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## Kinetics and isotherm studies for adsorptive removal of methylene blue from aqueous solutions using organoclay

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The presence of dyes in various industrial effluents has emerged as a global environmental concern. The removal of dyes from effluents thus becomes essential to reduce their risks to different life forms. Keeping this in view, raw bentonite (Ben) has been modified with hexadecyltrimethylammonium bromide (HDTMA-Br) by cation exchange to form HDTMA modified bentonite (HDTMA-Ben). Both Ben and HDTMA-Ben were analyzed using Brunauer–Emmet–Teller (BET) method, Scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy and Thermogravimetric analysis (TGA). Studies are conducted at room temperature to determine the behaviour of Ben and HDTMA-Ben towards the adsorptive removal of Methylene blue (MB) from aqueous solutions. Thermodynamics studies were carried out to assess the effect of temperature on adsorption behaviour of both the adsorbents. The experimental adsorption capacity of HDTMA-Ben at equilibrium time was found to be 93.14 mg g<sup>-1</sup>. Characterization results revealed insertion of alkylammonium chain in between the layers of bentonite. Thermodynamics data indicated that the adsorption is spontaneous, exothermic and enhanced on increasing temperature. HDTMA-Ben showed higher dye removal efficiency in comparison to Ben under all conditions. The adsorption data of both the adsorbents was better explained by Freundlich isotherm whereas the pseudo-second-order (PSO) model explained the adsorption kinetics of the adsorbents.

**Keywords:** Adsorption, Bentonite, Hexadecyltrimethylammonium bromide, Methylene blue, Surfactant

The discovery of synthetic dyes has revolutionized the coloring process due to their numerous advantages like colorfastness, cheapness, versatility etc. At present >10,000 commercial dyes are available which are being used in numerous industries like textiles, paper, plastic, rubber, leather, cosmetics and many others<sup>1,2</sup>. During the dyeing process, a significant amount of dyes remain unreacted that is discharged with effluents from industries using them for colouring<sup>3</sup>. In most of the developing nations like India, the colored effluents are released into the water bodies without any treatment. Most of the synthetic dyes are toxic and adversely affect human beings and other life forms<sup>4</sup>. Aquatic flora and fauna are highly affected as the color imparted by these effluents to the water bodies hinder sunlight to penetrate water and thereby adversely affecting the photosynthetic process in phytoplanktons<sup>5</sup>. Moreover, most of the synthetic dyes are highly water-soluble thus tend to resist degradation by physical, chemical and biological means<sup>4,6</sup>. In the present study, methylene blue had

been selected as a model dye because of its extensive utilization in textile, paper and many other industries<sup>1</sup>. It can cause nausea, vomiting and large doses may lead to abdominal and chest pain, profuse sweating, mental confusion<sup>7</sup>. Many physical, chemical and biological techniques have been employed to remove these toxic dyes from effluents till now. Unfortunately, most of them failed to show much impact during scale-up due to higher cost, operational difficulty, material availability, etc. Amongst all, adsorption has emerged as the most promising technique due to its versatility, simplicity and ease<sup>8,9</sup>. Nowadays, researchers are looking for adsorbents that not only possess high dye adsorption potential but are also cheap, eco-friendly and abundantly available. Bentonite, one of the naturally available clay minerals, may serve as an ideal material for the removal of the toxic dyes from coloured effluents. Intercalation of cationic surfactant in between the layers of bentonite not only changes its surface properties from hydrophilic to hydrophobic, but also

enhances the basal spacing of the layers<sup>5,10</sup>. Thus, hexadecyltrimethylammonium bromide (HDTMA-Br) was used to modify raw bentonite (Ben) by replacement of exchangeable cations with organic chain of surfactant to form HDTMA-Ben. The study was also conducted to evaluate the potential of HDTMA modified bentonite for the treatment of aqueous solutions containing methylene blue. The equilibrium data was evaluated through different isotherm models *viz.* Langmuir, Freundlich and Temkin. To understand the adsorption mechanism, various kinetic models such as pseudo-first order (PFO), pseudo-second order (PSO), and intra-particle diffusion (IPD) model were used.

### Experimental Section

Commercially available bentonite was obtained from CDH Ltd. (India). MB and HDTMA-Br were procured from Sigma-Aldrich, India and SD Fine Chemicals Ltd., Mumbai respectively. Double distilled water was used for the entire study. The solution pH was adjusted using 0.1 N HCl and 0.1 N NaOH solution. Shimadzu UV-1800 spectrophotometer was used for the quantitative analysis of MB in the solution. SEM analysis was done using Zeiss<sup>®</sup> EVO 18, FT-IR spectra was analyzed by Nicolet<sup>™</sup> iS50 FTIR Spectrometer, XRD pattern was studied using Panalytical X'Pert Pro and TGA analysis was done using Perkin Elmer Pyris Diamond analyzer. The surface area was determined based on BET method using Micromeritics 3 Flex 3500.

#### Preparation of HDTMA modified bentonite

Cation exchange capacity (CEC) was determined by an earlier reported method<sup>11</sup>. Bentonite and 0.1M NaCl solution (in 1:10 ratio) were stirred on a magnetic stirrer at 60°C for 6 h. The resultant mixture was centrifuged and washed several times with distilled water to obtain Na-bentonite through the replacement of all the exchangeable cations with the Na<sup>+</sup>. HDTMA-Ben was prepared through the cation exchange of Na<sup>+</sup> with alkylammonium ions of HDTMA. Na-bentonite was mixed with HDTMA (twice the CEC of bentonite) and the contents were stirred for 6 h at 60°C. This colloidal mixture was then centrifuged and finally dried at 70°C for 24 h to obtain HDTMA-Ben.

#### Adsorption studies

Batch studies were carried out at room temperature for determining the adsorption behavior of Ben and HDTMA-Ben on MB. The amount of MB remained

in the solution after adsorption was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad \dots (1)$$

where,  $q_e$  is the amount of MB at time  $t$  ( $\text{mg g}^{-1}$ );  $V$  is the volume of MB solution (L),  $C_0$  and  $C_e$  are the initial and the equilibrium MB concentration respectively ( $\text{mg L}^{-1}$ ) and  $M$  is the amount of the adsorbent (g).

#### Thermodynamic studies

To assess the adsorption behaviour of Ben and HDTMA-Ben at different temperatures, 200 mg of Ben was added to 200  $\text{mg L}^{-1}$  of 50 mL MB dye solution. The contents were shaken for 180 min on orbital shaker at different temperatures (298, 308 and 318K). The obtained solutions were then filtered and the filtrates were analysed with UV-Vis spectrophotometer. Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were calculated to determine the nature of the adsorption process. A similar procedure was followed with 100 mg of HDTMA-Ben and 200  $\text{mg L}^{-1}$  of MB at different temperatures to determine the above-mentioned parameters.

### Results and Discussion

#### Characterization of adsorbents

The N<sub>2</sub> adsorption-desorption isotherms of Ben and HDTMA-Ben are illustrated in Fig. 1. The isotherms of both the adsorbents were of type IV adsorption-desorption isotherm. The obtained surface area of HDTMA-Ben (41.865  $\text{m}^2 \text{g}^{-1}$ ) was higher in comparison to Ben (35.068  $\text{m}^2 \text{g}^{-1}$ ). This could be attributed to the higher availability of adsorption sites in comparison to bentonite. Fig. 1 shows the variation of pore volume with pore width. The pore diameter of Ben and HDTMA-Ben was found to be 13.54 nm and 15.48 nm, respectively that included major mesopores having diameter in the range of 2 to 50 nm. The length of a methylene blue molecule is 1.382 nm or 1.45 nm<sup>12</sup>, and the width is approximately 0.95 nm. Considering the length of the MB molecule and the pore sizes of adsorbents, MB molecules can easily enter into the pores of the adsorbents<sup>13</sup>. FT-IR spectra of both the adsorbents are shown in Fig. 2. The broad absorption bands in both adsorbents at 3620  $\text{cm}^{-1}$  were due to O-H stretching vibrations of the Si-OH (silanol) and Al-OH groups of

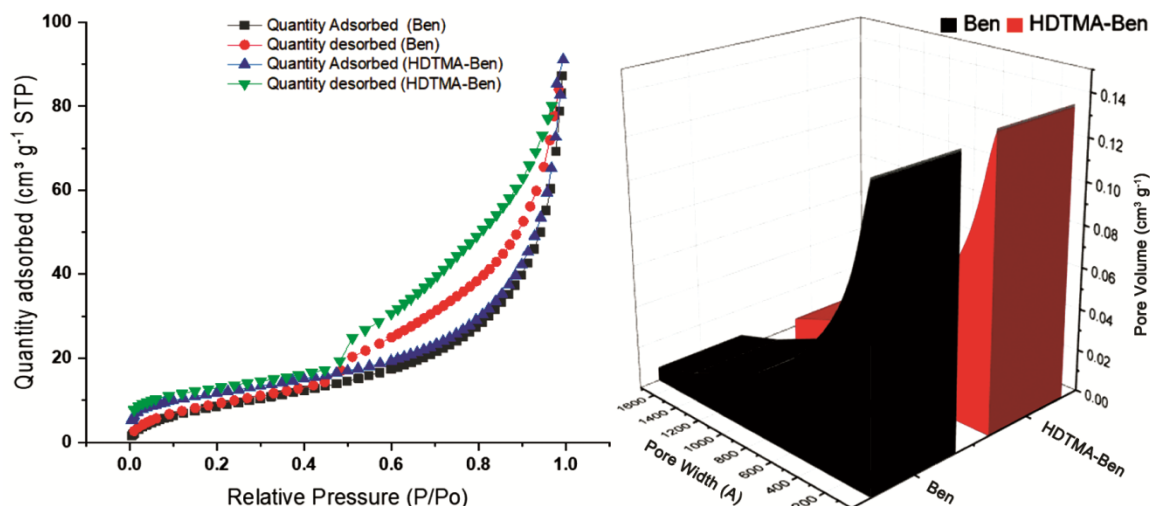


Fig. 1 — N<sub>2</sub> adsorption-desorption isotherm (left) and variation of pore volume with pore width (right)

Ben and HDTMA-Ben<sup>5</sup>. Two bands at 2850 cm<sup>-1</sup> and 2920 cm<sup>-1</sup> in HDTMA-Ben attributed to the asymmetric and symmetric stretching vibrations of the -CH<sub>3</sub> and -CH<sub>2</sub> groups of aliphatic chain of the HDTMA<sup>14,15</sup>. The band at 1640 cm<sup>-1</sup> corresponded to the -Si-O-H deformation vibration in raw bentonite. The deep bands at 1034 cm<sup>-1</sup> in Ben and HDTMA-Ben represented Si-O stretching in the Si-O-Si groups of the tetrahedral sheet<sup>15</sup>. The absorption band at 700 cm<sup>-1</sup> attributed to the -OH bending vibrations indicating octahedral sites occupied by Al<sup>3+</sup> ions<sup>16,17</sup>. The Si-O-Al and Si-O-Si bending vibrations appeared at 532 and 466 cm<sup>-1</sup>, respectively<sup>18</sup>. The SEM images of Ben and HDTMA-Ben (Fig. 3) revealed significant changes in the surface morphology of Ben after modification with HDTMA. As shown in Fig. 3(a), Ben exhibited a less porous surface whereas HDTMA-Ben [Fig. 3 (b)], showed a more porous surface with some fibers reaching out by the introduction of HDTMA, which further confirmed the intercalation of alkylammonium ions in between the layers of bentonite. The XRD patterns of Ben and HDTMA-Ben are shown in Fig. 4. The basal spacing of Ben was found to be 1.40 nm corresponding to the d<sub>001</sub> plane at 2θ = 6.27. After modification with HDTMA, the d<sub>001</sub> peak in HDTMA-Ben shifted to 2θ = 6.03 and the corresponding interlayer spacing of HDTMA-Ben increased to 1.46 nm, indicating enhanced basal spacing by insertion of alkylammonium ions in between the layers of raw bentonite<sup>19</sup>. The TGA of Ben and HDTMA-Ben has been represented in Fig. 4. The initial mass loss of 9% resulted due to the evaporation of water molecules from HDTMA-Ben (in the temperature range of 30-250°C). The second major mass loss of 23%

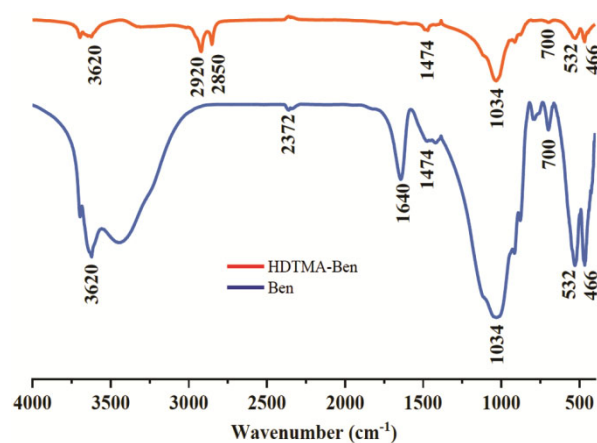


Fig. 2 — IR spectra of Ben and HDTMA-Ben

in the temperature range of 250-600°C corresponded to the decomposition and thermal degradation of cationic surfactant exposed. A small mass loss in the temperature range 600-800°C could be attributed to the dehydroxylation in aluminosilicate layers. In contrast, the raw bentonite TGA curve (Fig. 4) showed a major mass loss of 8% in the temperature range of 30-120°C due to the removal of adsorbed water molecules on the surface. In the temperature range of 120-600°C, raw bentonite showed high stability due to the absence of organic content or surfactant. After 600°C, a small mass loss was observed which could be attributed to the removal of the hydroxyl group (-OH) from the bentonite surface.

#### Adsorption studies

##### Effect of hydrogen ion concentration and adsorbent dose

The pH of dye solutions was varied from pH 3 to pH 11 using 0.1 N HCl and NaOH solutions keeping

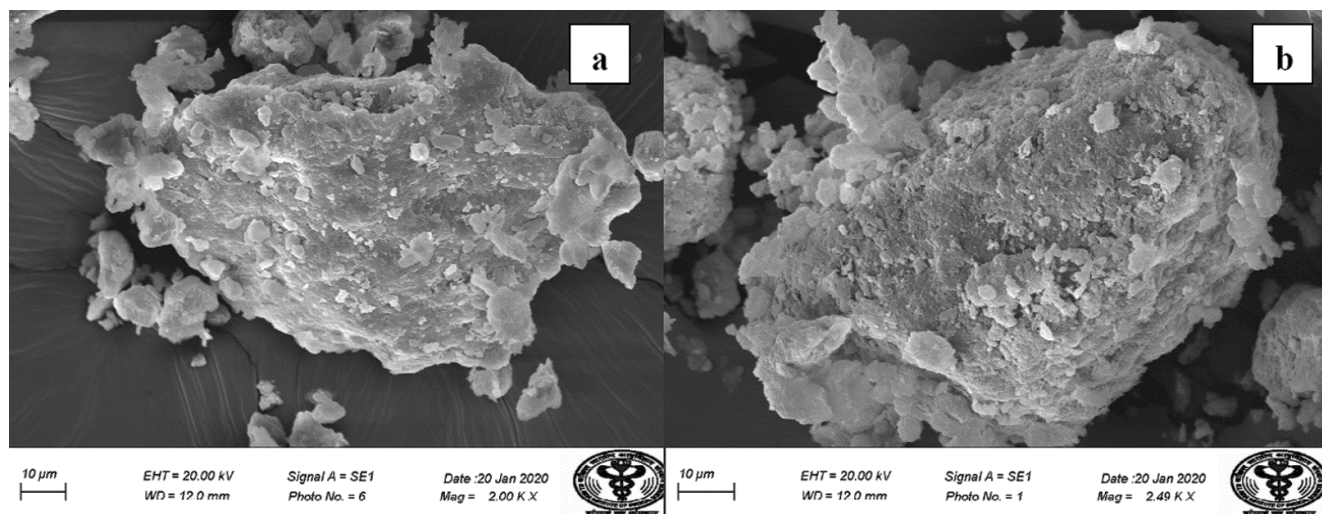


Fig. 3 — SEM images of Ben (a) and HDTMA-Ben (b)

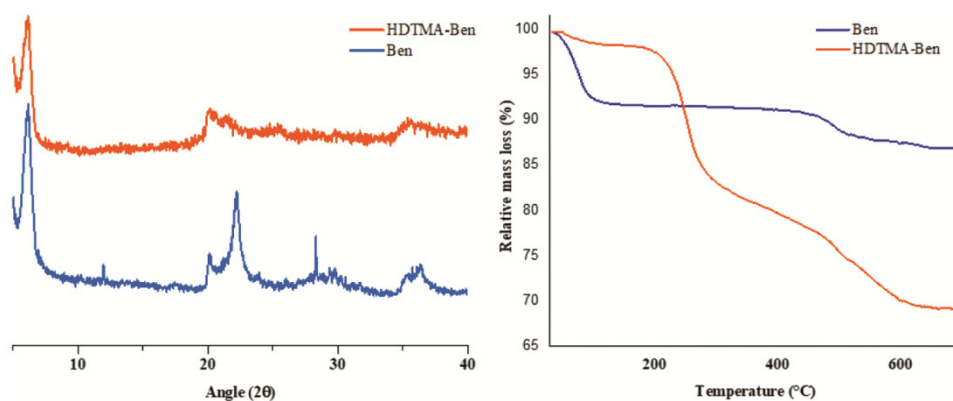


Fig. 4 — XRD pattern (left) and TGA curves (right) of Ben and HDTMA-Ben

the initial dye concentration of MB at  $200 \text{ mg L}^{-1}$ . For both the adsorbents, MB removal efficiency increased with an increase in  $pH$  upto 9 and thereafter became constant. Also, higher MB removal efficiency was observed in HDTMA-Ben in comparison to Bentonite. Because of the highest adsorption efficiency,  $pH$  9 was selected to carry out further adsorption studies. The enhanced adsorption capacity with an increase in  $pH$  is due to the decrease in positive charge on the surface and increase in the negatively charged sites assisting the uptake of MB<sup>5</sup>.

To determine the effect of adsorbent dose on adsorption capacity, the amount of adsorbent was varied from 25 to 250 mg for 50 mL of the dye solution (100 ppm) keeping other factors constant. On increasing adsorbent dose from 25 mg to 200 mg, per cent dye removal increased from 93 to 99. Further increase in the dose did not affect the per cent dye removal and adsorption capacity. Thus, 200 mg was

selected as the optimized dose for adsorption of MB onto Ben adsorbent. Similar results were obtained for HDTMA-Ben although saturation reached at a lower dose than Ben. 100 mg of HDTMA-Ben could effectively remove MB (99%) from 50 mL dye solution of 100 ppm concentration. But, a decrease in the specific adsorption capacity of both the adsorbents was observed with further increase in the dose due to the presence of relatively more active sites in comparison to dye molecules<sup>20</sup>. Also, adsorption capacity was found to be higher in HDTMA-Ben than Ben. Therefore, 100 mg of HDTMA-Ben was selected as the optimum dose for carrying out further studies.

#### *Effect of initial dye concentration and contact time*

The initial dye concentrations of MB were selected in the range of  $25\text{-}250 \text{ mg L}^{-1}$ . The adsorption capacity of both the adsorbents increased with an increase in the initial concentration of MB. At lower

MB concentrations, equilibrium reached at a faster rate due to less competition among dye molecules and the available active sites for adsorption. High initial concentration of MB provided the necessary driving force to overcome MB mass transfer resistance between the aqueous phase and the adsorbents<sup>21</sup>. It also resulted in the enhanced interaction between MB molecules and adsorbents thereby increasing the adsorption capacity. With increase in MB concentration from 25-250 mg L<sup>-1</sup>, the adsorption capacity of Ben increased from 6.165 mg g<sup>-1</sup> to 58.552 mg g<sup>-1</sup> whereas it was found to be in the range 12.491-117.351 mg g<sup>-1</sup> for HDTMA-Ben. The equilibrium time was found to be dependent on concentration of MB. It was found that at lower MB concentrations, the equilibrium time was found to be 20 min whereas time of 60 min was sufficient to attain the equilibrium at higher MB concentrations. Thus, the studies were conducted for 240 min to ensure the attainment of full equilibrium.

#### Adsorption isotherms

The adsorption data of both adsorbents were fitted with non-linear Langmuir, Freundlich and Temkin adsorption isotherms<sup>22</sup>. The adsorption isotherms were obtained at initial dye concentrations in the range 25-250 mg L<sup>-1</sup>. The isotherm parameters are shown in Table 1 and corresponding curves are depicted in Fig. 5. The results of adsorption studies indicated higher MB removal efficiency of HDTMA-Ben in comparison to Ben. Freundlich isotherm model was found to be best fitted with the obtained adsorption data for both the adsorbents. The value of coefficient of determination ( $r^2_{adj}$ ) was found to 0.984 and 0.951 for Ben and HDTMA-Ben, respectively. The results pointed towards adsorption of MB onto

Table 1 — Langmuir, Freundlich and Temkin isotherm parameters for the adsorption of MB onto Ben and HDTMA-Ben

Isotherm	Equation <sup>22</sup>	Parameters	Adsorbents
			Ben
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$q_{m,cal}$	249.821±164.25
		$q_{m,exp}$	47.004
		$K_L$	0.019±0.015
		$r^2_{adj}$	0.976
Freundlich	$q_e = K_F C_e^{1/n_F}$	$K_F$	6.148±1.155
		$n_F$	1.234±0.115
		$r^2_{adj}$	0.984
Temkin	$q_e = \frac{RT}{b_{Tem}} \ln A_{Tem} C_e$	$b_{Tem}$	197.022±50.156
		$A_{Tem}$	2.572±1.798
		$r^2_{adj}$	0.744

the heterogeneous surface of adsorbents<sup>23,24</sup>. The non-linearity and heterogeneity of MB adsorption could also be identified from the value of Freundlich adsorption constant ( $1/n_F$ ). The Freundlich adsorption constant value for Ben and HDTMA-Ben was found to be 0.810 and 0.348, respectively (less than 1) thus suggesting L-type adsorption. Moreover, the non-linear slope suggested physisorption involving weak Van der Waals forces<sup>25</sup>. Similar results were obtained by other researchers<sup>26,27</sup>.

#### Adsorption kinetics

Thenon-linear Pseudo-first-order (PFO) and Pseudo-second-order (PSO) models were utilized to compare the kinetics data<sup>28</sup>. The parameters for adsorption kinetics using PFO and PSO are depicted in Table 2 and their plots are shown in Fig. 6. Kinetic studies of MB adsorption on Ben and HDTMA-Ben revealed higher dye uptake on increasing the contact time though adsorption rates varied. On this basis, the equilibrium time was selected as 60 min because at this particular time nearly 95-99% dye was adsorbed. Kinetic studies revealed that MB adsorption onto Ben and HDTMA-Ben could better be explained by the PSO model in comparison to PFO although their  $r^2_{adj}$  values (0.998 and 0.999 respectively) were comparable. This slight difference suggested that the adsorption of MB on both the adsorbents was physisorption assisted by chemisorption<sup>29</sup>. Physisorption occurred due to the penetration of MB molecules into mesoporous structure of adsorbents whereas chemisorption took place due to the interaction of functional groups present on the surface

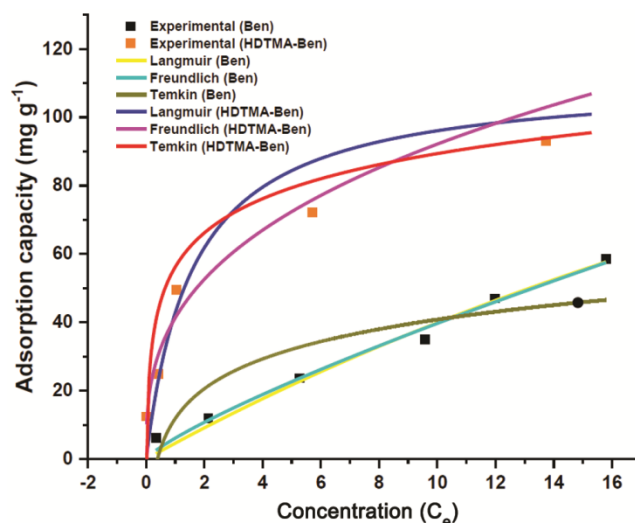


Fig. 5 — Plots of Langmuir, Freundlich and Temkin isotherm models for the adsorption of MB onto Ben and HDTMA-Ben

Table 2 — Non-linear model parameters and  $r^2_{Adj}$  of the studied kinetic models for Ben and HDTMA-Ben

Kinetic model	Equation <sup>28</sup>	Parameters	Adsorbents	
			Ben	HDTMA-Ben
PFO	$q_t = q_e(1 - \exp(-k_1 t))$	$q_{e,exp}$	47.004	93.137
		$q_{e,calc}$	46.467±0.262	92.132±0.498
		$k_1$	0.315±0.037	0.322±0.038
		$r^2_{Adj}$	0.998	0.998
PSO	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$	$q_{e,exp}$	47.004	93.137
		$q_{e,calc}$	47.110±0.171	93.334±0.327
		$k_2$	0.032±0.004	0.017±0.002
		$r^2_{Adj}$	0.999	0.999
IPD	$q_t = k_i t^{1/2} + C$	$k_i$	1.136±0.249	2.112±0.474
		$C$	43.053±0.713	85.794±1.359
		$r^2_{Adj}$	0.738	0.728

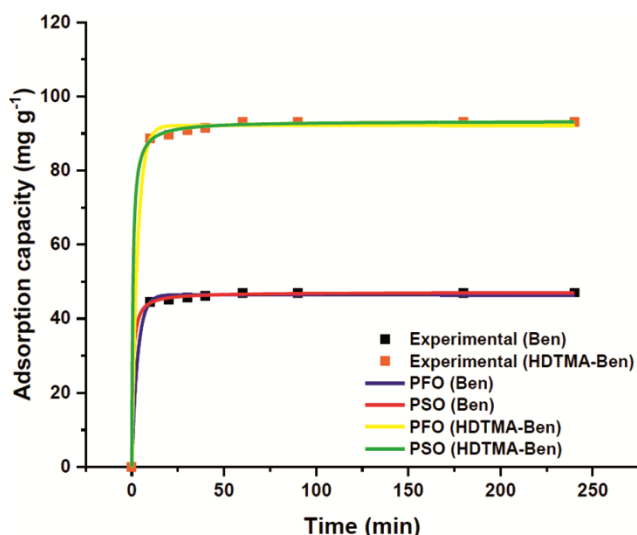


Fig. 6 — Plots of pseudo-first-order (PFO), pseudo-second order (PSO) models for the adsorption of MB onto Ben and HDTMA-Ben

of adsorbent and MB molecules. The results were also supported by studies carried out by other researchers on different adsorbents<sup>30-32</sup>.

#### Adsorption mechanism

The intra-particle diffusion (IPD) model was utilized to understand the adsorption mechanism behind the adsorption of MB onto Ben and HDTMA-Ben. The parameters are shown in Table 2 and the plots are represented in Fig. 7. The values of intercept provide an estimate of the boundary layer thickness<sup>21</sup>. The results showed that the boundary layer effect was significant in adsorption of MB onto HDTMA-Ben in comparison to Ben. Moreover, the intercept value was found to be higher for HDTMA-Ben in comparison to Ben. As observed in the IPD plots (Fig. 7), the plotted line did not pass through the origin indicating that the intra-particle diffusion alone was not the rate-control

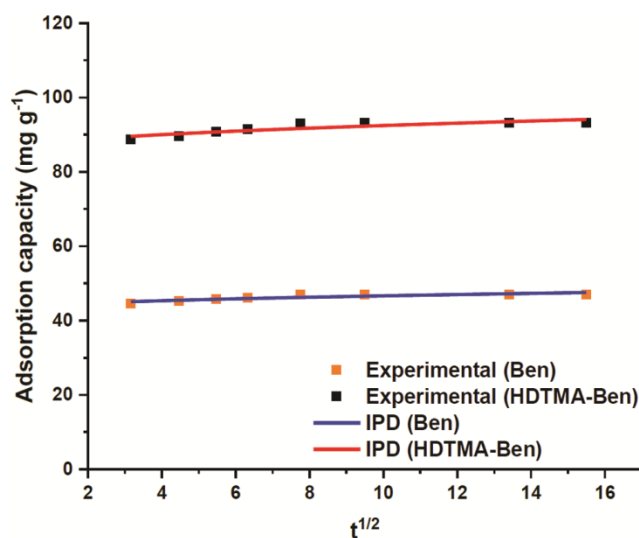


Fig. 7 — Plots of intraparticle diffusion model for the adsorption of MB onto Ben and HDTMA-Ben

ling factor and boundary layer diffusion also contributed to the adsorption process to some extent<sup>33</sup>. The maximum adsorption capacities of Ben and HDTMA-Ben for MB removal were compared with that of different adsorbents reported by other researchers and their values are presented in Table 3.

#### Adsorption thermodynamics

Thermodynamic studies were carried out to assess the spontaneity of adsorption process. The change in Gibbs free energy ( $\Delta G^\circ$ ) was determined using following equation<sup>26</sup>:

$$\Delta G^\circ = -RT \ln K_c \quad \dots (2)$$

where  $\Delta G^\circ$  is Gibbs free energy ( $\text{kJ mol}^{-1}$ ),  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is absolute

Table 3 — Comparison of maximum adsorption capacities of prepared adsorbents with other adsorbents

Adsorbent	Adsorption Capacity (mg g <sup>-1</sup> )	Reference
Clay-biochar composites	7.90	36
Magnetic chitosan-clay beads	82	37
Natural clay (Portugal)	22.2	38
Raw KT3B kaolin (Algeria)	52.76	39
Natural palygorskite (Jiangsu Province, China)	77.92	40
Alginate beads crosslinked	0.22	41
Alginate/almond peanut biocomposite	22.80	20
Magnetic porous carbon	61.65	42
Iron oxide modified Montmorillonite clay	71.12	43
Ben	47	This study
HDTMA-Ben	93.14	This study

Table 4 — Thermodynamic parameters for adsorption of MB onto Ben and HDTMA-Ben

Adsorbent (Dye)	T(K)	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Ben	298	-12.6178	-8.706	13.302
	308	-12.7633		
	318	-12.958		
HDTMA-Ben	298	-14.773	-11.686	10.281
	308	-14.8043		
	318	-14.9818		

temperature (K) and  $K_c$  is the equilibrium constant ( $C_s/C_e$ ).  $C_s$  and  $C_e$  represent the equilibrium concentration of dye on the adsorbent and in solution respectively (mg L<sup>-1</sup>). The values of enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were calculated from the Van't Hoff equation<sup>26</sup>:

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad \dots (3)$$

The values of thermodynamics parameters for Ben and HDTMA-Ben are represented in Table 4. With increase in temperature, the  $\Delta G^\circ$  values also decreased which suggested an increase in the feasibility of adsorption process.  $\Delta G^\circ$  values were found to be negative which indicated that the adsorption process was spontaneous. The negative values of  $\Delta H^\circ$  suggested that it is an exothermic process. The positive values of  $\Delta S^\circ$  suggested an increase in degrees of disorder and randomness at the solid-solution interface during the adsorption process<sup>34,35</sup>.

## Conclusion

Raw bentonite was modified with cationic surfactant (HDTMA) and used to remove MB from aqueous solution. Characterization studies revealed that the HDTMA modification induced changes in the structure and surface properties of raw bentonite due to the intercalation of alkylammonium ions in between the layers of bentonite. Higher adsorption capacity was observed for HDTMA-Ben in comparison to Ben. The adsorption process was found to be exothermic and spontaneous. The adsorption data of MB on both adsorbents followed PSO kinetic model and the Freundlich adsorption isotherm. Outcomes of this study suggested that HDTMA-Ben hold promise for the removal of cationic dyes and could be exploited on large scale.

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## Conflict of interest

The authors declare no conflict of interest.

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