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Adsorption of Congo Red by surfactant-impregnated bentonite clay

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ABSTRACT

Due to an ever-changing climate and invasive foreign plant species increase, South Africa struggles with limited water resources. Water is important for the sustenance of all living organisms and it has to be protected. The development of different water treatment techniques becomes more popular to achieve efficient and cost-effective ways of removing contaminants from water. In this study, the property of bentonite clay was altered through impregnation with surfactants such as benzyltrimethylammonium chloride (BTMA), hexadecyltrimethylammonium bromide (HDTM) and tris(hydroxymethyl)aminomethane (THMA) and then used for the removal of the anionic dye, Congo Red (CR), from solutions. The characterization of the different clay samples was done with the use of X-ray diffractometer, X-ray fluorometer and FTIR spectroscopy. To determine the bentonite adsorption affinity the pseudo-first- and second-order kinetic models were used as well as the Langmuir- and Freundlich isotherm models. Other influencing factors that were tested include the effects of adsorbent dosage, initial dye concentration and contact time. The natural bentonite (NB) and bentonite impregnated with BTMA or THMA only adsorbed CR to a certain extent with an adsorption affinity of $q_e = 5.00$ mg/g, $q_e = 1.87$ mg/g and $q_e = 2.76$ mg/g, respectively. The HDTM-impregnated bentonite performed very well in adsorbing CR with an adsorption affinity of $q_e = 16.04$ mg/g. Evaluation of thermodynamic parameters such as ΔG° and ΔH° indicated that the adsorption process was thermodynamically favourable and endothermic in nature. HDTM can therefore be considered to improve the adsorption capacity of natural bentonite clay for the removal of an anionic dye such as CR.

Keywords: Anionic dyes; Adsorption; Bentonite; Surfactant; Congo Red; FTIR

1. Introduction

Dyes can be very dangerous to the environment and to the health of any living organism, including human beings. About 20% of synthetic textile dyes enter the environment through industrial effluents. They are characterized by their low biodegradability, elevated salt content and they cause visual pollution because of their colour [1]. Congo Red is a synthetic anionic disazo dye also known as disodium; 4-amino-3-[[4-[4-[(1-amino-4-sulfonaphthalen-2-yl)diazenyl]phenyl]phenyl] diazenyl] naphthalene-1-sulfonate which is very stable in the environment and has the potential to cause cancer [2,3]. The colour intensity of dyes limits sunlight transmissions into surface water, inhibiting the growth of aquatic plants and this can have a negative effect on the aquatic ecosystem [4]. When dyes break down, hazardous products may be formed that are toxic,

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mutagenic or carcinogenic [5]. It is has been reported [6,7] that Congo Red contains a toxic metabolite namely benzidine which causes cancer of the bladder in humans. It is therefore very important to remove these dyes from the water to ensure environmental safety and to provide safer water for human consumption.

Conventional water treatment methods are not as effective in removing the dyes from solution due to the stability of dyes deriving from their synthetic origin. Anionic dyes are especially difficult to remove from solution because of their structure and negative charge. Adsorption is a favoured water treatment technique because it effectively removes pollutants that are too stable for other treatment methods. It produces a product of high quality and it is an inexpensive treatment method compared to other treatment techniques [4,8].

Various non-conventional materials exist and are proven effective for adsorption purposes. These include among others eggshell power [9], *Hibiscus cannabinus* fibre [10], hen feathers [11] and aluminosilicates such as clay [12,13]. When taking cost-effectiveness and adsorption efficiency into account, clay minerals are becoming more popular because they are easily obtainable and are low in cost [14]. Bentonite consists mainly of montmorillonite and a small fraction of other materials such as quartz, feldspar, volcanic glass, organic matter, gypsum and/or pyrite and the chemical structure consists of a hydrous alumina silicate which contains small amounts of alkali and alkaline-earth metals. The building blocks of montmorillonite are the repetition of an alumina octahedral sheet with a silica tetrahedral sheet [15]. Bentonite is a favoured adsorbent because it possesses a high specific surface area [4] and can disperse into colloid particles [15].

In a previous study natural bentonite clay was used for the removal of dyes from solution, which revealed that the clay hardly adsorbed anionic dyes due to the clay's natural anionic structure [16]. It is therefore necessary to alter the clay's structure with the use of surfactants to increase the clay's adsorption capacity for anionic dyes.

In this study, the adsorption of the anionic dye, Congo Red, onto natural bentonite clay is assessed and compared to the adsorption onto surfactant-impregnated bentonite clay.

2. Experimental

2.1. Materials

Natural bentonite clay (NB) was obtained from the Yellowstar mine near Koppies in the Free Sate, South Africa. It has a cation exchange capacity (CEC) of 62 cmol/kg and it was used as adsorbent during the experiments to remove the anionic dye from solutions. The clay was ground and sieved to obtain a particle size of 106 μm and smaller.

The anionic dye used in the experiments was Congo Red (CR), obtained from Sigma Aldrich. The clay's natural anionic charge causes it to hardly adsorb anionic dyes from solution and it was therefore necessary to alter the clay's structure with the use of surfactants such as benzyltrimethylammonium chloride and tris(hydroxymethyl)aminomethane, obtained from Sigma Aldrich, and also hexadecyltrimethylammonium bromide, obtained from ACE chemicals.

2.2. Preparation of impregnated clay

The impregnation of NB was done by adding 21 g of bentonite clay to 0.54 L of distilled water and then the mass of surfactant (BTMA, HDTM or THMA) added was equivalent to twice the clay's CEC. A temperature controlled orbital shaker was used to keep the mixture in suspension for 24 h at 160 rpm and 25℃. The impregnated clay was washed with distilled water and dried at 70℃ for 24 h.

2.3. Characterization of the clay

A Philips X'Pert pro MPD X-ray diffractometer (XRD) was used at 40 kV and 30 mA with scan speed: 2°/min, 2θ scan range: 3–90° and the step width: 0.01° to determine the clay's mineralogical composition.

A MagiX PRO & SuperQ Version 4 X-ray fluorometer (XRF) was used to determine the elemental composition of the clay at 50 kV and 125 mA.

The IRAffinity-1S Fourier transform infrared spectrophotometer from Shimadzu, with a spectral range from 4,000 to 400 cm^{-1}, was used to identify the functional groups present in the clay and to evaluate the surface activation.

2.4. Adsorption studies

To determine the equilibrium concentration of each dye solution, a UVmini-1240 UV–vis spectrophotometer was used. The calibration was done at a wavelength of 560 nm for CR.

The effects of adsorbent dosage (0.01–0.3 g), initial dye concentration (10–100 mg/L) and contact time (15–90 min) were tested, keeping constant the following parameters: temperature at 25℃, adsorbent particle size at 106 μm, rotation speed at 160 rpm and solution volume at 0.1 L. The effect of temperature on the adsorption performance of adsorbents exposed to 150 mg/L of CR was investigated at 30, 40, 50 and 60℃ for 40 min at a shaking speed of 160 rpm.

2.5. Isotherm and kinetic models

The dye adsorption by NB and bentonite impregnated with the different surfactants was evaluated using the Langmuir and Freundlich isotherm models [17–19].

The Langmuir isotherm model assumes monolayer adsorption in single solute systems. This model's linear form is given by:

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

The Freundlich model can be applied in heterogeneous systems and it is not limited to monolayer adsorption. This model's linear form can be given by:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{2}$$

In the two isotherm models given, C_e is the concentration of dye at equilibrium in (mg/L), q_e is the concentration of the dye at equilibrium in (mg/g), q_m is a Langmuir constant associated with the adsorption capacity in (mg/g), k is a Langmuir constant related to energy released during adsorption in (L/mg), k_F is the Freundlich adsorption capacity parameter in (mg/g) and n indicates the deviation of adsorption from linearity. To aid in identifying the adsorption rate the pseudo-first- and second-order models are used [19,20].

The pseudo-first-order kinetic model is given by:

$$\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303} \tag{3}$$

The pseudo-second-order kinetic model is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where q_e is the concentration of the dye at equilibrium in (mg/g), q_t is the amount of dye adsorbed at time t in (mg/g), k_1 is the first-order rate constant in (min^{-1}), k_2 is the second-order rate constant in (g/mg/min) and t is the time in (min).

3. Results and discussion

3.1. Mineralogical and elemental composition of the clay

The XRD results of NB indicated the presence of bentonite, quartz and albite. Alumina and silica were identified by the XRF analysis and the other elements identified included calcium, chloride, iron, magnesium, manganese, sodium and titanium. These other elements could promote electrostatic interaction on the binding sites available.

3.2. FT-IR analyses

The FT-IR results of the NB-, BTMA-, HDTM- and THMA-impregnated bentonite showed obvious differences throughout the FT-IR spectra as the surfactants affect the structure of the NB.

The group of adsorption peaks observed between 3,390 and 3,610 cm^{-1} indicates the stretching bands of the hydrogen bonded O–H groups that are present in the natural bentonite and impregnated bentonite [21]. The peak at 3,016 cm^{-1} is indicative of an unsaturated asymmetric stretching vibration of C=C–H that is visible after NB was impregnated with HDTM. In the region 2,918–2,848 cm^{-1} there are two strong peaks that were not part of the NB spectra. These peaks formed for HDTM-bentonite, indicating the symmetric and asymmetric stretching vibration of the C–H groups.

In the spectral range between 1,450 and 1,600 cm^{-1} respective peaks indicate the stretching symmetric and asymmetric vibrations of C–C=C aromatic ring double bonds that formed after surfactant impregnation. Within this range there are also peaks corresponding to the bending vibrations of N–H of primary amines after impregnation.

The increasing peak intensities between 1,471 and 1,487 indicate the bending vibration of N–H of secondary amines. These secondary amines are present in the structure of BTMA and HDTM. It is therefore expected that the BTMA- and HDTM-impregnated clays contain this functional group.

The band intensity for NB at 1,614 cm^{-1} was decreased after impregnation of each surfactant, also confirming the modification of NB.

The FT-IR spectra of the NB before and after adsorption of CR exhibited the most evident difference in the band at 1,614 cm^{-1}. This band corresponds to the stretching vibration of C=O in the NB structure and after adsorption of CR the intensity of this peak reduces.

The change observed in the FTIR-spectra for the adsorption onto the BTMA modified bentonite was not very noticeable but there was a change in the region 1,487–1,473 cm^{-1} which corresponds to asymmetric stretching vibration of C–C=C aromatic rings or the bending vibrations of N–H.

There was a change observed at 3,016 cm^{-1} between the FTIR spectra of HDTM before and after adsorption of CR, a peak at that band corresponds to an unsaturated asymmetric stretching vibration of C=C–H. This peak is reduced after the adsorption of CR. In the region 2,918–2,848 cm^{-1} there was a change in the band corresponding to the stretch vibration of C–H. In the region 1,490–1,470 cm^{-1} there was a change in the band corresponding to the stretching vibration of C–C in the aromatic ring or bending vibration of N–H of secondary amines. This band diminishes after the adsorption of the anionic dye.

From the FT-IR analysis of the adsorption onto THMA-bentonite there are no significant changes throughout the whole spectrum and from this it can be concluded that THMA-bentonite does not perform well during anionic dye adsorption.

3.3. Adsorption behaviour

The effect of adsorbent dosage, as seen in Fig. 1, was tested. A constant volume (0.1 L) of the dye solution was used with the initial concentration of the dye and contact time kept constant at 50 mg/L and 90 min, respectively. With an increase in adsorbent dosage there is an increase in surface area available for adsorption with more binding sites that are exposed. However, it was found that as the initial concentration of the adsorbent increased the adsorption capacity decreased; it was previously reported [22] that the adsorption capacity of metal ions is inversely proportional to the initial concentration of the adsorbent when the initial concentration of the metal ions is kept constant.

For the effect of initial dye concentration (see Fig. 2) the adsorbent dosage was kept constant at 0.3 g and the contact time was kept constant at 90 min. It can be observed that the adsorption of CR onto the HDTM-bentonite increased continuously as the dye concentration was increased. This was not the case for the other adsorbents which poorly removed the CR from solution, exhibiting an adsorption capacity below 5 mg/g that was relatively constant in the whole range of dye concentrations considered.

In Fig. 3, the effect of contact time on the adsorption of CR is shown. The parameters that were kept constant were the adsorbent dosage at 0.3 g and the initial dye concentration at 50 mg/L. When the contact time was increased, the amount of dye adsorbed also increased up until 60 min, after which the adsorption exhibited only a very small increase. During adsorption, time is required for sufficient exposure and interaction between the binding sites on the adsorbent and the adsorbate; after a period of time, most of the binding sites have been occupied and the rate of adsorption reduces since only a relatively small amount of metal ions can bind to the available binding sites on the adsorbent. Saturation of the adsorbent is eventually reached when binding sites are no longer available to interact with the metal ions, from this moment, the adsorption capacity will remain constant.

According to the trend observed in all the figures, the HDTM-bentonite adsorbed the most dye and it

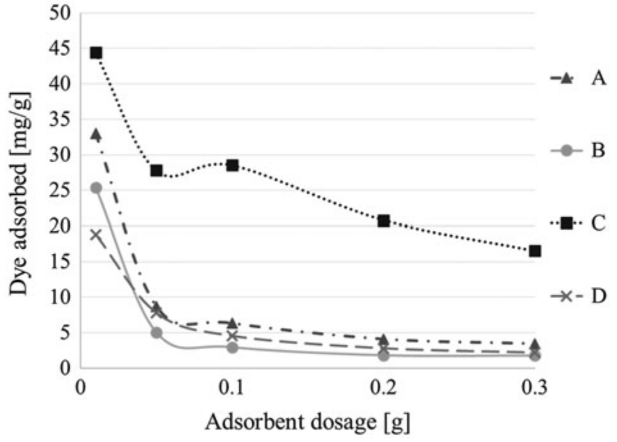

Fig. 1. Effect of adsorbent dosage on the adsorption of dye by (A) NB and bentonite impregnated with (B) BTMA, (C) HDTM and (D) THMA.

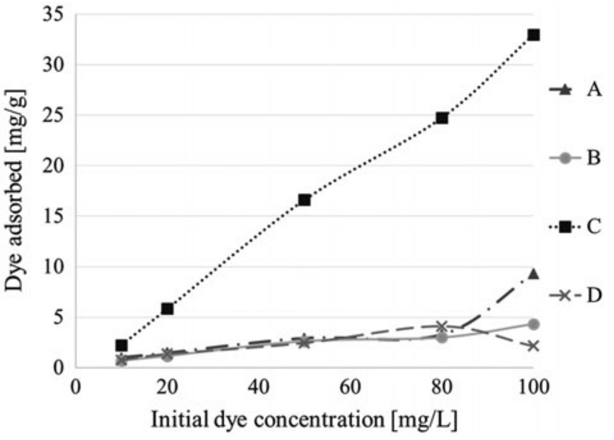

Fig. 2. Effect of initial dye concentration on dye adsorption by (A) NB and bentonite impregnated with (B) BTMA, (C) HDTM and (D) THMA.

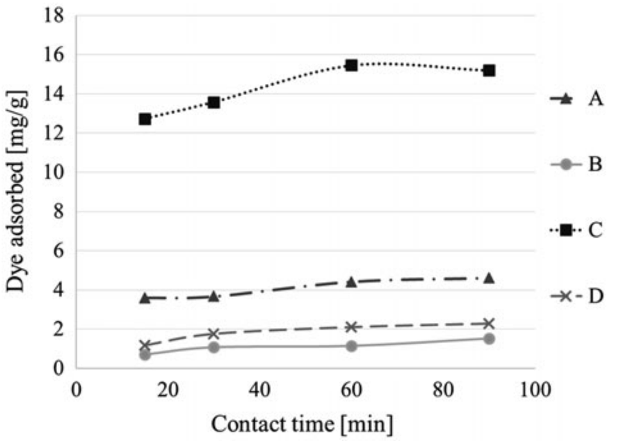

Fig. 3. Effect of contact time on the adsorption of dyes by (A) NB and bentonite impregnated with (B) BTMA, (C) HDTM and (D) THMA.

performed better than the natural bentonite. The THMA- and BTMA-bentonite however did not perform as well as the natural bentonite in adsorbing CR.

3.4. Isotherm and kinetic models results

To better understand the mechanism of adsorption of CR onto the various adsorbents, the Langmuir and the Freundlich isotherms were considered.

The Langmuir isotherm plots for the adsorption of CR by NB and bentonite impregnated with the various surfactants are depicted in Fig. 4 and were constructed by plotting C_e/q_t vs. C_e. To construct the Freundlich isotherm plots, $\log(q_e)$ was plotted as a function of $\log(C_e)$; the plots corresponding to the various adsorbents are shown in Fig. 5. The isotherm parameters were calculated from the intersections and slopes of the various plots.

From the coefficient of determination (R^2 values) in Table 1 it can be observed that overall; the Langmuir isotherm model showed a better fit of the adsorption of CR by the adsorbents than is the case with the Freundlich isotherm model; implying that the adsorption mechanisms could be dominated by the binding to the monolayer surface of the adsorbents [23,24]. However, the perfect fit was only observed in the case of the adsorption of CR by the BTMA-bentonite, predicted by the Langmuir isotherm model.

A prediction of the rate at which dye removal takes place is very important for a treatment process. A kinetic study can be performed to provide relevant data in this regard and allow the determination of the capacity of adsorbents. The pseudo-first and -second-order models are among the kinetic models frequently used for the prediction of the adsorbents behaviour [19]. The values of the kinetic parameters in Table 2 were obtained by plotting $\log(q_e - q_t)$ vs. t (Fig. 6) and t/q vs. t (Fig. 7) for the pseudo-first and -second-order models, respectively.

The suitability of the model to predict the adsorption behaviour can be determined by considering the value of the coefficient of determination (R^2); the closer this value is to the unity the better the fitness of the model to the adsorption data will be. The R^2 values in Table 2 show that the pseudo-first-order model is not suitable for the prediction of the adsorption behaviour, while for the pseudo-second-order model these values are closer to unity indicating the fitness of the model to the adsorption data.

As shown in Table 2, the adsorption capacities of BTMA-bentonite (q_e = 1.87 mg/g) and THMA-bentonite

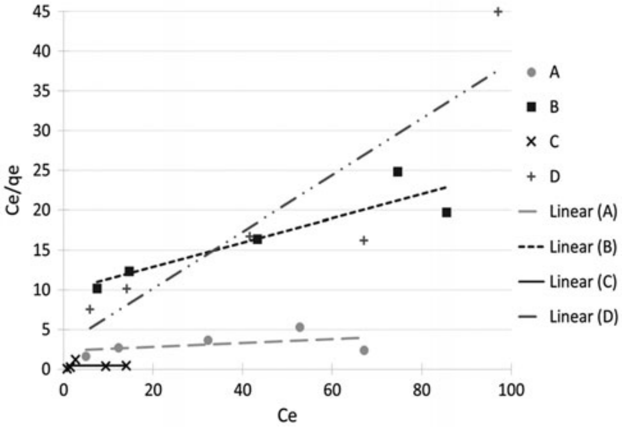

Fig. 4. Validation of the Langmuir isotherm model for the adsorption of CR onto (A) NB, (B) BTMA-bentonite, (C) HDTM-bentonite and (D) THMA-bentonite.

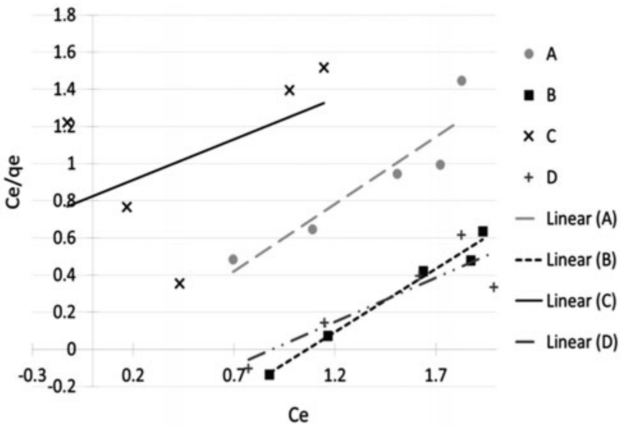

Fig. 5. Validation of the Freundlich isotherm model for the adsorption of CR onto (A) NB, (B) BTMA-bentonite, (C) HDTM-bentonite and (D) THMA-bentonite.

Table 1
Langmuir and Freundlich isotherm constants

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	k (L/mg)	R^2	n	k_F (mg/g)	R^2
NB	26.99	18.30×10^{-3}	0.848	ND	0.640	0.208
BTMA-bentonite	6.580	15.43×10^{-3}	0.979	1.470	0.190	0.827
HDTM-bentonite	ND	2.370×10^{-3}	0.236	ND	6.670	2×10^{-4}
THMA-bentonite	2.820	114.8×10^{-3}	0.765	2.110	0.380	0.800

Note: ND: Not determined.

Table 2
Pseudo-first- and second-order kinetic model parameters

Adsorbent	Pseudo-first-order kinetics				Pseudo-second-order kinetics			
	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	k_2 (g/mg/min)	R^2
NB	16.8	13.47	1.20×10^{-3}	0.934	16.8	5	24.9×10^{-3}	0.996
BTMA-bentonite	15.98	15.34	0.60×10^{-3}	0.905	15.98	1.87	20.6×10^{-3}	0.946
HDTM-bentonite	15.98	3.93	22.0×10^{-3}	0.709	15.98	16.04	15.0×10^{-3}	0.998
THMA-bentonite	16.33	15.17	0.90×10^{-3}	0.871	16.33	2.76	19.2×10^{-3}	0.999

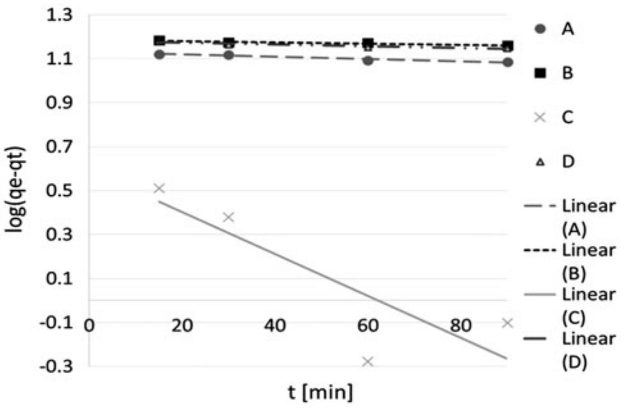

Fig. 6. Validation of the pseudo-first-order kinetic model for CR adsorbed by (A) NB and NB impregnated with (B) BTMA, (C) HDTM and (D) THMA.

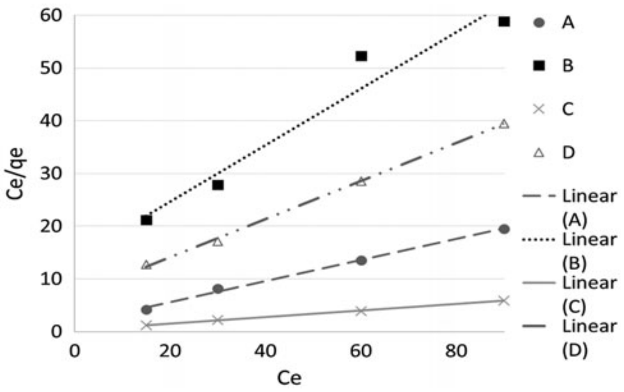

Fig. 7. Validation of the pseudo-second-order kinetic model for CR adsorbed by (A) NB and NB impregnated with (B) BTMA, (C) HDTM and (D) THMA.

($q_e = 2.76$ mg/g) are lower than that of NB ($q_e = 5.00$ mg/g). This suggests that there was a reduction of the already limited binding sites present in NB by impregnating with BTMA and THMA. However, the calculated values of q_e were significantly different to the experimental values for the following adsorbents, NB, BTMA and THMA. In the case of HDTM, the calculated value of q_e was closer to the experimental value, implying that the pseudo-second-order kinetic model was only suitable for the prediction of the adsorption behaviour of HDTM.

The HDTM-bentonite removed the most dye from solution with higher equilibrium adsorption capacities for the anionic dye, CR. The amount of dye HDTM-bentonite adsorbed at equilibrium for CR is $q_e = 16.04$ mg/g. This indicates successful impregnation of NB by using HDTM as a surfactant. Similar results were obtained in previous studies [25,26].

3.5. Thermodynamic study

Four different temperatures (30, 40, 50 and 60°C) were considered to investigate the effect of temperature

Table 3
Thermodynamic parameters for the adsorption of Congo Red onto NB, BTMA, THMA and HDTM

Adsorbent	Ka	Temperature (K)	ΔG (kJ/mol)	ΔS (J/mol/K)	ΔH (kJ/mol)
NB	2.12	303.15	−1,892.78	7.9	49.2
	2.18	313.15	−2,028.03		
	2.27	323.15	−2,206.98		
	2.34	333.15	−2,354.85		
BTMA	1.87	303.15	−1,583.75	115.4	8.85
	1.95	313.15	−1,740.98		
	2.18	323.15	−2,092.79		
	2.37	333.15	−2,394.98		
THMA	1.93	303.15	−1,651.36	88.2	8.26
	2.03	313.15	−1,847.35		
	2.12	323.15	−2,017.66		
	2.34	333.15	−2,354.85		
HDTM	16.55	303.15	−7,073.67	122.6	27.4
	18.64	313.15	−7,616.53		
	19.89	323.15	−8,033.19		
	21.30	333.15	−8,471.68		

on the adsorption of Congo Red by NB, BTMA, THMA and HDTM. It was found that the adsorption of CR increases with an increase of temperature. Parameters such as the Gibbs free energy (ΔG°, kJ/mol), entropy change (ΔS°, J/molK) and enthalpy change (ΔH°, kJ/mol) were calculated, based on the following equation:

$$\ln K_a = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{5}$$

where K_a (q_e/C_e) is the equilibrium constant or the linear adsorption distribution coefficient, T is the solution temperature (K), and R is the gas constant (8.314×10^{-3} kJ/mol/K).

The values of ΔS° and ΔH° were obtained from the intercept and slope of the plot ln K_a vs. $1/T$ and these values are shown in Table 3. The negative value of ΔG° indicates the spontaneous nature of the adsorption of CR onto the adsorbents; the positive value of ΔH° indicates that the dye adsorption process was endothermic in nature; whereas the positive value of ΔS° suggests increased randomness at the solid/liquid interface with some structural changes obtained in the adsorbate and adsorbent system for the adsorption of CR [27,28]. These changes are likely to be more pronounced for HDTM which has higher value of ΔS° than the other adsorbents.

4. Conclusion

In this study, the removal of the anionic dye, Congo Red, from solution with the use of surfactant-impregnated bentonite clay was investigated. It was demonstrated throughout this study that bentonite modification with HDTM enhanced the performance of natural bentonite as adsorbent for this particular dye.

An increase in initial dye concentration in the solution increased the amount of CR dye adsorbed onto the HDTM-bentonite. However, at an initial dye concentration of 50 mg/L and higher, the adsorption onto the modified clay remained more or less the same in all except CR adsorbed by HDTM-bentonite.

The batch kinetic studies revealed that the Langmuir isotherm model could better explained the adsorption of CR by NB and BTMA-bentonite, which implies that the binding of CR on those adsorbents occurred on a monolayer. The adsorption of CR onto HDTM-bentonite and THMA-bentonite could not be predicted by the isotherm models as these models did not fit the adsorption patterns. The pseudo-second-order kinetic model was the model suitable to predict the adsorption capacity of all the adsorbents and confirmed the higher performance of the HDTM-bentonite over the rest of adsorbents.

The adsorption process was found to be thermodynamically favourable and endothermic in nature, when using all four adsorbents.

From the results obtained, it can be concluded that the surfactants, BTMA and THMA, cannot be used to improve the adsorption of NB for the removal of anionic dyes. HDTM-bentonite on the other hand is an effective adsorbent in the removal of the anionic dye, CR, from solution. It can also be utilized in industrial wastewater treatment for the removal of anionic dyes.

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