Removal of Organic Pollutants by Using Surfactant Modified Bentonite

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Summary: Naturally abundant bentonite clay minerals have high cation exchange capacity (80–120 meq/g), greater surface area, enhanced swelling properties with micro and meso-porosity. However, their hydrophilic surface limits their adsorption ability. In the present study, bentonite clay (BT) was modified with a cationic surfactant by using cation exchange reaction to modify its surface from hydrophilic to hydrophobic; thus making it a better adsorbent for the removal of pollutants from contaminated water. The modified clay was characterized through fourier transform infrared spectroscopy, and thermo gravimetric analysis. It was used as an adsorbent for the removal of methyl orange and deltamethrin from aqueous solutions. The results showed that modified bentonite has strong tendency to remove organic pollutants from water. About 97% removal of methyl orange was observed with surfactant modified bentonite in contrast to only 56% removal with unmodified bentonite. Similarly, modified bentonite removed up to 98% deltamethrin as compared to only 47% removal with unmodified bentonite. Kinetic study of both experiments showed that the absorption process follows a pseudo second order equation.

Keywords: Bentonite; CTAB-BT; Deltamethrin; Methyl orange, Adsorption.

Introduction

Ground water gets polluted by mixing of waste materials which affects all living organisms including plants [1]. A wide variety of pollutants including dyes and pesticides are excessively introduced into aquatic environment at high pH and at high temperature from various sources including agricultural runoff, industrial waste, and chemicals spill [2].

Dyes are excessively used in paper and textile industries, while pesticides are widely used in agricultural fields to limit the growth of weeds and insects on plants [3]. Methyl orange is water soluble azo dye used as pH indicator and also has many applications in industries. Prolong exposure of methyl orange causes abrasive damage to skin [4]. Its LD_{50} value is 60 mg/kg (rat/oral). Deltamethrin is a white colored synthetic pyrethroid insecticide basically used for crop protection, and to protect stored cargoes. High concentration of Deltamethrin insecticide damages aquatic life and causes skin irritation. Its US EPA limit is 0.05ppm in drinking water and food items. The toxic nature of organic dyes and pesticides are harmful to both aquatic life and human beings. Hence these should be removed from water [5].

Various physiochemical treatment procedures have been used for the removal of organic pollutants such as photocatalytic degradation, photodegradation, photo-oxidation and adsorption. Among all, adsorption method is extensively used for the treatment of polluted water due to its effectiveness, low cost, simplicity in design, easy operation and it does not create secondary pollutants [6]. In the most recent couple of decades, distinctive sorts of adsorbents have been utilized for the removal of pollutants from wastewater [7-9].

Bentonite clay consists of 85% Montmorillonite $Al_2Si_4O_{10}(OH)_2nH_2O$ that belongs to Semectite group [10, 11]. An octahedral sheet of alumina $[AlO_3(OH)_3]^{6-}$ is fused with two external tetrahedral silica $[SiO_4]^4$ layer. As a result, the octahedral sheet and tetrahedral sheets belong to same oxygen ions. Negative charge inside the bentonite layer is due to isomorphic substitution and is stabilized by exchangeable cations, such as, K^+ or Na^+ Ca^{2+} [12].

Natural bentonite is hydrophilic in nature and is not an efficient adsorbent for dyes and pesticides from contaminated water. Therefore, in the present study, bentonite clay is modified with a simple cation exchange method by using cationic surfactant cetyltrimethylammonium bromide (CTAB) [13]. The exchange of inorganic cations by organic cations in the interlayer of bentonite is irreversible. Van der Waals interactions between the organic surfactant cations and the reduced solvent shielding of ions in the inter-lamellar environment, change bentonite surface from hydrophilic to hydrophobic. This in turn should markedly increase the adsorption of methyl orange and deltamethrin on the surface of the modified clay.

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In this paper we report the modification process of bentonite with a cationic surfactant cetyltrimethyl ammonium bromide (CTAB). The adsorption of methyl orange and deltamethrin in aqueous solution on the modified bentonite (CTAB-BT) was studied. Different operational parameters like pH effect, time effect and adsorbent concentration effect were premeditated to check the adsorption efficiency. Kinetic studies were applied on the data to determine the order of reaction.

Experimental

The chemicals used in this work are bentonite (Sigma Aldrich), cationic surfactant cetyltrimethylammonium bromide (BDH), deltamethrin (Selmore), methyl orange (Sigma Aldrich), $AgNO_3$ (Merck). All other reagents and chemicals were purchased from Merck.

Synthesis of Na- Bentonite

The Na-BT was synthesized by dispersing bentonite (2.0g/200ml) in distilled water in a round bottom flask. Sodium chloride (NaCl-2.92g/50ml-distilled water, 1N) was added in the solution. The reaction mixture was vigorously stirred on hot plate at 60°C for 24 hours, and the product was washed to remove all chloride ions. Silver nitrate (1 M) test was used to confirm the removal of chloride ions. Purified clay was dried in oven at 80°C for 24 hours. Mortar pestle was used to obtain fine powder of dried sodium bentonite.

Synthesis of Surfactant Modified Bentonite

2.0g Sodium bentonite (Na-BT) was added in 200 ml of distilled water and vigorously stirred in a conical flask for 60 minutes to achieve homogeneity. Aqueous solution of cationic surfactant (0.03M, 0.545gm) cetyltrimethylammonium bromide was slowly introduced to the resultant suspension and again stirred at room temperature for 12 hours.

The synthesized organoclay was centrifuged, washed, dried at 80 °C for 24 hours and grinded to obtain a fine powder.

Adsorption experiment

The adsorption experiments were performed under various conditions to observe the effect of various parameters like effect of contact time, effect of pH (2–12) and effect of adsorbent concentration for the adsorption of methyl orange and deltamethrin from the aqueous solution. 50ml of methyl orange 10, 20, 30, 40, 50ppm (for deltamethrin 100, 200ppm) were taken in two conical flasks and 0.2gm of CTAB-BT was added in each solution separately. Then resultant sample solutions were shaken on shaker at 250 rpm. 5 ml from the solutions was taken out after every 10 min, and centrifuged (4000 rpm for 5 min) at room temperature. The clear filtrate was analyzed by UV-Vis spectrometer.

For pH effect, 10 ml of 10ppm methyl orange (for deltamethrin 100ppm) solution was prepared and pH was adjusted (2, 4, 6, 8, 10, 12). 0.02gm of CTAB-BT was added in each solution separately. Then resultant sample solutions were shaken on shaker at 250 rpm. After 30 min, 5 ml from each solution were taken out and centrifuged (4000 rpm for 5 min) at room temperature. Clear filtrates were analyzed by UV-Vis spectrometer.

For adsorbent concentration, 10 ml of 10ppm methyl orange, (for deltamethrin 100ppm) were taken in conical flasks and 0.01, 0.02, 0.05, 0.1gm of CTAB-BT were added in each solution separately. The resultant sample solutions were shaken on shaker at 250 rpm. After 5 min, 5 ml suspension solutions were taken out and centrifuged (4000 rpm for 5 min) at room temperature. The clear filtrates were analyzed by UV-Vis spectrometer.

The adsorption efficiency for methyl orange and deltamethrin was calculated by using the equation: [2]

$$qe = \frac{(Co - Ce)V}{m} \quad (1)$$

In this,

qe = amount of adsorbent for methyl orange or deltamethrin (mg/g),
Co = initial concentration of methyl orange or deltamethrin (mg/l),
Ce = equilibrium concentration of (methyl orange or deltamethrin) in solution (mg/l),
m = adsorbent mass (g) and
V = volume of solution.

Results and Discussion

FT-IR

FTIR spectra of bentonite (BT) and CTAB-BT are shown in Figure 1 and 2 respectively. In the FTIR spectrum of bentonite, stretching and bending vibrations of water were observed at 3625 cm^{-1} and 1636 cm^{-1}. Asymmetric and symmetric stretching vibrations of Si-O-Si were visible at 988 cm^{-1} and 1118 cm^{-1}.

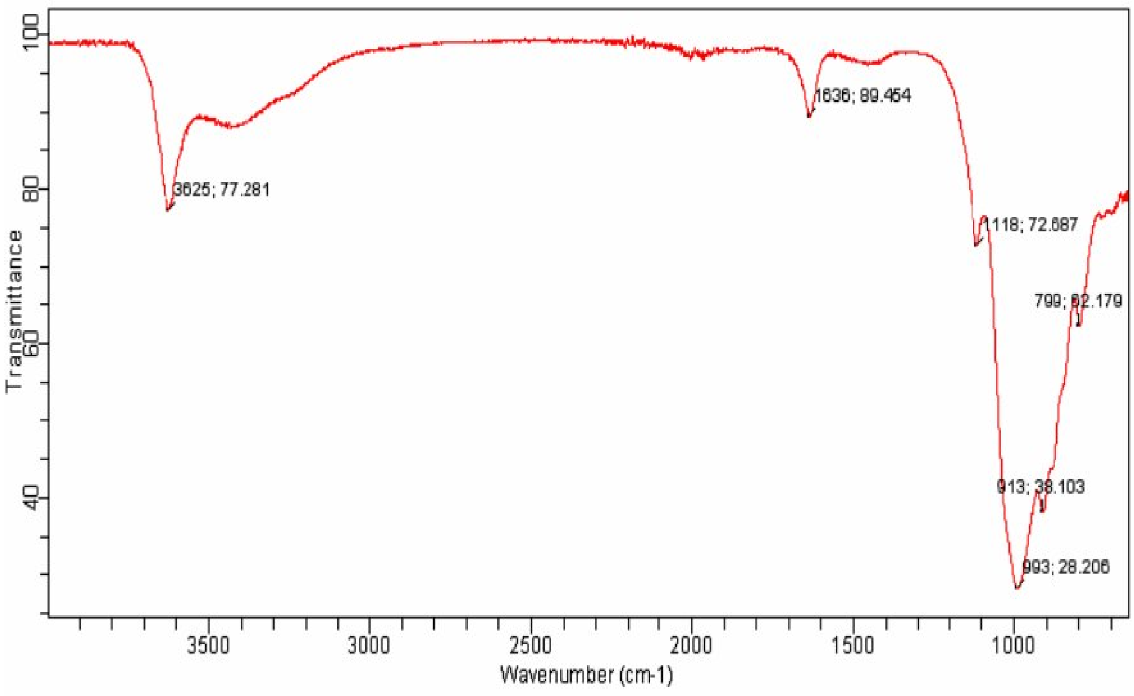


Fig. 1: FT-IR Spectrum of Bentonite.

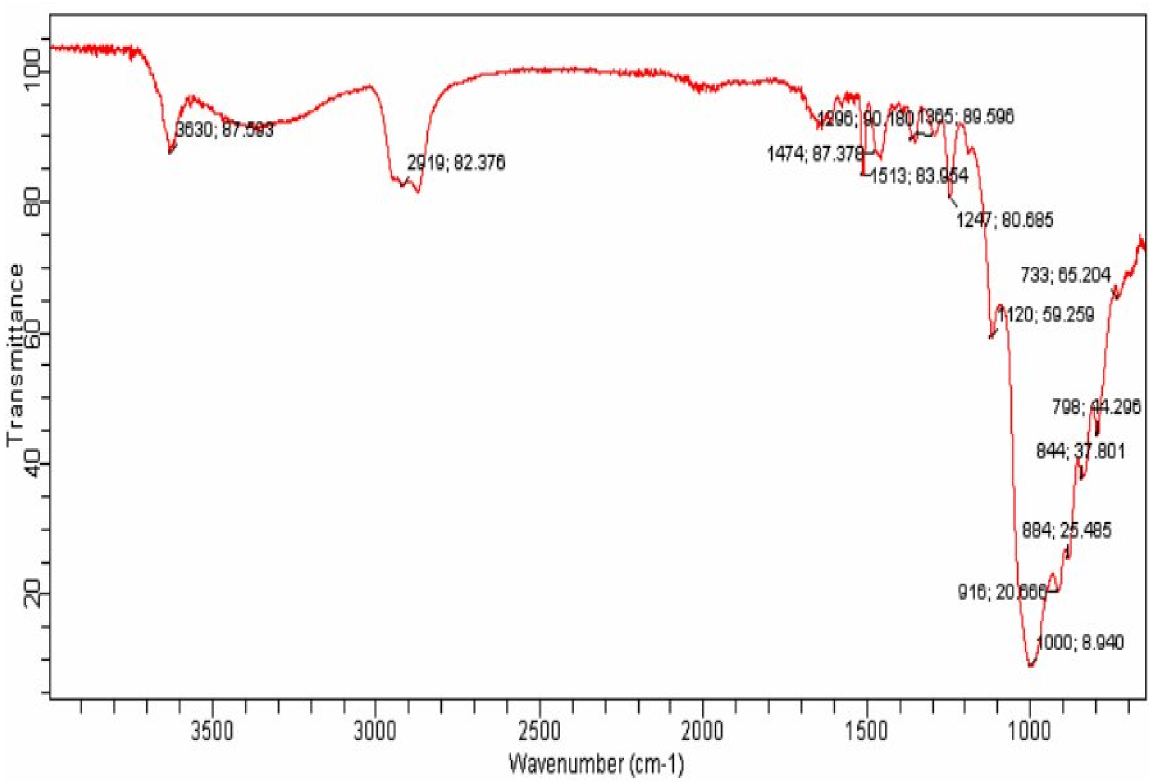


Fig. 2: FT-IR Spectrum of CTAB-Bentonite.

In the FTIR of CTAB-BT, symmetric and asymmetric vibrations of C-H bond were observed at 2857 cm^{-1} and 2920 cm^{-1} respectively. The presence of these bands confirms the attachment of CTAB within the layer of BT. The A small peak at 1475 cm^{-1} corresponds to the presence of NH_4^+ ions that helps in the binding of surfactant to the bentonite surface. Hence FTIR results confirm the incorporation of CTAB on bentonite surface as desired.

Thermogravimetric Analysis (TGA)

Weight loss of modified bentonite with increasing temperature is calculated with TGA graph in Fig. 3. Four steps were included in the weight loss of clay.

1. The evaporation of water molecules from modified clay caused 3% initial weight loss (in temperature range of 30-250 °C).
2. The decomposition and thermal degradation of cationic surfactant exposed second (about 7%) major weight loss in the temperature range of 250-600°C.
3. The dehydroxylation in aluminosilicate layers displayed (about 3%) third weight loss between 600-800°C.

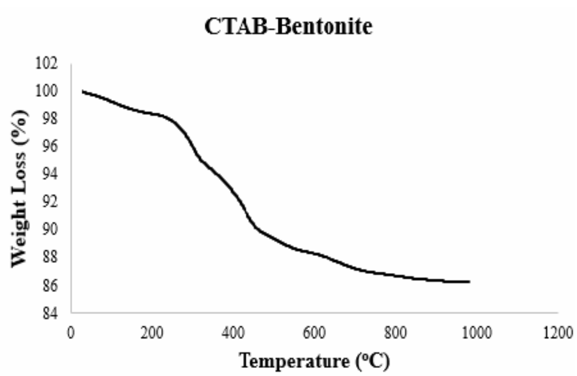


Fig. 3: TGA of CTAB-BT.

In contrast, parent bentonite TGA curve (shown in Figure 4) shows a major weight loss of 6% due to the removal of adsorbed water molecules on the surface between temperature range of 40-120°C. After that the sample showed high stability up to 600°C due to the absence of organic content or surfactant. After 600°C, however a small weight loss was observed that corresponds to the removal of hydroxyl group (OH) from bentonite surface.

Removal of pollutants by using CTAB-BT

As synthesized CTAB-BT was applied for the removal of organic pollutants methyl orange and deltamethrin from aqueous samples. Several adsorption conditions were studied to enhance the removal efficiency of CTAB-BT.

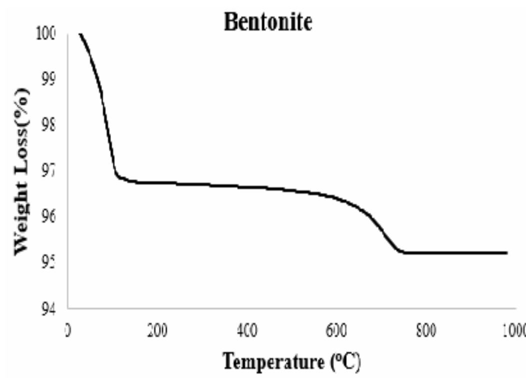


Fig. 4: TGA of BT.

pH Effect

The adsorption tests for pollutants (methyl orange and deltamethrin) were conducted in the pH range 2–12 and results are shown in fig 5 and 6. From acidic to basic, change in pH also changed the adsorption of dye after 30min interaction with the adsorbent.

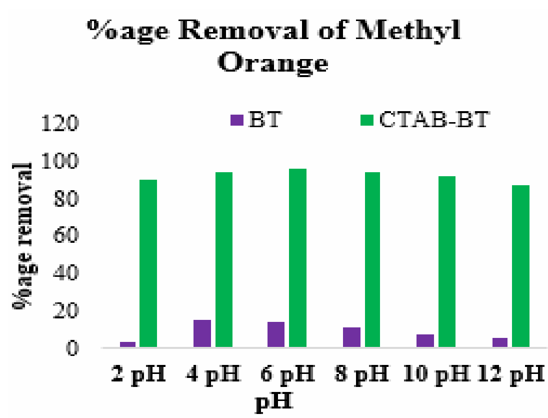


Fig. 5: pH Effect of Methyl Orange.

Methyl orange showed maximum adsorption (96% removal) at pH 6 with CTAB-BT, while only 13% removal was observed with BT. At higher pH, slight decline in adsorption of dye was observed owing to the repulsive forces between anionic character of methyl orange and excess concentration of hydroxyl group (OH^-). Still, substantial adsorption was observed at pH = 8 due to chemical interactions between dye and CTAB-BT.

In case of deltamethrin, maximum removal was observed at pH 8. A marked increase in the removal of deltamethrin was observed with CTAB-BT as compared to BT. At 8 pH, 30 min contact with CTAB-BT gave 97% removal as compared to only 25% removal with BT. Hence modification of bentonite has increased its adsorption ability for deltamethrin.

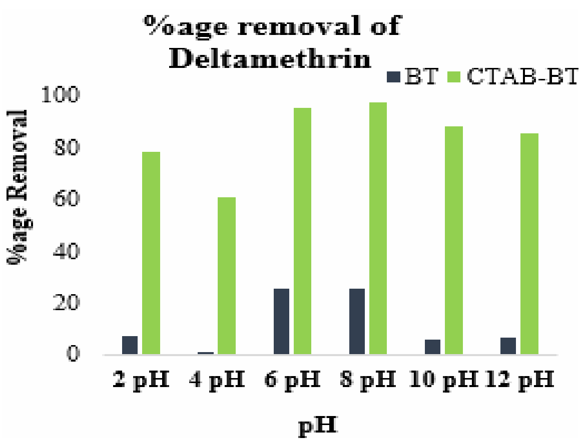


Fig. 6: Effect of pH for adsorption of deltamethrin.

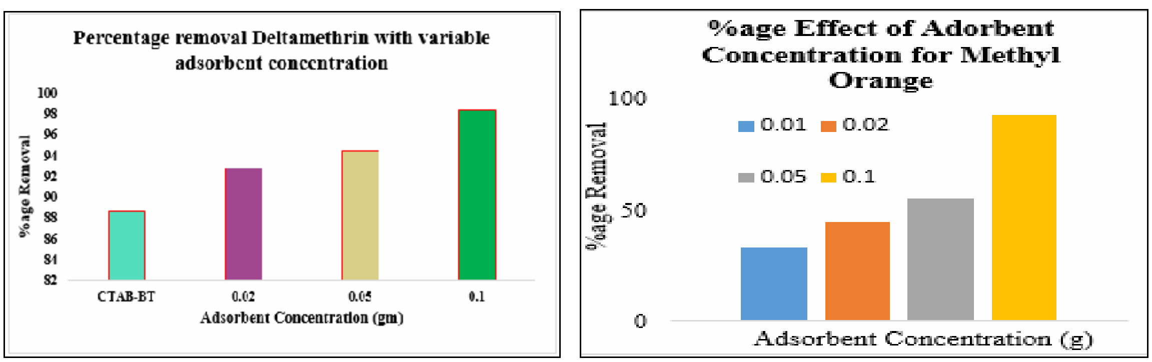
Concentration Effect

Removal of the pollutants from aqueous solutions (dye 10ppm, deltamethrin 100ppm) at different adsorbent concentration ranging 0.01–0.10gm, after 30 min contact time were studied at room temperature. The adsorption efficacy of modified bentonite was found to increase by increasing adsorbent concertation for both pollutants. Maximum adsorption was achieved by using 0.1gm of adsorbent, as shown in Figure 7.

0.1 gm CTAB-BT with 30 min contact time resulted in 93% removal of Methyl orange while 98% deltamethrin was removed under the same conditions. Hence there is a direct relationship between the rate of adsorption of pollutant and to the adsorbent concentration.

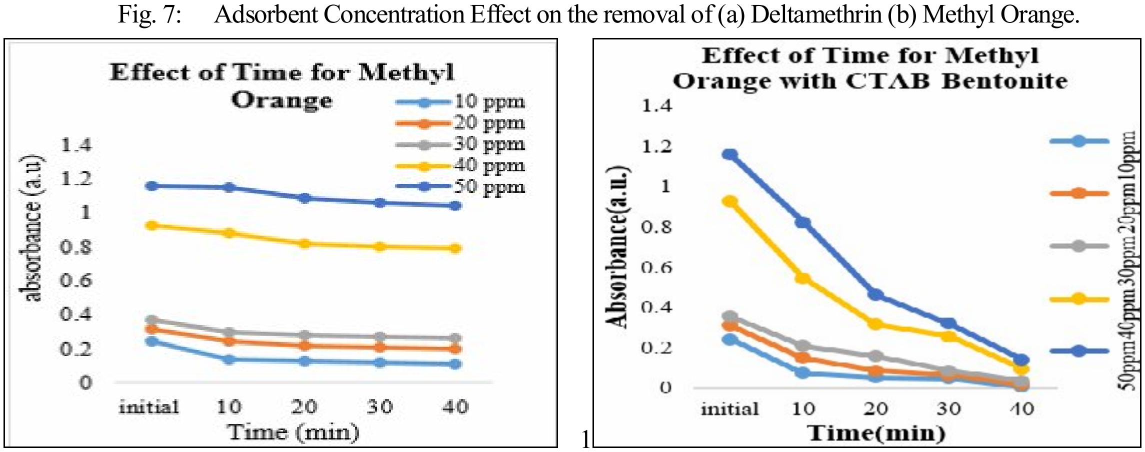
Time Effect

The adsorption process of methyl orange (10–50 ppm solutions) and deltamethrin (100ppm and 200ppm solutions) on BT and CTAB-BT was studied at various time intervals. Only a small decrease in the absorbance of methyl orange solutions shows a very limited adsorption ability of BT. However, when modified bentonite was used as adsorbent, a marked decrease in methyl orange absorbance was detected.



(a) (b)

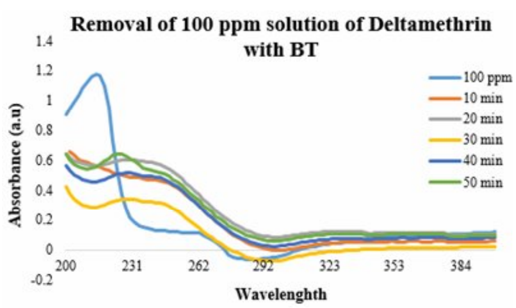
Fig. 7: Adsorbent Concentration Effect on the removal of (a) Deltamethrin (b) Methyl Orange.



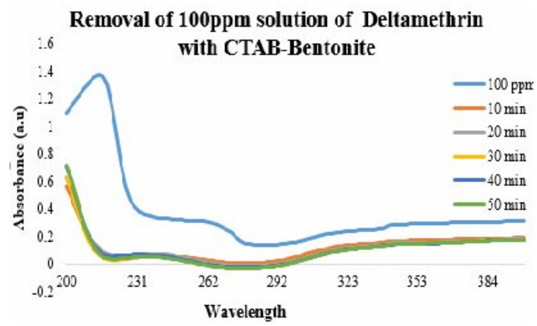
(a) (b)

Fig. 8: Time effect for the removal of Methyl Orange with (a) BT (b) CTAB-BT.

Surfactant modified bentonite (CTAB-BT) showed increased adsorption capacity at low as well as at high concentration of methyl orange. After 40min in 50ppm dye solution, 97% dye was removed while only 56% dye was removed with BT. Hence it can be concluded that CTAB-BT is an efficient adsorbent as compared to BT for the removal of methyl orange from aqueous solutions.



(a)



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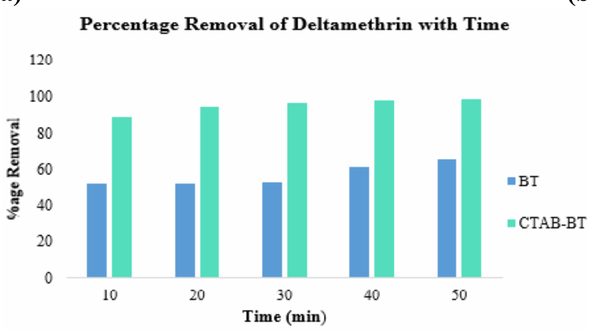
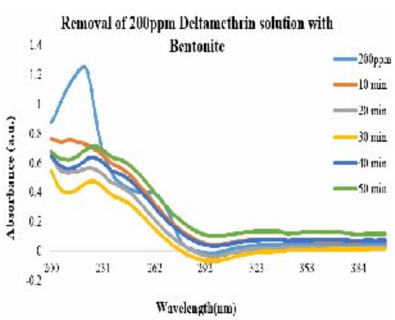


(c)

Fig. 9: Removal of Deltamethrin (100ppm) with (a) BT (b) CTAB-BT (c) Percentage removal.



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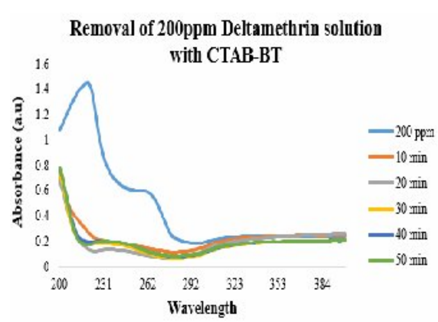

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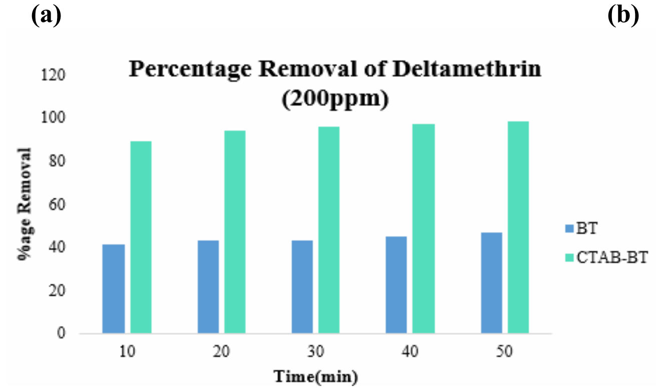


(c)

Fig. 10: Removal of Deltamethrin (200ppm) with (a) BT (b) CTAB-BT (c) Percentage removal.

After 50min BT displayed only 47% removal of deltamethrin from 200ppm solution as compared to 98% removal with CTAB-BT. Hence, we can conclude that synthesized CTAB-bentonite is an exceptional adsorbent for the removal of deltamethrin in highly concentrated solutions.

Kinetic Study

Kinetic study examines the adsorption mechanism of deltamethrin and dye on the adsorbents. The experimental data were checked by using pseudo-first-order and pseudo-second-order models.

Lagergren equation for pseudo first order, kinetic equation is expressed in the form,

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

where q_e and q_t are the values of dyes and deltamethrin at equilibrium and at the time t in mg/g, respectively, and pseudo first order rate constant is k_1 (min^{-1}).

The linear graph of pseudo first order at various initial concentrations of methyl orange and deltamethrin were plotted and it was observed that, this model is not appropriate with the facts and is not suitable for the adsorption of methyl orange and deltamethrin on CTAB-BT.

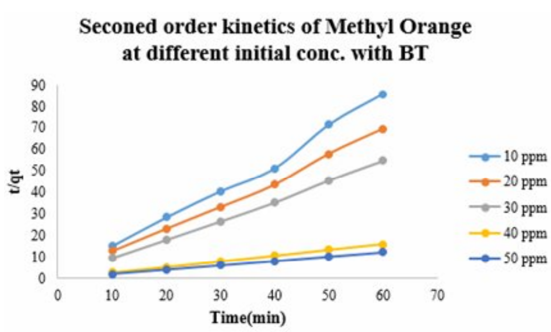
The kinetics equation for pseudo second order reaction was given by Mckay and Ho and is given below. [2]

$$\frac{t}{qt} = \frac{1}{k2qe2} + \frac{t}{qe} \qquad (3)$$

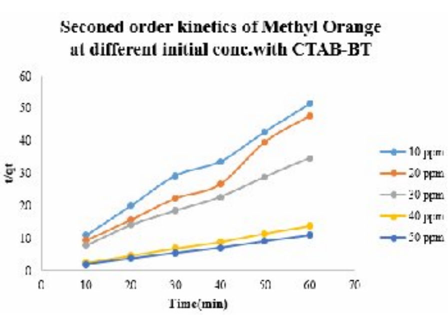
In this, qe is the value of dye and deltamethrin at the equilibrium (mg/g), while qt is the value of dye and deltamethrin at the time t (mg/g), and pseudo second order rate constant is k_2 (min^{-1}).

The linear graph of pseudo second order reaction at various initial concentration of dye and deltamethrin are showed in Fig 13 and 14. Outcomes of pseudo second order equation and the assessed correlation coefficients of each concentrations for the linear graph displayed best agreement of 0.99 for each experimental value and is consistent with previous literature. [3] Hence, it seems that the rate of the dye and deltamethrin adsorption mechanism is followed by chemical method including valency forces by exchange or sharing of electrons between adsorbate and adsorbent.

The calculated kinetic parameters for methyl orange and deltamethrin have been potted in Table-1 and 2.



(a)

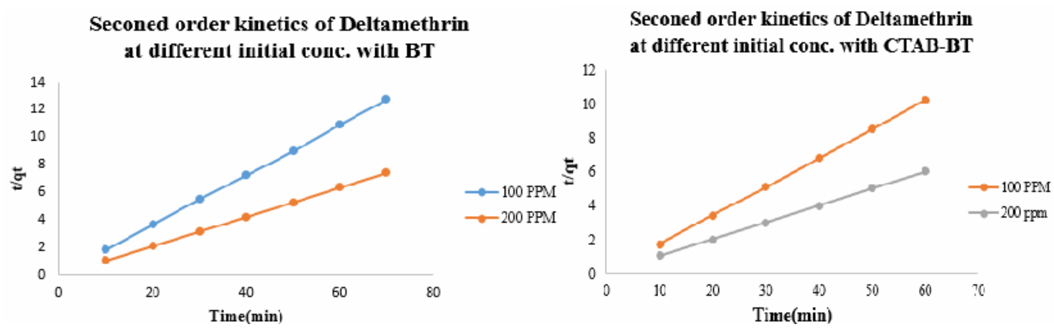


(b)

Fig. 11: Second order kinetics at different initial concentrations of dye (a) with BT (b) with CTAB-BT.

Table-1: Second order kinetics at different initial concentrations of dye.

Initial concentration (ppm)	Pseudo second order					
	BT			CTAB-BT		
	qu (mg/g)	K_2 (1/min)	R^2	qe (mg/g)	K_2 (1/min)	R^2
10	0.713	3.8125	0.9909	1.2702	0.1608	0.9933
20	0.772	3.586	0.9959	1.3055	7.6453	0.9971
30	1.2207	4.566	0.9989	1.9091	0.0976	0.9969
40	14.077	4.496	0.9999	4.438	0.417	0.9985
50	23.951	2.413	1	5.5897	0.3135	0.9989



(a) (b)

Fig. 12: Second order kinetics at different initial concentrations of deltamethrin (a) with BT (b) with CTAB-BT.

Table-2: Second order kinetics at different initial concentrations of deltamethrin.

Initial concentration (ppm)	Pseudo second order					
	BT			CTAB-BT		
	qu (mg/g)	K_2 (1/min)	R^2	qe (mg/g)	K_2 (1/min)	R^2
100	5.513	0.7616	0.9998	5.878	1.65	1
200	6.246	0.7767	1	10.02	0.25	0.998

The adsorption isotherms namely, Langmuir and Freundlich adsorption isotherm models were fitted to experimental data. The applicability of these isotherms was compared by analyzing the correlation coefficients R^2. Fitting of equilibrium data with these isotherms using HA has been reported in Fig.13, 14.

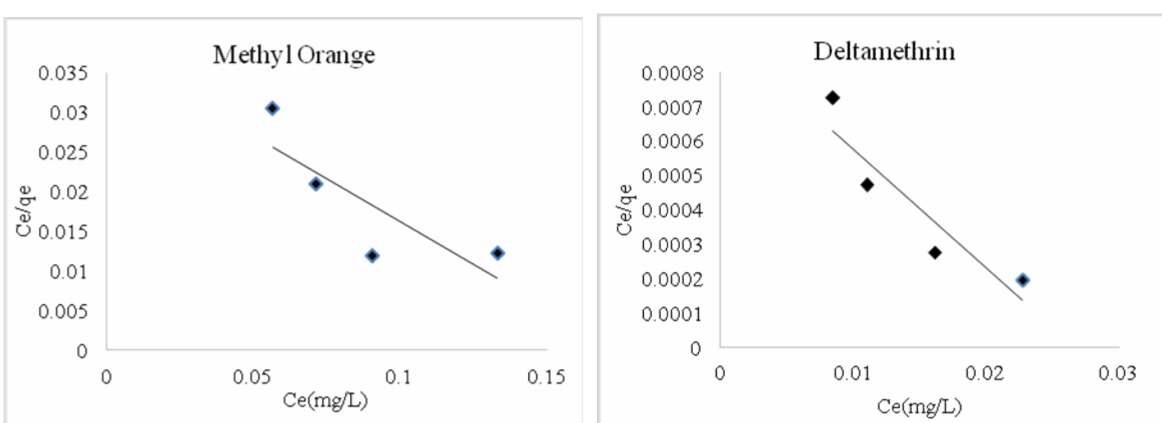
The Langmuir adsorption isotherm is valid for monolayer sorption onto specific homogeneous surface with a finite number of identical sites and with negligible interaction between adsorbed molecule [14].

The Langmuir isotherm model estimates the maximum adsorption capacity produced from complete monolayer coverage on the adsorbent surface [15]. The Langmuir isotherm can be linearized into this form.

$$C_e/q_e = C_e/q_m + 1/(K_a.q_m) \quad (4)$$

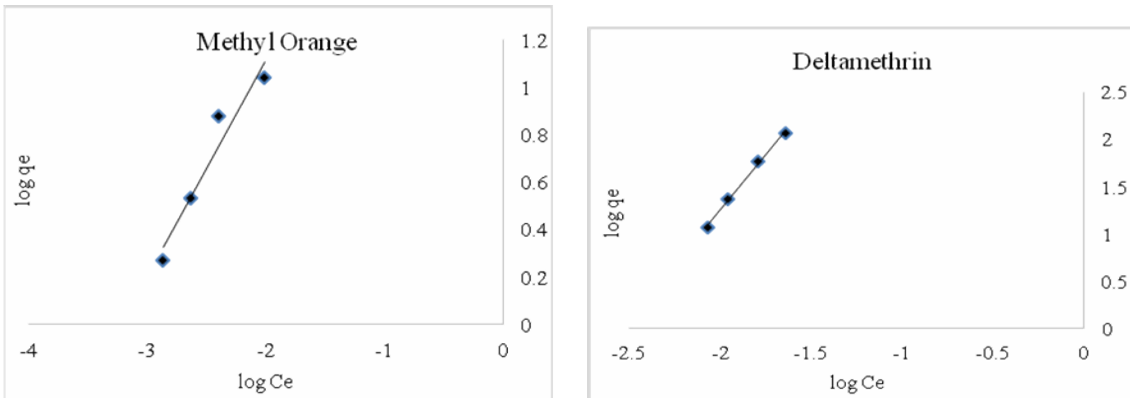
where q_m (mg/g) is the amount adsorbed per unit mass of the adsorbent corresponding to formation of a complete monolayer, K_a (L/mg) is the Langmuir equilibrium constant. C_e (mg/L) and q_e (mg/g) are the equilibrium liquid phase concentrations and amount of solute adsorbed at equilibrium, respectively [16].

The Freundlich isotherm model is applicable to the adsorption of heterogeneous surface with interaction between adsorbed molecules. The Freundlich model is the earliest known empirical equation and is shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surfaces. The Freundlich equation is expressed as: [17]



(a) (b)

Fig. 13: Langmuir isotherm model for (a) Methyl orange (b) Deltamethrin.



(a) (b)

Fig. 14: Freundlich isotherm model for (a) Methyl orange (b) Deltamethrin.

$$q_e = K_f C_e^{1/n} \quad (5)$$

where K_f (mg/g (L/mg)$^{1/n}$) is the adsorption capacity of the sorbent and related to the bonding energy or distribution coefficient. The magnitude of the exponent, 1/n, is the heterogeneity factor and it is a measure of the deviation from linearity of adsorption. Values of $n < 1$ represent unfavorable adsorption condition [14]. Eq. (5) may be written in the logarithmic form as

$$\text{Log } q_e = \log K_f + 1/n \log C_e \quad (6)$$

Values of K_f and n are calculated from the intercept and slope of the plot.

The value of 1/n obtained in the present study was greater than unity, indicating that adsorption of Methyl orange and Deltamethrin onto CTAB-bentonite was favorable.

Table-3: Isotherm parameters for adsorption

Pollutants	Isotherm parameters for adsorption					
	Langmuir			Freundlich		
	qm (mg/g)	K_a (dm^3/mg)	R^2	1/n	K_f (mg/g)(mg/L)$^{1/n}$	R^2
Methyl Orange	-0.2173	120.482	0.6689	1.089	19.281	0.9323
Deltamethrin	-0.0344	32362.45	0.8476	2.3265	369.564	0.9968

It can be seen that the data fits Freundlich adsorption isotherm better than Langmuir isotherm and corresponds to an inhomogeneous adsorption surface.

Conclusion

Modified clays are widely used as adsorbents due to their extensive inter layer expansion, swelling properties and their peculiar structure. In the present study, bentonite was successfully modified with a cationic surfactant (CTAB) by a simple cation exchange method. The prepared modified bentonite was characterized by using Fourier transform infrared spectroscopy and thermogravimetric analysis. The modified bentonite was used to remove methyl orange and deltamethrin from aqueous solutions. A marked increase in the adsorption capacity of CTAB-BT was observed for both pollutants that can be related to the attachment of cationic surfactant (CTAB) on bentonite as compared to plain bentonite. The absorption capacity depended on operational parameters like concertation of CTAB-BT, effect of pH and effect of contact time of the adsorbent and the adsorbates (methyl orange and deltamethrin). Better removal of both methyl orange and deltamethrin was observed in acidic pH. Kinetic study of methyl orange and deltamethrin showed that the adsorption process was best fitted for pseudo second order equation having correlation coefficients (R^2) 0.99. Freundlich adsorption isotherm model well explained the adsorption process for both methyl orange and deltamethrin.

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