, 1% carbonate, 5% calcite and 0.5% organic matter. The family to which the clay minerals belong was determined by X-ray diffraction by measuring the displacement of the main line (0 0 1) under specified treatments. This material was supplied by ENOF ((an Algerian manufacture specialized in the production of non-ferric products and useful substances).

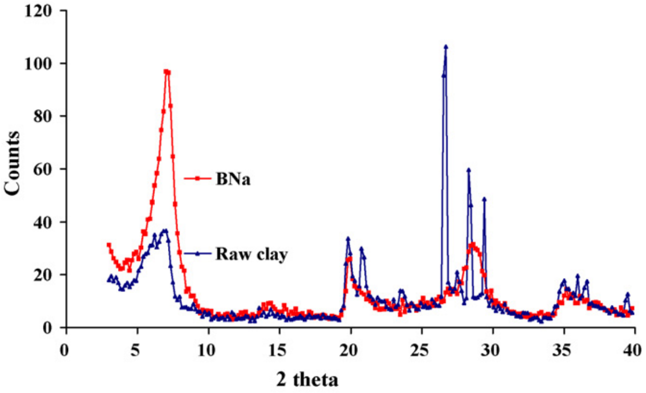

Fig. 1. Diffraction of X-ray of Raw and sodium exchanged bentonite.

It was purified in laboratory to remove carbonates, iron hydroxide and organic matter.

A suspension in distilled water enabled us to obtain, a colloidal suspension after 12 h. The clay used was purified by sedimentation based on the law of Stokes to obtain lower size granulometric fraction <2 μm. It was treated by solution of HCl (0.05 M) in order to destroy carbonates in the clay particles, followed by a treatment with oxygenated water in order to eliminate the organic matters. 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 bentonite or Na-bentonite, whose mineralogy was evaluated by X-ray diffraction. The X-ray diffractogram is presented in Fig. 1. Its structural formula 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} $(OH)_2$.

2.2. Preparation of CTAB–bentonite

The organic clay was prepared by exchanging the inorganic cation of bentonite with quaternary ammonium cation at the following percentage of the clay's CEC: CTAB cations at 100%. The quantity of organic cation added the bentonite was determined by

$$f = \frac{M_{\text{cation}}}{\text{CECM}_{\text{clay}}\text{GMW}_{\text{cation}}X} \quad (1)$$

where f is the fraction cation exchange capacity satisfied by organic cation (dimensionless), M_{cation} the mass organic cation required to achieve desired fraction of CEC (mass), CEC the cation exchange capacity of clay (equivalents/mass), M_{clay} the mass clay (mass), GMW cation the gram molecular weight of organic cation (mass/mol) and X is the moles of charge per equivalent = 1 mol/equiv. for the cations used in this study (mol/equiv.). Theoretically, the cation exchange capacity represents the maximum amount of organic cation that can be exchanged onto the clay's surface. The measured total organic content exchanged onto the organoclay agreed well with the calculated theoretical value [23].

Organophilic clay was prepared by adding amounts of surfactant equivalent to 100% of the value of CEC in which the maximum uptake of CTAB was 371.74 mg/g clay. The surfactant was dissolved in 1 L of distilled water at approximately 30 °C, and 10 g of the base clay (Algerian bentonite) was added to the solution. This amount of CTAB is desired to saturate the cation exchange capacity of bentonite. After agitation during 24 h, the modified clay was recovered by centrifugation, washed until the supernatant solution was free of bromide ions, as indicated by the $AgNO_3$ test and dried at 60 °C. The CTAB organoclay is symbolized hereafter by CTAB–bentonite. Cetyltrimethyl-ammonium bromide (99%), of chemical formula $C_{19}H_{42}NBr$ obtained from ACROS ORGANICS consists of a 16 carbon chain tail group attached to a trimethyl quaternary amine head group with a permanent +1 charge.

2.2.1. *Characterization methods*

Samples were analyzed using the Siemens D-5000 diffractometer with Cu Kα radiation. The X-ray tube was operated at 40 kV and 30 mA beam current. The clays were examined over the range 3–40° 2θ at a scan speed of 2° 2θ/min. 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 mg of pure potassium bromide and 1 mg of sample were compressed under vacuum at room temperature. The transparent disc was fixed on a support.

2.2.2. *Experimental procedures*

Analytical-grade disazo direct dye, Benzopurpurin 4B, Direct Red 2 (CI 23500), with a molar mass 724.73 g/mol ($C_{34}H_{26}N_6O_6S_2Na$) was provided by ACROS ORGANICS. The purity of the dye used was >95% on a weight. It was dried in vacuum and was used without further purifications. The visible absorption spectrum of direct dye exhibits an absorption maximum at 500 nm (A SAFAS bundle of type mc^2 spectrophotometer was used for the absorbance measurements).

Adsorption experiments were conducted in a batch mode using aqueous of Benzopurpurin 4B solutions to obtain equilibrium data. The batch technique was selected because of its simplicity. A stock solution of the dye with a concentration of 200 mg/L was prepared in bidistilled water. From the stock solution, various concentrations were prepared by dilution. Ionic strength was not adjusted during adsorption tests. The direct dyes presented approximately of 30–50 mg/L as an influent concentration. The sorption characteristics to organophilic clay should therefore be evaluated at the top of a similar range of concentrations.

Kinetic experiments were carried out by batch adsorption method at temperature (20 ± 2 °C) on water bath-cum-shaker using 150 mL capped Pyrex glass bottles containing 100 mL of 45, 75 and 120 mg/L of Benzopurpurin 4B solutions and 100 mg of the adsorbent. At different time intervals of 5, 10, 15, 20, 30, 45, 50, 60, 75, 120 and 140 min, aliquots were removed from the suspension and centrifuged at 5000 trs/min. The concentration of dye in the supernatant was determined by spectrophotometer at $\lambda = 500$ nm and was substrated from the initial concentration to determine the adsorbed amounts in each case.

Effect of temperature on the kinetics of the adsorption of Benzopurpurin 4B was studied by adding a 100 mg of adsorbent to each 100 mL volume of dye aqueous solutions having an initial concentration 120 mg/L. The experiments were carried out at 20, 40 and 60 °C. Isothermal studies to determine the sorption capacity were conducted by adding different doses of adsorbate and a fixed concentration of adsorbent and agitating the reaction mixture for the equilibrium time at different temperature 20, 40 and 60 °C.

The effect of the initial pH solution on the amount of adsorbed dye was studied by adjusting the pH of the dye-adsorbent system to different values from pH 3 to pH 11. Dilute HCl and NaOH were used for pH adjustment in order not to increase the volume of samples too much and keep the error created by pH adjustment in a reasonable range. The residual dye color in the reaction mixture after equilibrium contact time was analyzed by centrifuging the reaction mixture and then measuring the absorbance of the supernatant at the wavelength that correspond. Generally, each experiment was performed twice at least under identical conditions. Reproducibility of the measurements was mostly within 4%.

The amount adsorbed (mg/g) was calculated using the following equation:

$$q_{\mathrm{e}} = (C_i - C_{\mathrm{e}})\frac{V}{m} \tag{2}$$

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.

3. Kinetics model

Ho [24] developed a pseudo-second order kinetic expression for the sorption system of dye onto fly ash. This model has since been widely applied to a number of direct dye/adsorbent sorption systems [25,26]. To investigate the mechanism of sorption and the rate constants for the adsorption of Benzopurpurin 4B onto CTAB–bentonite, the pseudo-second order equation given below was used:

$$q_t = \frac{K q_{\mathrm{e}}^2 t}{1 + Kt} \tag{3}$$

The differential equation is as follows:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k(q_{\mathrm{e}} - q_t)^2 \tag{4}$$

Integrating Eq. (4) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\frac{1}{q_{\mathrm{e}} - q_t} = \frac{1}{q_{\mathrm{e}}} + kt \tag{5}$$

when Eq. (5) is linearized it gives:

$$\frac{t}{q_t} = \frac{1}{Kq_\mathrm{e}^2} + \frac{1}{q_\mathrm{e}}t \tag{6}$$

where q_e is the amount of Benzopurpurin 4B adsorbed at equilibrium (mg/g), q_t the amount of Benzopurpurin 4B adsorbed at time t (mg/g) and k is the rate constant of the pseudo-second order sorption (g/mg min).

The initial sorption rate can be obtained as q_t/t approaches zero:

$$h = Kq_\mathrm{e}^2 \tag{7}$$

where h is the initial sorption rate (mg/g min).

4. Isotherm models

We will examine the traditional models of adsorption, suggested to describe the experimental isotherms of adsorption. The Langmuir sorption isotherm [27], which has been widely applied to describe experimental adsorption data based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbate surface with a constant energy and there is no transmigration of adsorbate in the plane of adsorbate surface. The saturated monolayer isotherm can be represented as:

$$q_\mathrm{e} = \frac{q_\mathrm{m} k_\mathrm{b} C_\mathrm{e}}{1 + k_\mathrm{b}} \tag{8}$$

The above equation can be rearranged to the following linear form:

$$\frac{C_\mathrm{e}}{q_\mathrm{e}} = \frac{1}{K_\mathrm{b} q_\mathrm{m}} + \frac{1}{q_\mathrm{m}} C_\mathrm{e} \tag{9}$$

where C_e is the equilibrium concentration (mg/L), q_e the amount of dye adsorbed (mg/g) at equilibrium, q_m the amount of dye adsorbed for a complete monolayer (mg/g) and K_b is sorption equilibrium constant (L/mg).

And another empirical isotherm given by the Freundlich equation is the earliest known relationship describing the sorption equation [28]. This fairly satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous sorption and is expressed by the following equation:

$$q_\mathrm{e} = k_\mathrm{f} C^{1/n} \tag{10}$$

where q_e is the amount adsorbed (mg/g), C_e the equilibrium concentration of the adsorbate ions (mg/L) and k_f and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

5. Results and discussion

5.1. Characterization of bentonite

Table 1
The variations of the basal distance according to tests of behaviour's clay

Samples $d_{0\,0\,1}$ (Å)	
Raw clay	15.65
Solvatation of ethylene glycol	17.77
Saturation of K+	12.12
Hofmann–Klemen test	9.61

The absence of lines characteristic of expanding chlorite on the diffractogram (not shown) shown that our clay can be smectite or vermiculite. Saturation of the clay by K^+ changed the diffraction from 15.65 to 12.12 Å (Table 1). It is thus a smectite. Vermiculite gave a reading of 10.5 Å after this test. The irreversible collapse of the layers of a smectite at 9.6 Å after saturation with lithium, heating overnight to 250 °C and immersion in glycerol, shows that the mineral is a montmorillonite. Saponites and swelling beidellites give a reading of 17.7 Å after this treatment. So our clay thus consists of montmorillonite.

Diffractograms of the samples (Raw clay and Sodium exchanged clay) showed that after treatment the lines of the impurities at 26.68° (2θ) were disappearance in great quantity, which confirms the effectiveness of one protocol of purification (Fig. 1). The characteristic montmorillonite peak at 7.16° (2θ) was more intense and two others at 19.96° (2θ) and 28.76° (2θ). The spectrum of Sodium exchanged clay gives $d_{0\,0\,1} = 12$ Å corresponding to mineral with a monolayer's water. The cation exchange capacity and the surface have been determinate in previous paper [29]. The cation exchange capacity (CEC) was 101.25 mequiv./100 g of clay and the surface area calculated after Brunauer, Emmett and Teller (BET-surface) was 110.07 m^2/g [29].

Bentonite modified by large alkyl cations such as CTAB gives organophilic clay. The experimental value of organic contents of the prepared organoclay (17.67%) was fairly close to 100% CEC. General characteristics of the clay and organoclay samples are listed in Table 2. The interlayer spacing increased with the amount of cationic surfactant used in synthesis (figure not shown). The X-ray diffraction patterns of organophilic bentonite exhibit an interlayer spacing at 19 Å. The increase in the basal spacing for the modified clay is attributed to the intercalation of cationic surfactant into the interlayer of bentonite with a bilayer arrangement, giving a thickness of about 7 Å. The orientation of alkyl ammonium ions between silicated layers is variable. Alkylammonium ions form a monolayer (13.7 Å), a double layer (17.7 Å), a pseudotrimoleculaire layer (21.7 Å) or a parafinic complex (>22 Å) [30].

As shown in Fig. 2, the infrared spectra show the strong bands at 2921 and 2850 cm^{-1} attributed to asymmetric and symmetric stretching vibrations of C–H groups. In addition to this, strong

Table 2
General characteristics of the clay and surfactant-modified bentonite

Property	Sample	
	Na$^+$ bentonite	CTAB–bentonite
Cation formula	–	$C_{19}H_{42}N_+$
Molecular weight of cation	–	364,46
CEC(meq/100 g clay)	101.25	–
S BET (m^2/g)	110.07	–
Organic carbon content (%)	0.05	17.67

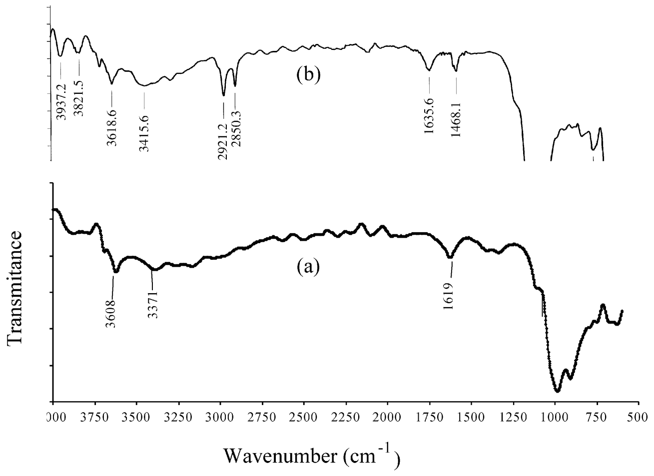

Fig. 2. FTIR spectra of sodium exchanged bentonite (B-Na) (a) and organophilic bentonite (CTAB–bentonite) (b).

absorption peak occur at 1468 cm^{-1} can be related bending vibrations of NH_4^+ and their bonding supporting the intercalation of surfactant molecules between the silica layers. The attributions of absorption at 988 cm^{-1} can be due to Si–O–Si and Si–O–Al stretching and 885 cm^{-1} can be the deformation of Si–OH. Normally the absorption related stretching vibrations of Si–O–Si and Si–O–Al occur at 1100–1000 cm^{-1} but this absorption is changed for lower wave number after modification of bentonite.

5.2. *Effect of pH*

The effect of initial pH on the removal of Benzopurpurin 4B was investigated at an initial concentration of 60 mg/L and 20 °C. The initial pH values of dye solutions affect the chemistry of a dye molecule. In this study, blank studies for Benzopurpurin 4B were done in the pH range of 2–13. The solution was kept for 1 h after the pH adjustment and, thereafter, the absorbance of the solution was found out. It is found that the colour is stable over a pH range of 3–11. The results indicated that the molecular form of Benzopurpurin 4B in solution medium changed markedly in the pH below 3, and at a high alkaline pH of 12. At low of 3 the dye solution changed its color form red to dark blue and there were a lot of fine particles in suspension in the solution and at a high pH of 12, the degree of red color was different from the original red. Similar result was reported in Ref. [31]. Therefore, the pH of the solution was examined between 3 and 11 in the presence of CTAB–bentonite.

The surface charge of adsorbent plays a significant role in the adsorption of ionisable matters. Na-bentonite had no affinity for the dyes. Na-bentonite carries a permanent negative charge in their structural framework. The hydration of Na^+ ions in clay and the nature of Si–O groups impart a hydrophilic nature to the mineral surface. Because of this property, water is preferentially adsorbed by this surface, and large organic compounds cannot compete with strongly held water for adsorption sites on the clay surface. The dye exists in anionic form, so no adsorption takes place on Na-bentonite, as both have negative charge. The surface charge of CTAB–bentonite is positive in the examined pH-range, the addition of CTAB with R a large alkyl group [e.g., cethyltimetylmmonium R = $-C_{19}H_{39}$] with a loading equal to 100% of the CEC of Na-bentonite and an interlayer spacing d_{001} = 19 Å with double layer of quaternary ammonium results an extensive hydrophobic bonding of CTAB molecules and could to result in a build up of positive charge on the clay surfaces, This is likely caused by tail-tail interactions between CTAB cations such the charged moiety is oriented outwards towards the bulk solution. Xu and Boyd [32] pointed out that larger HDTMA was initially adsorbed by cation exchange in the interlayer, which caused extensive clay aggregation. As loading increased, HDTMA adsorbed to the external surfaces of aggregates via cation exchange and hydrophobic bonding, the latter causing positive charge development on surfaces and ultimately clay dispersion.

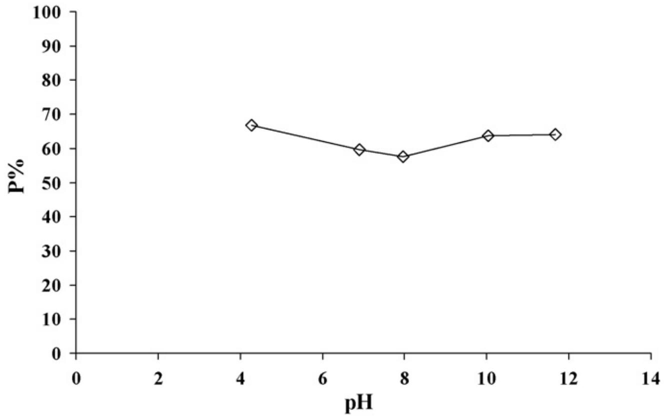

Fig. 3. Effect of initial pH on adsorption of Benzopurpurin 4B on CTAB–bentonite.

As can be seen in Fig. 3 the uptake of dye remains constant. Thus, using a surfactant template realizes electrostatic attraction between the negatively charged SO_3^- anionic groups of dye and quaternary ammonium groups in bentonite layers.

5.3. *Effect of initial dye concentration on kinetics*

Fig. 4 shows the amount of dye removal at various initial solute concentrations by organo-bentonite as a function of time at concentration of adsorbent 1 g/L, pH 6.3 and $T = 20\,^{\circ}C$. From this figure, it was observed that the amount of dye uptake, q_e (mg/g) and the amount of dye adsorbed per time increases with contact time at all initial dye concentrations. All curves have similar characteristics, showing an important and fast adsorption, between $t = 0$ and 40 min, and a slower adsorption at until equilibrium was accomplished and the removal of Benzopurpurin 4B on CTAB–bentonite became constant. The sorption capacity at equilibrium increases from 41.843 to 74.275 mg/g with an increase in the initial dye concentration from 45 to 120 mg/L (Table 3). The higher initial sorption rate may be due to an increased number of vacant adsorption sites available at initial stage of the adsorption process which results in an increased concentration gradient between the solute in solution and the solute on the adsorbent surface. This increased concentration

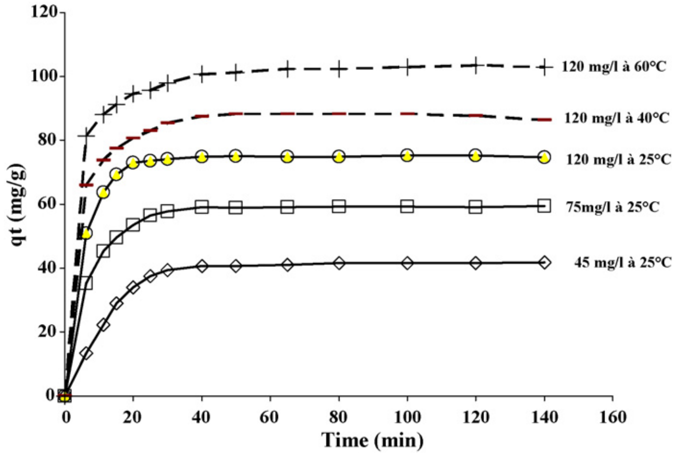

Fig. 4. Effect of contact time on adsorption of Benzopurpurin 4B on CTAB–bentonite at pH 6.3, adsorbent concentration of 1 g/L under different conditions of concentrations (45–75 and 120 mg/L) at temperature of 20 °C and concentration of dye $C_0 = 120$ mg/L at temperature of 20–40 and 60 °C.

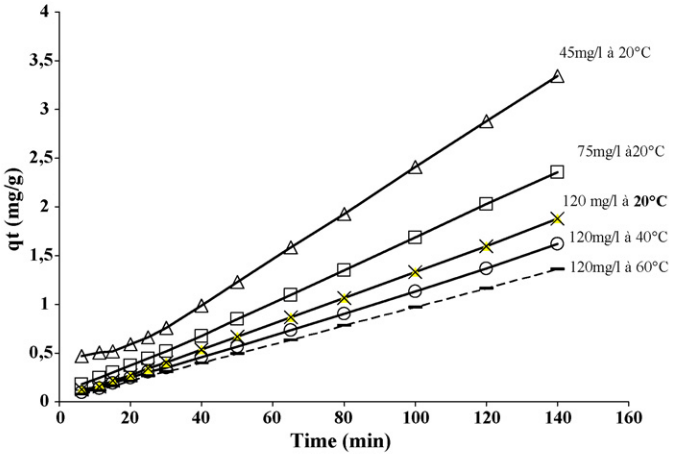

Fig. 5. Pseudo-second order Kinetic plot for adsorption of Benzopurpurin 4B on CTAB–bentonite at pH 6.3, adsorbent concentration of 1 g/L under different conditions of concentrations (45–75 and 120 mg/L) at temperature of 20 °C and concentration of dye $C_0 = 120$ mg/L at temperature of 20–40 and 60 °C.

gradient tends to increase the rate at which dye is adsorbed at the initial stage of adsorption. The dye adsorbed increases for greater initial dye concentrations. This is obvious, since at for higher C_0 values, a more efficient utilisation of the adsorptive capacity of the adsorbent is expected due to greater driving force.

The increased adsorption capacity of clay treated with cetyltrimethylammonium ions for this dye is due to the alkyl chains in the interlamellar spaces and the structure's form of dye. The sorption of this dye on CTAB–bentonite may occur via different mechanisms or additional mechanisms, because Benzopurpurin 4B has two sulfonic groups ($-SO_3$) and has an anthraquinone ring in its molecular structure and, the resultant organoclay (CTAB exchanged bentonite) have low surface areas and act as partitioning media in the sorption [33].

The results were also analyzed using the pseudo-first order and pseudo-second order models. Data obtained gave poor fits with the pseudo-first order model but very good fits with the pseudo-second order model at all reaction times as shown by the correlation coefficients in Fig. 5 shows a linear variation of t/q_t with time, t (Eq. (6)) for CTAB–bentonite at different initial dye concentration. The initial sorption rate h, pseudo-second order rate constant k, amount of Benzopurpurin 4B adsorbed at equilibrium q_e obtained from the pseudo-second order model are given in Table 3. The correlation coefficients for the linear plots of t/q_t against time from the pseudo-second order rate law are greater than 0.997. This suggest that the pseudo-second order model, based on the assumption that the rate-limiting step may be chemical sorption involving valence forces through sharing or exchange electrons between adsorbent and adsorbate, provides the best correlation of the data [34]. Namasivayam and Kavitha [35] reported similar findings for the adsorption of Congo red on activated carbon prepared from agricultural waste. Similar phenomenon was observed for the adsorption of Acid Blue 9 onto mixture of activated carbon and activated clay [36], and also in biosorption of reactive dyes on biomass [37,38]. Increasing dye concentration increased the initial sorption rate h (Eq. (7)) from 58.137 to 58. 137 mg/g min as Benzopurpurin 4B concentration was increased from 45 to 120 mg/L. The amount of direct dye adsorbed at equilibrium, q_e, was following this trend. This is due to a higher driving force that should result in a more rapid change in the rate at which Benzopurpurin 4B is adsorbed initially onto organophilic clay. However, there was an observed increase in the pseudo-second order rate constant, k, for the adsorption of dye on adsorbent, as initial dye concentration was increased. The values of the rate constants k were found to increase from 2.94×10^{-3} to 10.13×10^{-3} g/mg min as the initial concentration increased from 45 to 120 mg/L (Table 3), this trend indicates that the time for the adsorption of dye to reach equilibrium is not extended with increased initial dye concentration. In many cases, the equilibrium sorption capacity is unknown and when chemisorption tends to become unmeasurably slow, the amount adsorbed is still significant smaller than the equilibrium amount [39].

Lee et al. [40] reported that organic cations with large hydrocarbon moieties (C16) would be most effective because they formed a highly effective partition medium for removing nonionic organic compounds from water. Sheng et al. [41] presented that the sorption mechanisms of aromatic hydrocarbons onto

Table 3
Kinetic parameters for the adsorption of Benzopurpurin 4B on B-CTAB at various concentrations (pH 6.3 and $T = 20$ °C)

C_0 (mg/L)	k (g/mg min)	q_m (mg/g)	h (mg/g min)	R^2	k_i (mg/g min$^{1/2}$)	R_i^2
45	2.947×10^{-3}	44.843	5.926	0.997	1.0897	0.930
75	6.085×10^{-3}	60.975	22.623	0.999	0.902	0.895
120	10.130×10^{-3}	75.757	58.137	0.999	0.895	0.775

hexadecyltrimethylammonium (HDTA)-clays were the combination of solvating and partitioning. The major interactions were the Van der Waals forces between solutes and organoclay and the electric charge attraction between cationic surfactants' head groups and solutes. Surfaces modified by surfactants were considerably less homogeneous and the surface roughness was larger than for unmodified clay. However, there exist a Van der Waals force and an electric charge attraction between the preadsorbed cationic surfactant and the anionic dyes.

The linearity of the plots of the pseudo-second order model in Fig. 5 indicates that chemical reaction rather than physisorption is the main rate-controlling step throughout most of the adsorption process [42] and that the mechanism follows a pseudo-second order reaction scheme.

The corresponding linear plots of k, h and q_e can be expressed as a function of C_0 for Direct Red 2:

$$k = 2 \times 10^{-7} C_0^2 + 6 \times 10^{-5} C_0, \qquad r^2 = 0.993 \tag{11}$$

$$h = 0.0031 C_0^2 + 0.1844 C_0 - 8.651, \qquad r^2 = 1 \tag{12}$$

$$q_e, \text{predicted} = \frac{C_0}{0.0078 C_0 + 0.6525}, \qquad r^2 = 0.999 \tag{13}$$

5.4. *Effect of temperature on kinetics dye adsorption*

The temperature dependence of sorption was studied at pH 6.3 with a constant initial dye concentration of 120 mg/L, CTAB–bentonite dose 1 g/L at various sorption temperatures (20, 40 and 60 °C) and shown in Fig. 4. The equilibrium sorption capacity was found to increase from 74.275 to 102.900 mg/g for an increase in the solution temperatures from 20 to 60 °C. It is clear that the sorption of dye on CTAB–bentonite is an endothermic process. This variation is due to the decrease of the relative escaping tendency of dye molecules from the solid phase to the bulk phase and may suggest that increasing temperature may increase the driving force of dye onto the adsorbent. The sorption capacity at equilibrium is favoured by increasing in the temperature, which indicates that the strong interactions exist between modified clay and the dye. Adsorption of the Benzopurpurin 4B on CTAB–bentonite is favoured at high temperature. The initial sorption rate increases with an increase in the temperature. Table 3 shows that h vary from 58.13 to 73.47 mg/g min for a temperature variation from 20 to 60°C. This trend suggests that a chemisorption reaction or an activated process was becoming more predominant in the rate-controlling step. The values of pseudo-second order rate constant, k were found to decrease from 10.13×10^{-3} to 4.82×10^{-3} g/mg min, for an increase in the solution temperature from 20 to 60 °C. These observations are in line with those of Tsai et al. [43] for adsorption of basic violet 4 on regenerated bleaching earth, by Ghosh and Bhattacharyya [44] for kaolinite and methylene blue, by Low et al. [45] for carbonized SBE and basic blue 3 and methylene blue, and also by Dogan and Alkan [46] for perlite and methyl violet (i.e., basic violet 1).

There is a linear relationship between the pseudo rate constant and temperature with correlation coefficients of 0.9094. Linear variation was observed as shown in Fig. 6. Therefore the rate constant k at different temperatures listed in Table 3 was then applied to estimate the activation energy of the adsorption of Benzopurpurin 4B on CTAB–bentonite by the Arrhenius equation:

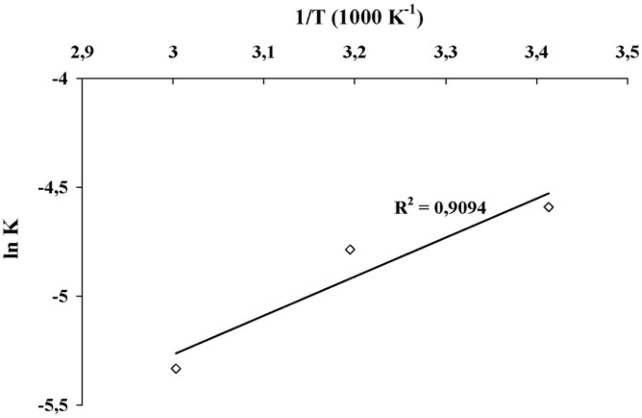

Fig. 6. Plot of ln(K) against reciprocal temperature for Benzopurpurin 4B adsorption onto CTAB–bentonite.

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \tag{14}$$

where k is the rate constant of sorption (g/mg min), k_0 the temperature independent factor (g/mg min), E the activation energy of sorption (kJ mol^{-1}), R the gas constant (8.314 J mol^{-1} K^{-1}) and T is the solution temperature (K).

The slope of the plot of $\ln k$ versus $1/T$ was used to evaluate E_a. Linear variations were observed as shown in Fig. 6 Thus, the relationship between k and T can be represented in an Arrhenius form as: $k = 2.41 \times 10^{-5} \exp(+14.86/8.314T)$

From this equation, the rate constants of sorption, k_0, is 2.41×10^{-5} g/mg min and the activation energy of sorption, E_a, is +14.86 kJ mol^{-1}. Since sorption is an endothermic process, it would be expected that an increase in solution temperature would result in an increase in sorption capacity. These results imply that a chemisorption-like mechanism may play an important role for the adsorption of direct dye and the organophilic clay.

The variation in the quantity adsorbed with the contact time at various concentrations and temperature was further processed to evaluate the role of diffusion (as the rate-controlling step) in the adsorption process. Adsorption is often a process at several stages which introduces the migration of adsorbate from bulk solution to outer surface of the solid by molecular diffusion, known as external (or) film diffusion, the transport of adsorbate from the particles surface into interior sites and the sorption of the solute particles from the active sites into the interior surface, this last is often a relatively slow process which is in fact rate-limiting step [47]. In order to examine the suitability of intraparticle diffusion in fitting our data, the rate constant for intraparticle diffusion was given by Weber and Morris [48]:

$$q_t = k_i t^{1/2} \tag{15}$$

where q_t is the amount adsorbed (mg/g) at time t (min). Fig. 7 presents the amount of color adsorbed, q_t versus the square root

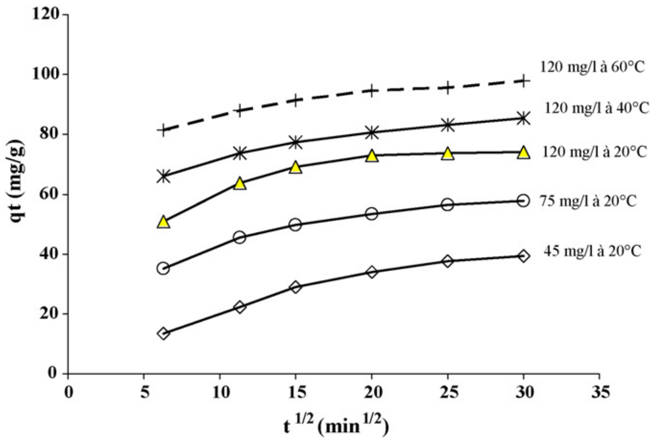

Fig. 7. Intra-particle diffusion plot for adsorption of Benzopurpurin 4B on CTAB–bentonite at pH 6.3, adsorbent concentration of 1 g/L under different conditions of concentrations (45–75 and 120 mg/L) at temperature of 20 °C and concentration of dye $C_0 = 120$ mg/L at temperature of 20–40 and 60 °C.

of time. The intra-particle diffusion correlation coefficient R_i^2 is based on the results for the first minutes only. The k_i (intra-particle diffusion rate in mg/g min$^{0.5}$) values were obtained from the slope of the straight-line portions of plots of q_t versus $t^{0.5}$ for various dye concentrations and temperatures. The values of constants, k_i, for intra-particle diffusion kinetics have been given in Tables 3 and 4. The results show that decreasing initial solute concentration and decreasing temperatures increased the intra-particle diffusion rate constant. Ho and McKay [49] found that k_i the constant of intra-particle diffusion decreases from 0.644 to 0.166 mg/g min$^{0.5}$ when the temperature increases from 18 with 80 °C for adsorption of Acid Blue 25 onto peat. Our constants speed of intra-particle diffusion k_i decrease from 0.895 to 0.632 mg/g min$^{0.5}$ with the increase in the temperature from 20 to 60 °C (Tables 3 and 4), and are higher than those found in the literature [50,51]. From this figure, it may be observed that the straight lines did not pass through the origin and this further indicates that the intra-particle diffusion is not the only rate-controlling step. Weber and Morris [48] have proposed that if the uptake of the adsorbate varies with the square root of time, intra-particle diffusion can be taken as the rate-limiting step. Ho and McKay [49] has shown that it is essential for the q_t versus $t^{0.5}$ plots to go through the origin if the intra-particle diffusion is the sole rate-limiting step. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further indicates that the intra-particle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. Since this was also not the case in the present work, it may be concluded that surface adsorption and intra-particle diffusion were concurrently operating during the Benzopurpurin 4B and CTAB–bentonite interactions

5.5. Equilibrium studies

Adsorption isotherms of Benzopurpurin 4B at 20, 40 and 60 °C expressing the adsorbed amounts as a function of equilibrium concentration at different temperatures are presented in Fig. 8. It is obvious from this figure that the adsorption isotherms of dyes on CTAB–bentonite are L-type according to the Giles classification [52]. In this type of isotherm, the initial portion provides information about the availability of the active sites to the adsorbate and the plateau signifies the monolayer formation. The initial curvature indicates that a large amount of dye is adsorbed at a lower concentration as more active sites of CTAB–bentonite are available. As the concentration increases, it becomes difficult for a dye molecule to find vacant sites, and so monolayer formation occurs. The types of system which give this curve do in fact fulfil these conditions. Thus they have one of the following characteristics: (i) the adsorbed molecules are most likely to be adsorbed flat or (ii) if adsorbed end-on, they suffer little solvent competition. Examples of (ii) are: (a) systems with highly polar solute and adsorbent, and a nonpolar solvent; (b) systems with monofunctional ionic subtances with very strong intermolecular attraction. It is possible that in the system (b) cases the adsorbed ions may have become associated into very large clusters and just adsorption takes place. Where the sites are few and widely separated, the surface has large hydrophobic regions.

The adsorption of the dye Benzopurpurin 4B tends to increase as temperature increases. This perhaps, evidences that the adsorption takes place chemically, because chemisorption principle dictates that there is a relation between temperature and adsorption rate. The amount of dye increases with increasing temperature due to the reduction of the desorption step in the mechanism. For an interval of concentration of 20 at 200 mg/L, the equilibrium sorption capacity, q_{m}, increases from 107.98 to 150.98 mg/g for an increase in the solution temperature from 20 to 60 °C. This phenomenon indicates that the sorption of Benzopurpurin 4B on organophilic clay is an endothermic process. Furthermore, the increasing trend of adsorption with temperature is mainly due to the strongly of adsorptive forces between the active sites of organophilic clay and adsorbate species, and also due to the weakening forces between the adjacent molecules of adsorbed phase. These results are in agreement with those found by Glosh et al for adsorption of the blue of methylene on kaolinite [44], by Dogan et al. for adsorption methyl violet onto perlite [46] and by Singh et al. of methylene blue and malachite green on chemically treated Psidium Guyava leaves [53].

Table 4
kinetic parameters for the adsorption of Benzopurpurin 4B on B-CTAB at various temperatures (pH 6.3 and $C_0 = 120$ mg/L)

T (°C)	k (g/mg min)	q_{m} (mg/g)	h (mg/g min)	R^2	k_i (mg/g min$^{1/2}$)	R_i^2
20	10.130×10^{-3}	75.757	58.137	0.999	0.895	0.775
40	8.345×10^{-3}	88.495	65.352	0.999	0.750	0.921
60	4.826×10^{-3}	105.263	73.473	1	0.632	0.903

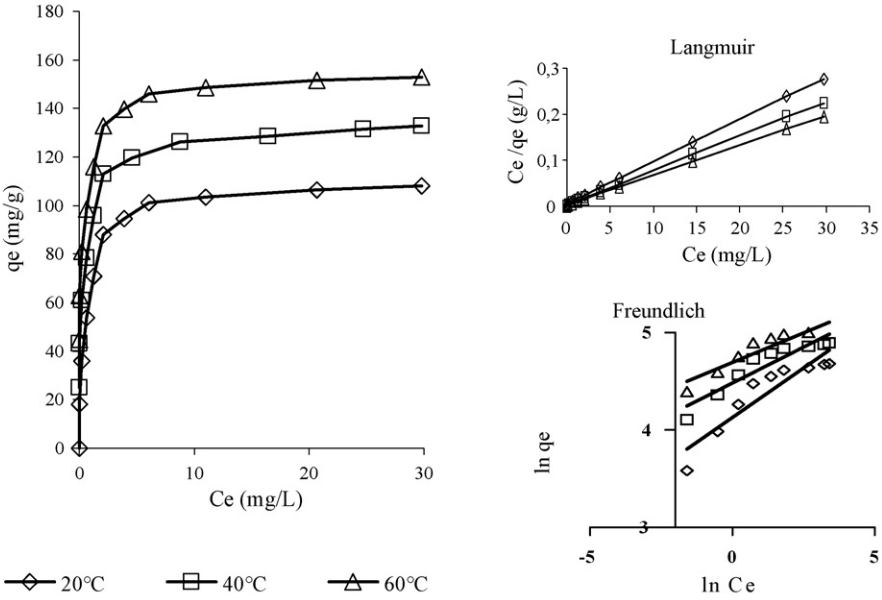

Fig. 8. Isotherms for the adsorption of dye Benzopurpurin 4B onto CTAB–bentonite at various temperatures.

Table 5
Adsorption isotherm constants for adsorption of Benzopurpurin 4B on CTAB–bentonite at various temperatures

T (°C)	Langmuir			Freundlich		
	q_m (mg/g)	k_b (L/mg)	R^2	k_f (L/g)	$1/n$	R^2
20	109,89	2,068	0.999	62.010	0.204	0.851
40	133,33	2,205	0.999	88.375	0.148	0.870
60	153,84	2,503	0.999	108.98	0.122	0.879

The linear plots of C_e/q_e versus C_e for the wastewater samples show that adsorption follows Langmuir isothermal model (Fig. 8). Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of CTAB–bentonite surface, i.e., each dye molecule/CTAB–bentonite adsorption has equal adsorption activation energy; the results also demonstrate the formation of monolayer coverage of dye molecule at the outer surface of adsorbent. Similar observation was reported for the adsorption of dyes onto organophilic clay [33]. Values of q_m and K_b were calculated from the intercept and slope of the linear plots, respectively, and are presented in Table 5. The equilibrium adsorption capacities evaluated from the Langmuir equation and the pseudo-second order rate model show that the evaluated values are reasonable.

When log q_e is plotted against log C_e, a straight line with slope $1/n$ and intercept log k_f is obtained (Fig. 8). This reflects the satisfaction of Freundlich isotherm model for the adsorption of dye. The intercept of line, log K_f, is roughly an indicator of the adsorption capacity and the slope, $1/n$, and is an indicator of adsorption intensity [28]. The Freundlich parameters for the adsorption of Benzopurpurin 4B on CTAB–bentonite are also given in Table 4. It is evident from this data that the surface of Cetyltrimethylammonium bromide–bentonite (CTAB–bentonite) is made up of heterogeneous adsorption. It is evident from these data that the surface of CTAB–bentonite is made up of homogeneous and heterogeneous adsorption patches. In other words, all of isotherm models fit very well when the r^2 values are compared in Table 4. The Langmuir model correlation coefficients are 0.999, the Freundlich model correlation coefficients between 0.851 and 0.879.

6. Conclusion

This study investigates the equilibrium and the dynamics of the adsorption of direct dye on the cetyltrimethylammonium bromide exchanged montmorillonite. The modification of Bentonite clay with cetyltrimethylammonium bromide enhanced the rate at which Direct dye Benzopurpurin 4B is adsorbed on Na-bentonite. Increasing concentration Benzopurpurin 4B in solution increased the amount of dye adsorbed ono cetyltrimethylammonium bromide–bentonite (CTAB–bentonite). The increased adsorption capacity of clay for Benzopurpurin 4B treated with Cetyltrimethylammonium ions is due to the alkyl chains in the interlamellar spaces of CTAB–bentonite functioning as organic solvent in partitioning and electrostatic attraction with positively organoclay surfaces and anionic dye molecules. Chemical interaction is observed: Our results support the existence of two modes of adsorption:

1. A strong mode of binding exists in between sulfonic groups of dye and positively charged development in surface clay with intercalating CTAB in silicate interlayers.
2. The second mode of binding, which is hydrophobic, and this latter between dye and CTAB was stronger because the volume of aromatic ring of Benzopurpurin is an anthraquinone ring.

However, there was an increase in the overall rate of adsorption of dye onto the adsorbent with increasing initial Benzopurpurin 4B concentration in aqueous solution because the time for the adsorption of dye to reach equilibrium is not extended with increased initial dye concentration, where the real equilibrium is not reached.

The adsorption reaction was found to be endothermic, this indicates that increase in Benzopurpurin 4B solution temperature will enhance the amount of Benzopurpurin 4B adsorbed from aqueous solution by cetyltrimethylammonium bromide–bentonite. The adsorption of Benzopurpurin 4B onto CTAB–bentonite was found to follow the pseudo-second order reaction. The mechanism of adsorption onto CTAB–bentonite was deduced to be chemisorption and the rate-limiting step is being controlled mainly by external mass transfer. The activation energy of adsorption can be evaluated using the pseudo-second order rate constants. The intra-particle diffusion is not the only rate-limiting step, the surface adsorption and intra-particle diffusion were concurrently operating during the Benzopurpurin 4B and CTAB–bentonite interactions. The adsorption of Benzopurpurin 4B onto the CTAB–bentonite is favoured at higher concentrations of dye solution, high temperatures and solution pH. The Freundlich and Langmuir adsorption models were used for the mathematical description of the adsorption equilibrium of Benzopurpurin 4B by CTAB–bentonite. The obtained results showed that the adsorption equilibrium data fitted very well to both models. Surface of CTAB–bentonite is made up homogeneous and heterogeneous adsorption patches. The equilibrium data in the Langmuir model of adsorption, showed the formation of monolayer coverage of dye molecules at the outer surface of the CTAB–bentonite. No studies were carried out relating to the recovery of dyes from organophilic clay. However, bentonite is used extensively as a cheap material and therefore by dewatering the spent organophilic clay of dye, it can be burned and new matrix generated. It may also be possible to recover the dyes by solvent extraction; however, the leaching out of other components from the clay is likely.

From the foregoing experiments the reasonable concludes that CTAB–bentonite is an effective adsorbent for removing BP.4B from aqueous solution, it can be represented as a suitable adsorbent and environmentally clean utilization of wastewater.

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