Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.816872

52 (2014) 6703–6711
October

Taylor & Francis
Taylor & Francis Group

Application of natural clay as a potential adsorbent for the removal of a toxic dye from aqueous solutions

Subhransu Sahoo[a], Uma[b], Sushmita Banerjee[c], Yogesh C. Sharma[b,*]

[a]*UG, Department of Chemical Engineering and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi 221 005, India*
[b]*Department of Applied Chemistry, Indian Institute of Technology (Banaras Hindu University), Varanasi 221 005, India*
Tel. +91 542 6702865; Fax: +2368428; email: ysharma.apc@itbhu.ac.in
[c]*Department of Chemistry, University of Allahabad, Allahabad, 211 002, India*

Received 19 February 2013; Accepted 5 June 2013

ABSTRACT

Application of natural clay (NC) was investigated for the removal of a toxic dye, methylene blue (MB) from aqueous solutions. Extensive characterization of NC was carried out. Effect of various parameters on the removal of MB was investigated. During the study of the effect of adsorbent dose, almost a 100% removal was achieved at a higher dose of natural clay. The experiments were carried out at an initial MB concentration of 60 mg/L and at 298 K. The removal of MB by the application of natural clay was feasible, spontaneous, and endothermic in nature. The process of removal was better explained by Langmuir isotherm model.

Keywords: Adsorption; Isotherm; Removal; Methylene blue; Natural clay

1. Introduction

The industries use colors and dyes at large scale for making the articles attractive. The pulp and paper, textile, and dye manufacturing industries use large quantities of dyes and colors in a number of operations and finally dispose the residual quantities in water sources, etc. [1,2]. The textile industry alone discharges about 1.5×10^6 tonnes of dyes annually with its wastewaters. Effluents discharged from dyeing industries are highly colored. These effluents are characterized by high Biochemical Oxygen Demand (BOD) and high chemical oxygen demand (COD). Disposal of this water into the water sources has been reported to be toxic to aquatic fauna and flora [3]. The dyes largely disrupt the biological activity in the water sources. Most of the dyes are mutagenic and carcinogenic and are reported to pose severe health problems to aquatic life and man. They also result in the malfunctioning of kidney, reproductive system, liver, brain, and cause neurological disorders [4]. The health effects of methylene blue are well documented [5,6]. Currently, several physical or chemical processes are applied to treat colored wastewaters. Physical methods have some advantages and disadvantages of the dye removal from wastewaters. Adsorption is one of the most common methods used to remove dyes from the effluents and has an advantage over the other methods due to its low maintenance cost and simple design. Commercial activated carbon has excellent adsorption capacity due to its large surface area and

*Corresponding author.

porous structure, but commercially available activated carbons are very expensive and limit the application to developed nations [3,7,8]. Alternative materials like cellulosic materials, clay minerals, polymers, composite materials including clay, and clay minerals have been applied for the treatment of dye-containing effluents. Natural clay (NC) is a clay mineral, which is mainly composed of alumina and silica [9–11]. Alumina and silica enhance the adsorption capacity of this natural adsorbent and make it an excellent adsorbent for the treatment of wastewaters. The natural abundance of NC makes the process of removal of the pollutants from aqueous solutions cost-effective. Further, it could be used effectively to treat the wide range of dye-laden wastewaters [12–14]. In the present work, NC has been used as a low-cost adsorbent for the removal of MB from its aqueous solutions. Kinetics and equilibrium studies of the process of the removal of methylene blue by NC have been reported in this article. Also, a comparison of the adsorption capacities of NC with other low-cost adsorbent materials has been discussed.

2. Materials and methods

2.1. Adsorbate

The dye methylene blue, C.I. Number 52015, was obtained from Merck, Mumbai, India. The chemical formula of MB is $C_{16}H_{18}C.N_3S.{}_3H_2O$, and the molecular weight is 373.91, and λ_{max} 663 nm. Stock solution of the dye was prepared by dissolving 1.0 g MB in 1,000 mL double distilled water. Working solutions (60–90 mg/L) of the dye were prepared by diluting the stock solution with double distilled water prior to adsorption experiments.

2.1.1. Adsorbent

The natural clay was collected locally from sediments of the river Ganges at Varanasi (25˚18´N, 83˚03´ E). The Ganges is the largest river system of India. The clay was sieved and then washed properly with distilled water. It was then dried in a hot-air oven maintained at 110˚C. The dried sample was ground and sieved to obtain desired particle size (150 μm) and stored in desiccators for further use without any modification.

2.1.2. Analysis of the adsorbent

The FT-IR spectral absorption studies were carried out to assess the presence of various functional groups on the surface of the adsorbent by infrared spectrometer (Simadzu/8400S, Japan). The pellets were prepared by mixing the adsorbent with KBr. The spectral wavelength was covered in 0–4,500 cm^{-1} range.

X-ray diffraction (XRD) analysis of the adsorbent was carried out using X-ray diffractometer (Rigaku, Poeder Diffractometer, Japan) to determine the phase characterization of natural clay. The scanning electron microscopy (SEM) was carried out on a Jeol, Japan, JSM 6390LV microscope equipped with an Oxford Links-Isis energy dispersive X-ray analyzer (EDS). X-ray fluorescence (XRF) analysis (Thermoscientific, ARL uptimx 166) of the sample was carried out to determine its chemical composition.

Point zero charge of the NC was determined by titrimetric method by using NaOH /HCl. About 50 ml of 0.01 M NaCl was taken to know the charge on the surface of clay material.

2.1.3. Batch adsorption studies

Batch adsorption studies for the removal of MB by natural clay were conducted to determine equilibrium time. About 0.25 g of natural clay was mixed with 50 ml of solution of different concentrations of MB in 250 ml stopperd conical flasks. The dose of adsorbent was decided experimentally. All the adsorption experiments were conducted at 298 K, and at the agitation rate of 150 rpm on a thermostatic shaking water bath. After equilibrium time viz. 100 min., the adsorbent was separated from the aqueous phase by centrifugation at 10,000 rpm for 10 min using a centrifuge (Remi 21, India). Except for the study of the effect of pH on the removal of MB, all the experiments were carried out at 6.5 pH.

The residual concentration of dye in supernatant was determined by a UV–visible spectrophotometer (Spectronic 20, Bausch and Lomb) at 663 nm.

The percentage removal of methylene blue at equilibrium on solid phase, q_e (mg/g), was calculated using the following relationship:

$$\% \text{ Removal of MB} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Amount of adsorbed dye per g of solid was determined as under:

$$q_e = \left(\frac{C_i - C_e}{w}\right) \times V \quad (2)$$

where C_0 (mg/l) is the initial concentration of methylene blue, C_e (mg/l) is the equilibrium residual concentration of dye in solution, V is the volume of solution (l) and w (g) is the mass of the natural clay.

3. Results and discussion

3.1. Textural characterization

3.1.1. Infrared studies of natural clay

The IR spectral absorption studies of the adsorbent were carried out on an infrared spectrometer (Shimadzu/8400S). The FT-IR of natural clay has been given in Fig. 1 which clearly reveals the major peaks of natural clay. The band near 3,620.21 cm^{-1} confirmed presence of stretching vibrations of the surface hydroxyl groups (Si–Si–OH, or Al–Al–OH). The other vibration at 1,635.34 cm^{-1} is attributable to the bending of adsorbed water (Fig. 1). In the low frequency range (1,200–650 cm^{-1}), the maximum absorption of silicate minerals was observed at 1,018.49 and 991.23 cm^{-1}, respectively, for NC. Other vibrations at 787.61 and 471.63 cm^{-1} are also the characteristics of silicate minerals. Quartz usually gives two characteristic bands near 800.31 and 787.61 cm^{-1}, as was the case of the studied clay materials reported elsewhere [15].

3.1.2. X-ray diffraction analysis

X-ray diffraction analysis of the adsorbent was carried out by X-ray diffractometer. For the analysis, a copper target with nickel as the filter medium was used. The powder sample for XRD was prepared by putting a thin layer of powder smeared over a glass plate Goniometer. The speed was maintained at 1°$min^{-1}$and orientation was kept from 0° to 100°. The phase of natural clay was determined by using XRD results and using the diffraction peaks from Scherrer formula:

$$X_s = \frac{0.9\lambda}{\mathrm{FWHM}\cos\theta} \quad (3)$$

where X_s = crystallite size (nm), λ = wavelength of monochromatic X-ray beam (nm), $\lambda = 0.154056$ nm for CuKα radiation. FWHM = full width at half maximum for the diffraction peak under consideration (rad), θ = diffraction angle (degree). X-ray diffraction shows (Fig. 2) that the nature of natural clay was crystalline. Natural clay sample consisted mainly of calcite and the additional peaks of quartz. For natural sample, main peak is attributable to clay minerals combined with subordinate peak of quartz. XRD pattern of the randomly oriented powder is shown in Fig. 2.

3.1.3. Scanning electron micrograph

Scanning electron microscopy (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent materials. It is useful for determining the particle shape, porosity and appropriate size distribution of the adsorbent. The SEM studies of the adsorbent were carried out on a Jeol, Japan, JSM 6390LV SEM equipped with an Oxford Links-Isis energy dispersive X-ray analyzer (EDS). The SEM measures the surface morphology of conducting and non-conducting materials by analyzing back scattered electron (BSE) and secondary electron (SE). The chemical compositions are analyzed by EDS.

The SEM image of natural clay (NC), the adsorbent, is shown in Fig. 3 which revealed the presence of dolomite and calcite. The images show a rough surface of the NC. It has many pores and humps along with platy flakes on the surface [16].

3.1.4. X-ray fluorescence

Chemical analysis of NC was carried out by X-ray fluorescence (XRF) (Thermoscientific ARL uptimx 166). The analysis shows that Silica, alumina, and iron oxides are the main constituents of the adsorbent. The analysis has been given in Table 1. The results

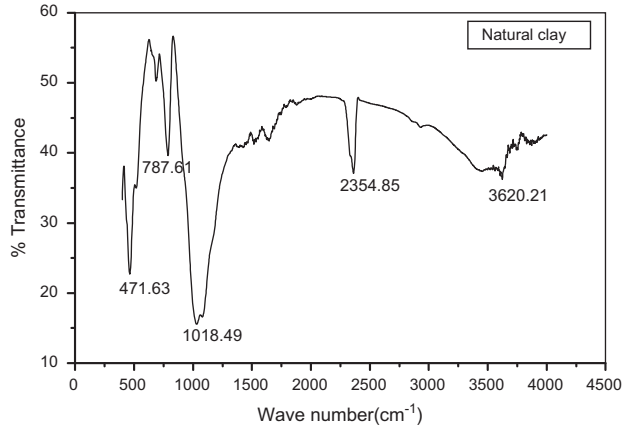

Fig. 1. FTIR of natural clay.

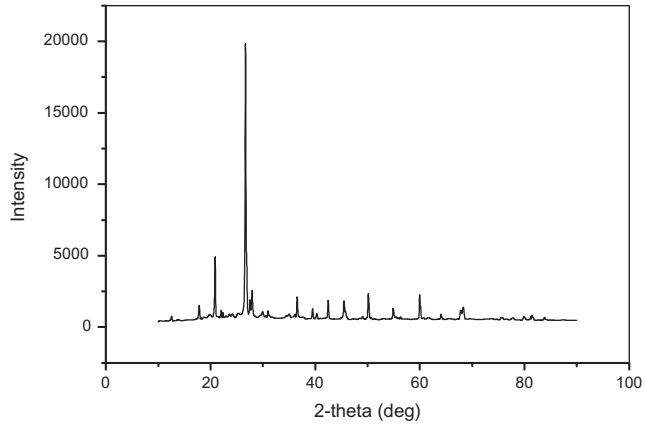

Fig. 2. XRD of natural clay.

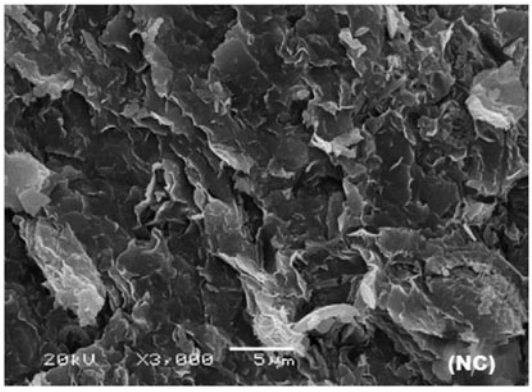

Fig. 3. SEM of natural clay.

indicated that clay contained high amount of calcium and its chemical composition significantly affected the adsorption sites. It should be emphasized that the presence of SiO_2, Al_2O_3, and CaO contents were significant in clay. Such composition would contribute to higher removal of methylene blue due to the presence of these groups at the surface of the natural clay. NC is, in fact a composite of these materials and others which are present in the adsorbent. Authors would like to comment that, depending on the geographical locations, almost all clays possess these compounds in different amounts.

3.1.5. Determination of pH_{zpc}

Determination of pH_{zpc} was done to investigate the surface charge of natural clay by titrimetric method. For the determination of pH_{ZPC}, 0.01 M NaCl was prepared and its pH was adjusted between 2.0 and 12.0 by using NaOH /HCl. About 50 ml of 0.01 M NaCl was taken in the 250 ml Erylenmeyer flasks and 0.20 g of the adsorbent, and NC was added to the solutions. These flasks were kept for 48 h and the pH of the solutions was measured by using a two point calibration pH meter. Graphs were then plotted between "pH_{final} vs. $pH_{initial}$" (Fig. 4). The point of intersection of the curves of "pH_{final} vs. $pH_{initial}$", which comes at 8.04 is the pH_{ZPC} of natural clay [17].

Table 1
Physico-chemical properties of the studied clay samples (% by weight)

Compounds and properties	Natural clay (NC) (% wt)
SiO_2	47.62
Al_2O_3	19.28
Fe_2O_3	7.17
CaO	16.08
MgO	3.21
TiO_2	0.93
K_2O	5.14
Others	0.57
SBET (m^2/g) 16.67	16.67
Total pore volume (cm^3/g)	0.06
pH_{zpc}	8.04

3.2. Effect of contact time and initial concentration

Adsorption experiments were carried out for different initial concentrations and contact time with a fixed adsorbent dosage of 5 g/l (Fig. 5). The removal of methylene blue by NC was found to be rapid in the initial stages and then, it became slow and stagnant with increase of contact time. The equilibrium reached in 100 min after which the removal of MB became steady. For the initial concentration 60 mg/l, the removal increased from 91.25 to 97.84% by decreasing the initial concentration of methylene blue from 90 to 60 mg/l. It is evident that for lower concentrations of dye, the extent of removal (%) is greater and the percent removal of dye decreases with increase in initial concentrations [17,18].

3.3. Effect of temperature

Temperature is an important parameter for adsorption processes and generally has significant impact on extent of removal. It has significant influence on the removal of methylene blue by natural clay also. The effect of temperature was investigated in the temperature range of 298–313 K. The experimental results show that the removal of MB increased from 93.2 to 99.16% by increasing the temperature from 298 to 313 K (Fig. 6) indicating that the process of removal in present case is endothermic [19,20].

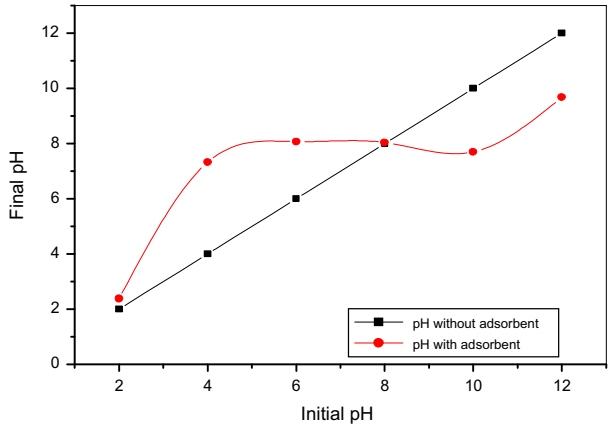

Fig. 4. pH_{zpc} of natural clay.

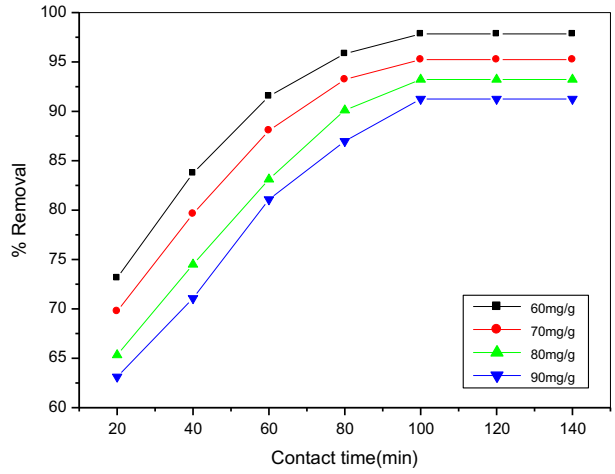

Fig. 5. Maximum removal of methylene blue by adsorption on natural clay at different concentration.

3.4. Kinetic studies

In order to analyze the adsorption kinetics of methylene blue on natural clay, two kinetic models; pseudo-first-order and pseudo-second-order kinetic models were applied for the experimental data. Kinetic studies were made by taking 50 ml of the dye solutions in 100-ml reagent bottles and adding suitable amount of the adsorbent material: 0.25 g of natural clay in 50 ml of solution. The solutions were shaken at regular intervals and after equilibrium the adsorbent was separated from the solutions by centrifugation. Residual concentration of the dye in aliquot was determined spectrophotometrically. For the kinetic studies, the experiments were conducted at 298, 303, 308, and 313 K. Kinetic studies were performed to evaluate the rate constants for the adsorption of methylene blue from aqueous solutions onto natural clay.

3.4.1. Pseudo-first-order kinetic model

The pseudo-first-order kinetic model, also known as Lagergren model is widely used to study adsorption kinetics. The pseudo-first-order kinetic model assumes that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time [19,20]. For the present system, the adsorption kinetics of methylene blue was also studied by pseudo-first-order kinetic equation [20]:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

where q_e and q (both in mg/g) are amounts of methylene blue adsorbed at any time and at equilibrium, respectively, and k_{ad} (min^{-1}) is the rate constant of adsorption. The straight line plots of "log $(q_e - q)$ vs. t" (Fig. 7) confirm that the process of removal of MB by adsorption on NC is governed by first-order kinetics. The values of the rate constant of adsorption were determined by slopes of Fig. 7.

Fig. 7 represents the pseudo-first-order kinetic plots for methylene blue adsorption on natural clay. The value of pseudo-first-order rate constant increased with the increasing temperature for the present system (Table 2). It reveals that higher temperature favors the adsorption of methylene blue on natural clay and confirms that the removal of MB is governed by an endothermic process.

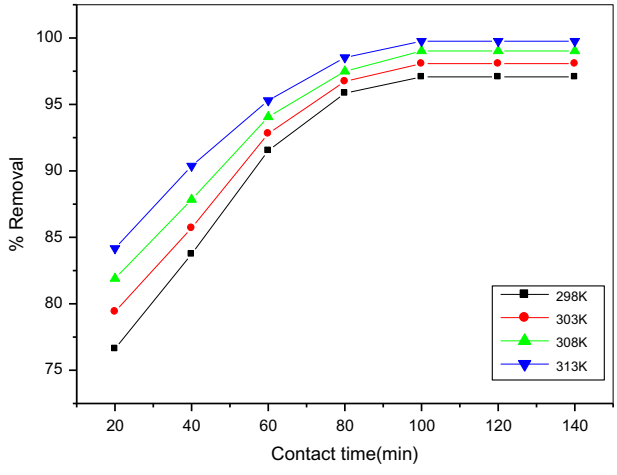

Fig. 6. Maximum removal of methylene blue by adsorption on natural clay at different temperature.

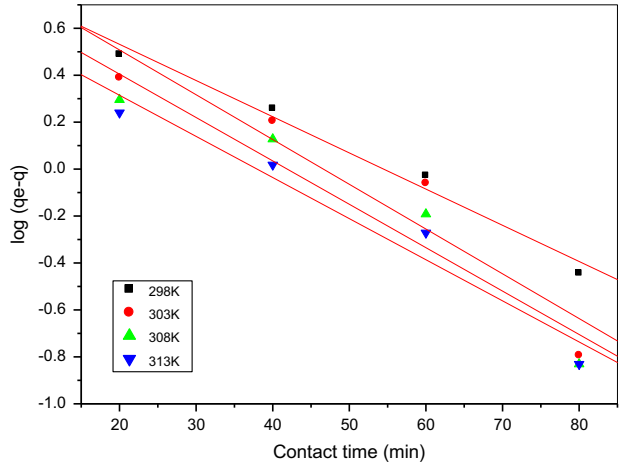

Fig. 7. Pseudo-first-order kinetic plots for the adsorption of methylene blue onto natural clay at different temperature.

Table 2
Values of rate constants of pseudo-first-order ($\times 10^{-2}$ min^{-1}) and pseudo-second-order ($\times 10^{-3}$ $gmg^{-1}min^{-1}$) reaction at different temperatures for the removal of MB by adsorption on natural clay

Temperature (K)	k_1 ($\times 10^{-2}$ min^{-1})	R^2	k_2 (10^{-3} g $mg^{-1}min^{-1}$)	R^2
298	1.54	0.981	2.82	0.998
303	1.75	0.979	2.13	0.997
308	1.84	0.952	1.52	0.997
313	1.90	0.923	1.12	0.997

3.4.2. Pseudo-second-order kinetic model

The adsorption of methylene blue on natural clay is also tested with the second-order kinetic model. The second-order model assumes that the adsorption process is of pseudo-order and that the uptake takes place through chemisorption. The application of the second-order kinetics by plotting "t/q_t vs. t" as shown in Fig. 8, yielded the second-order rate constant k_2, estimated equilibrium capacity q_e, and the coefficient (R^2) for the initial methylene blue concentration ranging from 60 to 90 mg L^{-1} (Table 2). The calculated q_e values show a good agreement with the corresponding experimental values. The values of coefficient of determination (R^2) are more than 0.997 which indicate that the second-order kinetic model describes the removal of methylene blue by adsorption on natural clay better. The second-order kinetic model is expressed as follows [21]:

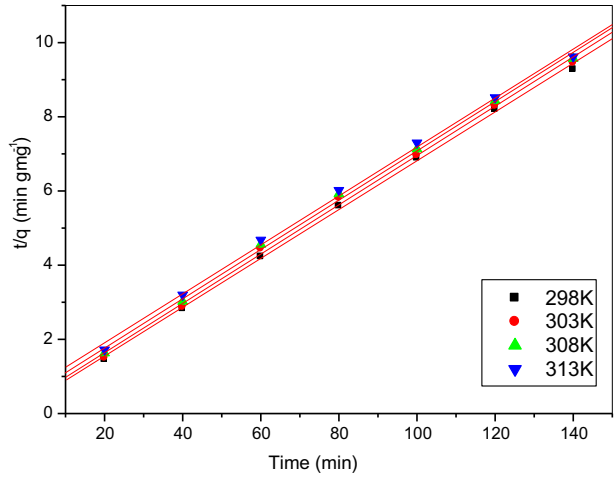

Fig. 8. Pseudo-second-order kinetic plots for the adsorption of methylene blue onto natural clay at different temperature.

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

where k_2 (g/mg min) is the rate constant of pseudo-second-order equation. The integrated form of the above reaction can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{6}$$

$$h = k_2 q_e^2 \tag{7}$$

where h is the initial adsorption rate. The value of q_e and k_2 can be determined by the slope and intercept of the straight line of the plot t/q_t vs. t, respectively.

The values of pseudo-second-order rate constant, k_2 for the removal of methylene blue by the adsorption on natural clay at different temperatures were calculated from the straight line plots of Fig. 8 and their values are given in Table 2. The linear plots (Fig. 8) indicate applicability of this model to the present system. These results indicate that the adsorption of methylene blue on clay follows pseudo-second-order kinetics better than the first-order model. The R^2 value of pseudo-second-order kinetics was greater than the R^2 values for pseudo-first-order kinetics. This further supports the validity of this model for the present system.

3.5. Adsorption isotherms

3.5.1. Langmuir isotherm

Langmuir isotherm model is based on the assumption that the adsorption energy is constant and independent of surface coverage. The maximum adsorption occurs when the surface is covered by monolayer of methylene blue. The linear form of Langmuir isotherm is given as follows [22]:

$$\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \frac{C_e}{Q^\circ} \tag{8}$$

where C_e (mg/l) is the equilibrium concentration of the solute (mg/l), q_e is the amount adsorbed at equilibrium (mg/g), and Q^o (mg/g) and b (l/mg) are constants related to the adsorption capacity and the energy of adsorption, respectively. The plots of "C_e/q_e vs. C_e" (Fig. 9) are smooth and linear indicating that the equilibrium data fit the Langmuir's model. The values of Q^o and b were determined by the slopes and intercepts of Fig. 9 and are given in Table 3.

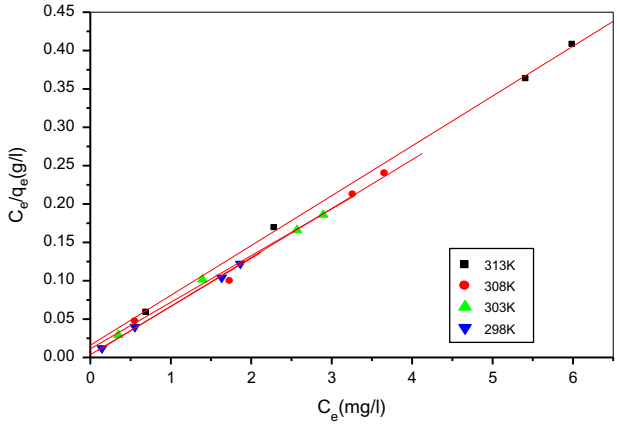

Fig. 9. Langmuir plots for adsorption of methylene blue on natural lay at different temperatures.

3.5.2. Freundlich isotherm

Freundlich model is based on the adsorption of the species on a heterogeneous surface. The adsorption data for the removal of MB on natural clay were fitted to the linear form of Freundlich isotherm [23]:

$$\log q_e = \ln K_f + \frac{1}{n} \log C_e \quad (9)$$

where $\log q_e$ is the amount adsorbed per unit mass of the adsorbate, C_e the equilibrium concentration, and $1/n$ and K_f are Frendulich constants. The constant K_f is related to the degree of adsorption, n provides the tentative estimation of the intensity of the adsorption. The values of these parameters were determined from the straight line plots of "$\log q_e$ vs. $\log C_e$" (Fig. 10).

The values of K_f and n calculated as above are given in Table 3. It may be noted that the value of K_f and n increase with an increase in temperature for the removal of methylene blue on natural clay indicating that the adsorption is favorable at higher temperatures. When the value of n is 1, the adsorption is a linear isotherm. When the value of $n<1$ or $n>1$, which implies that the adsorption process is related to a chemical or favorable physical process, respectively. As shown in Table 3, the value of all n are >1, indicating favorable adsorption process for the removal of methylene blue. As seen in Table 3, the Freundlich isotherm model also fits the experimental better than the Langmuir's model (correlation coefficient $R^2>0.99$), whereas, the Langmuir has the low correlation coefficients ($R^2<0.98$). The monolayer adsorption capacity according to this model was 15.58 mg/g at 298 K.

As the adsorbent used in the present studies is a non-conventional adsorbent, its capacity has been compared with other non-conventional adsorbents

Table 3
Values of constants of Langmuir and Freundlich, isotherms for adsorption of methylene blue on natural clay

Isotherms	Temperature (K)	Parameters		
		Q^o (mg/g)	b (l/mg)	R^2
Langmuir	298	15.40	5.80	0.988
	303	15.70	1.014	0.987
	308	15.93	0.985	0.998
	313	16.28	0.946	0.999
		K_f (l/g)	$1/n$ (l/g)	
Freundlich	298	1.091	0.111	1.0
	303	1.108	0.147	0.989
	308	1.132	0.132	0.977
	313	1.170	0.108	0.999

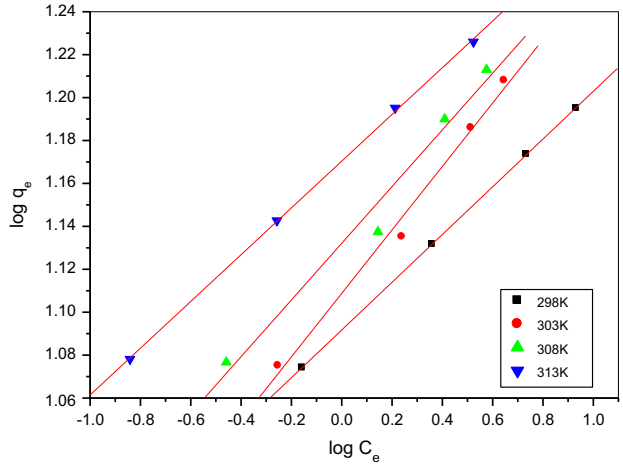

Fig. 10. Freundlich plots for adsorption of methylene blue on natural clay at different temperatures.

(Table 4). Being a well-known adsorbent, the activated carbon has not been included in this table. A comparison of the adsorption capacity of natural clay based on previous studies, the amount of dye adsorption by various other low-cost adsorbents for removal of methylene blue from aqueous solutions is shown in Table 4 [24–34]. Also, the adsorption capacity of NC was compared with silica nano sheets and Ilmenite nano particles [35] which displayed adsorption capacities of 11.77 and 71.9 mg/g. It is clear from Table 4 that NC displayed a higher adsorption capacity than silica nano sheets. In the current study, natural clay samples demonstrated a substantial removal of methylene blue, and it was observed that the adsorption capacity of natural clay for the removal of MB, though not maximum, but is significant and can be used for

Table 4
Comparison of adsorption capacity of several low-cost adsorbents for the uptake of methylene blue from its aqueous solutions

Adsorbents	Sorption capacity Q^o (mg/g)	References
Activated date pits	12.9	[24]
Neem leaf powder	5.87	[26]
Banana peel	20.8	[27]
Corncob based activated carbon	0.84	[28]
Orange peel	18.6	[27]
Fly ash	5.57	[28]
Almond shell-activated carbon	1.33	[4]
Fir wood based activated carbon	1.21	[28]
Glass	2.24	[31]
Clay	6.3	[32]
Aspergillus niger	18.54	[33]
Silica nano-sheets	11.77	[34]
Ilmenite nanoparticles	71.9	[35]
Natural clay	15.4	This study

the removal of methylene blue from aqueous solutions.

3.6. Thermodynamic study

Thermodynamic parameters, such as change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) of adsorption for the removal of MB by adsorption on NC were calculated at 298, 303, 308, and 313 K, respectively. The thermodynamic parameters were calculated using the following equations [36]:

$$K_c = \frac{C_{ac}}{C_e} \tag{10}$$

$$\Delta G^\circ = -RT \ln K_c \tag{11}$$

$$\Delta H^\circ = R\left(\frac{T_2 T_1}{T_2 - T_1}\right) - \ln\left(\frac{K_2}{K_1}\right) \tag{12}$$

$$\Delta S^\circ = \left(\frac{\Delta H^\circ - \Delta G^\circ}{T}\right) \tag{13}$$

where K_c is the equilibrium constant and C_{ac} and C_e (both mg L^{-1}) are the equilibrium concentrations of methylene blue on the surface of (unmodified) clay and the equilibrium concentration of methylene blue in the solution, respectively. The values of these parameters have been given in Table 5. It is clear from Table 5 that the values of ΔG° are negative at all values of temperatures revealing a spontaneous nature of the process of removal of MB in present studies. The values of enthalpy change ΔH° were positive indicating endothermic nature of the process of removal. The value ΔS° was found to be 34.8 calmol^{-1} K^{-1} at 298 K.

Table 5
Thermodynamic parameters for adsorption of toxic dye (methylene blue) onto natural (unmodified) clay at different temperatures

Temperature (K)	ΔG° (kcal mol^{-1})	ΔH° (kcal mol^{-1})
298	−7.029	3.356
303	−7.709	7.388
308	−9.055	14.213
313	−11.508	

4. Conclusions

This study has shown the effectiveness of natural clay as the adsorbent for the removal of methylene blue from aqueous solutions. The NC contained high amounts of carbonates, kaolinite, calcium oxides, and silicates which are responsible for excellent adsorption of MB from aqueous solutions. The FT-IR spectrum of natural clay shows the position of the functional groups available for methylene binding to natural clay. The FT-IR spectroscopy study indicated that the presence of silicates and quartz with hydroxyl groups were the sorption sites for interaction with dye molecules. X-ray diffraction analysis, demonstrated the reordering of the structures on the surface of natural clay. SEM analysis of the natural clays shows that flaky structures are available on the surface. By X-ray fluorescence (XRF) analysis silica, aluminum, and iron oxides are the main components of natural clay. The removal of methylene blue by adsorption on NC was found to be higher in low concentration ranges and this finding has industrial implications. The removal of MB was governed by both pseudo-first- and pseudo-second-order kinetics and the equilibrium data followed Frendulich isotherm better than Langmuir's model. The process of removal of the dye was endothermic, and the thermodynamic studies revealed that the removal of MB is feasible. The experimental data can be used to design treatment plants for the treatment of dye house effluents.

Acknowledgement

The authors are thankful to AICTE, Govt. of India for funding the Scheme (Dev 4061) which supported this work.

References

[1] A. Mittal, J. Mittal, A. Malviya, D. Kaur, V.K. Gupta, Adsorption of hazardous dye crystal violet from wastewater by waste materials, J. Colloid Interface Sci. 343 (2010) 463–473.

[2] C.H. Weng, Y.F. Pan, Adsorption of a cationic dye (methylene blue) onto spent activated clay, J. Hazard Mater. 144 (2007) 355–362.

[3] K. Kadirvelu, C. Karthika, N. Vennilamani, S. Pattabhi, Activated carbon from industrial solid waste as an adsorbent for the removal of Rhodamine-B from aqueous solution: Kinetic and equilibrium studies, Chemosphere 60 (2005) 1009–1017.

[4] A. Aygun, S.Y. Karakas, I. Duman, Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties, Micropor. Mesopor. Mater. 66 (2003) 189.

[5] R. Han, D. Ding, Y. Xu, W. Zou, Y. Wang, Y. Li, L. Zou, Use of rice husk for adsorption of congo red from aqueous solution in column made, Bioresour. Technol. 99 (2008) 2938–2946.

[6] V.V.B. Rao, S.R.M. Rao, Adsorption studies on treatment of textile dyeing industrial effluent by flyash, Chem. Eng. J. 116 (2006) 77–84.

[7] P.S. Kumar, S. Ramalingam, C. Senthamarai, M. Niranjana, P. Vijayalakshmi, S. Sivanesan, Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions, Desalination 261 (2010) 52–60.

[8] A. Gil, F.C.C. Assis, S. Albeniz, S.A. Korili, Removal of dyes from wastewaters by adsorption on pillared clays, Chem. Eng. J. 168 (2011) 1032–1040.

[9] Y.C. Sharma, B. Singh, A. Agrawal, C.H. Weng, Removal of chromium by riverbed sand from water and wastewater: Effect of important parameters, J Hazardous Mater. 151 (2008) 789–793.

[10] Z. Li, C. Po-Hisang, J. Wei-The, J. Jiin-Shuh, H. Hanlie, Mechanism of methylene blue removal from water by swelling clays, Chem. Eng. J. 168 (2011) 1193–1200.

[11] C.A.P. Almeida, N.A. Debacher, A.J. Downs, L. Cotteta, C.A. D. Mello, Removal of methylene blue from colored effluents by adsorption on montmorillonite clay, J. Colloid Interface Sci. 332 (2009) 46–53.

[12] V. Gomez, M.S. Larrechi, M.P. Callao, Kinetic and adsorption study of acid dye removal using activated carbon, Chemosphere 69 (2007) 1151–1158.

[13] H. Azejjel, J.M. Ordax, K. Draoui, M.S. Rodríguez-Cruz, M.J. Sánchez-Martín, Effect of cosolvents on the adsorption of ethofumesate by modified Moroccan bentonite and common clay, Appl. Clay Sci. (2010) 120–126.

[14] S.S. Tahir, N. Rauf, Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay, Chemosphere 63 (2006) 1842–1848.

[15] S. Harti, G. Cifredo, J.M. Gatica, H. Vidal, T. Chafik, Physicochemical characterization and adsorptive properties of some Moroccan clay minerals extruded as lab-scale monoliths, Appl. Clay Sci. 36 (2007) 287–296.

[16] A. Sdiri, T. Higashi, T. Hatta, F. Jamoussic, N. Tase, Evaluating the adsorptive capacity of montmorillonitic and calcareous clays on the removal of several heavy metals in aqueous systems, Chem. Eng. J. 172 (2011) 37–46.

[17] Y.C. Sharma, Uma, S.N. Upadhyay, An economically viable removal of methylene blue by adsorption on activated carbon prepared from rice husk, The Canadian J. Chem. Eng. 89 (2011) 377–383.

[18] A. Pala, E. Tokat, Color removal from cotton textile industry wastewater in an activated sludge system with various additives, Water Res. 36 (2002) 2920–2925.

[19] Jiwan Singh, Uma, S. Banerjee, Y.C. Sharma, A very fast removal of Orange G from its aqueous solutions by adsorption on activated saw dust: Kinetic modeling and effect of various parameters, Intl. Rev. Chem. Eng. 4 (2012) 1–7.

[20] J. Song, W. Zou, Y. Bian, F. Su, R. Han, Adsorption characteristics of methylene blue by peanut husk in batch and column modes, Desalination 265 (2011) 119–125.

[21] Y.S. Ho, J.C.Y. Ng, G. McKay, Kinetics of pollutant sorption by biosorbents: Review, Sep. Purif. Method. 29 (2000) 189–232.

[22] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[23] H.M.F. Freundlich, Uber die adsorption in losungen, Z. Phys. Chem. 57 (1906) 385–470.

[24] F. Banat, S. Al-Asheh, L. Al-Makhadmeh, Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters, Process Biochem. 39 (2003) 193–202.

[25] D. Kavitha, C. Namasivayam, Experimental and kinetic studies on methylene blue adsorption by coir pith carbon, Bioresour. Technol. 98 (2007) 14–21.

[26] K.G. Bhattacharyya, A. Sharma, Kinetics and thermodynamics of methylene blue adsorption on neem (*Azadirachta indica*) leaf powder, Dyes Pigments 65 (2005) 51–59.

[27] G. Annadurai, R. Juang, D. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, J. Hazard. Mater. B92 (2002) 263–274.

[28] R.L. Tseng, S.K. Tseng, F.C. Wu, Preparation of high surface area carbons from corncob using KOH combined with CO_2 gasification for the adsorption of dyes and phenols from water, Colloids Surf. A 279 (2006) 69–78.

[29] K.V. Kumar, V. Ramamurthi, S. Sivanesan, Modeling the mechanism involved during the sorption of methylene blue onto fly ash, J. Colloid Interf. Sci. 284 (2005) 14–21.

[30] F.C. Wu, R.L. Tseng, High adsorption capacity NaOH-activated carbon for dye removal from aqueous solution, J. Hazard. Mater. 152 (2008) 1256–1267.

[31] S. Chakrabarti, B.B. Dutta, On the adsorption and diffusion of methylene blue in glass fibers, J. Colloid. Interf. Sci. 286 (2005) 807–811.

[32] A. Gürses, S. Karaca, Ç. Doğar, R. Bayrak, M. Açıkyıldız, M. Yalçın, Determination of adsorptive properties of clay/water system: Methylene blue sorption, J. Colloid Interf. Sci. 269 (2004) 310–314.

[33] Y. Fu, T. Viraraghavan, Removal of a dye from an aqueous solution by fungus *Aspergillus niger*, Water Qual. Res. J. Can. 35 (2000) 95–111.

[34] M. Zhao, Z. Tang, P. Liu, Removal of methylene blue from aqueous solution with silica nano-sheets derived from vermiculite, J. Hazard. Mater. 158 (2008) 43–51.

[35] Y.H. Chen, Synthesis, characterization and dye adsorption of ilmenite nanoparticles, J. Non-Cryst. Solids 357 (2011) 136–139.

[36] Y.C. Sharma, B. Singh, A. Agrawal, C.H. Weng, Removal of chromium by riverbed sand from water and wastewater: Effect of important parameters, J. Hazard. Mater. 151 (2008) 789–793.