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Adsorption of Crystal Violet Dye on Modified Bentonites

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The adsorption of basic crystal violet dye on bentonite and four modified bentonite with different fatty acids (bentonite FA1, bentonite FA2, bentonite FA3 and bentonite FA4) was investigated. The surface of each bentonite samples was examined before and after adsorption of dyes by FTIR technique. The effect of pH solution, initial concentration of dye and contact time on the adsorption of basic dye onto bentonites was studied. The results showed that the adsorption capacity of basic crystal violet was high on bentonites and modified bentonites with different degree. The Langmuir and Freundlich adsorption models were used to describe the adsorption process and to determine the isotherm constant. Based on the equilibrium data, which analyzed by two models and correlation coefficient, the Langmuir model was a good fit of experimental data than Freundlich model. This referred to the homogeneous surface for adsorption process.

Keywords: Adsorption, Crystal violet, Langmuir isotherm, Freundlich isotherm.

INTRODUCTION

Several synthetic dyes including cationic (basic dyes) [1,2], anionic dyes (direct, acid and reactive dyes) [3-8] and non-ionic dyes (disperse dyes and vat dyes) [9,10] are widely used in textile, leather and paper dyeing. These factories produce coloured wastewater causing serious problems to living organisms [11]. Different methods such as filtration, coagulation, photodegradation [11,12] and adsorption [5,13,14] have been used for the removal of dyes from wastewater effluents.

Among the different adsorbents (active carbon, alumina, silica) largely used for dyes removal [15,16], bentonite, a widely available natural mineral with a layer structure unit composed of one octahedral alumina sheet existed between two tetrahedral silica sheets, is applied in many fields due to their low cost, high surface area and high cationic exchange capacity [11,17]. Bentonite is used in ceramic industries, cement, paints and dyes removal [18-23].

Eren and Afsin [24] reported the adsorption of crystal violet basic dye on bentonite and treated bentonite with cobalt, nickel and zinc. Meanwhile, removal of crystal violet on MgO-bentonite was conducted at different factors like initial concentration of dye, contact time and temperature [25]. In the same way, adsorption of three basic dyes (methylene blue, crystal violet and rhodamine B) from aqueous phase on cationic surfactant modified bentonite has also been described [26]. Recently, Gao *et al*. [27] reported that iron modified bentonite may be used as an inexpensive adsorbent to rapidly remove rhodamine B from the treated effluent.

The aim of this work is to study the adsorption of basic crystal violet dye onto bentonite and fatty acids modified bentonite. The adsorption capacity was investigated by using adsorption isotherm technique. The experimental results were fitted into Langmuir model isotherm and Freundlich model isotherm equations in order to know which of these models gives better correlation to experimental results.

EXPERIMENTAL

Bentonite was provided from Sinai company for manganese, Egypt. Four different samples of bentonite were prepared by using different fatty acids. The fatty acids dimethyl dihydrogenated tallow ammonium chloride, ethanaminium, 2-hydroxy-N-(2-hydroxyethyl)-N,N-dimethyl-, esters with C16-18 and C18 unsaturated fatty acids and dibenzyl dihydrogenated tallow ammonium chloride were supplied by Aldrich chemical company. The modified bentonite named as bentonite FA1, bentonite FA2, bentonite FA3 and bentonite FA4.

TABLE-1
WEIGHTS OF USED REAGENTS

Weight of bentonite (g)	Weight of sodium carbonate (g)	Name and weight of fatty acid	Name of modified bentonite
10	0.5	Dimethyl dihydrogenated tallow ammonium chloride 5.0 g	Bentonite FA1
10	0.5	Dimethyl dihydrogenated tallow ammonium chloride 8.50 g	Bentonite FA2
10	0.5	Ethan aminium, 2-hydroxy-N-(2-hydroxyethyl)-N,N-dimethyl-, esters with C16-18 and C18 unsaturated fatty acids 5.0 g	Bentonite FA3
10	0.5	Dibenzyl dihydrogenated tallow ammonium chloride 8.50 g	Bentonite FA4

Crystal violet cationic dye (Color index: 42555, λ_{max}: 592 nm, m.w.: 407.99, m.f.: $C_{25}H_{30}N_3Cl$) was purchased from Sigma chemical company. The other reagents were used all of analytical grade.

Preparation of modified bentonite: 20.0 mL deionized water in a beaker of 250 mL heated to 70 °C, a known weight of bentonite (Table-1) was added, sodium carbonate in 5 mL hot deionized water was added under stirring. A known weight of molten fatty acid was added slowly to the content of beaker with continuous stirring for 40 min. After cooling at room temperature, the mixture was dried in the oven for 24 h. The obtained solids were milled to get 200 mesh size.

Characterization techniques: The chemical analysis of bentonite was measured by energy dispersive X-ray spectrometer (EDX) attached to scanning electron microscope (SEM).

The FT-IR spectra of bentonites and dye before and after adsorption were done using Fourier transform infrared spectroscopy (FTIR), Nicolet iS 10 Thermo-scientific. The samples were dried and mixed with pure KBr (1:20 w/w), then pressed to obtain IR-transparent pellets. The FT-IR was first calibrated for background signal scanning with a control sample of pure KBr. The spectra were recorded within a scanning range of 4000-400 cm^{-1}.

Dye adsorption: The adsorption studies were carried out with 0.5 g of bentonites and treated bentonites samples and 50 mL of crystal violet dye with different concentrations, pH and contact time. The solution of dye and adsorbents were shaking with a constant speed of 130 rpm at 25 °C, after that the solution was centrifuged at 4000 rpm for 10 min and the concentration of dye was determined using UV/visible spectrophotometer (UV-1800 SHIMADZU, Japan) at the maximum absorption of wavelength 592 nm for crystal violet.

The adsorption capacity q_e of the dye per gram adsorbent bentonites (mg/g) was calculated using the equation:

$$q_e = (C_i - C_e)\,V/m$$

where q_e is the equilibrium concentration of dye molecule on adsorbents (mg/g), C_i is the initial concentration of dye solution (mg/L), C_e is the equilibrium concentration of dye solutions (mg/L), m is the mass of adsorbent (g) and V is the volume of dye solution (L). To conduct the adsorption isotherm different concentration of dye solution were used from 200 to 800 mg/L on adsorbent (0.5 g/L) at pH = 6 and contact time 360 min.

The effect of pH on the adsorption of dye was studied with initial concentration of 600 and 400 mg/L for crystal violet dye, in the range of pH from 2 to 12. The pH of dye was adjusted by addition of few drops from HCl or NaOH solution.

For kinetic adsorption of crystal violet on bentonite FA1 and bentonite FA3, different concentration of crystal violet solution on adsorbent was stirred at time periods ranging from 10 to 150 min.

RESULTS AND DISCUSSION

The chemical composition of bentonite is given in Table-2. This analysis was done by EDX analysis. It is clear that silica and alumina exist as major components in the constituents of bentonites and the other metal oxides exist as minor components.

TABLE-2
CHEMICAL CONSTITUENTS OF BENTONITE AND PERCENTAGE OF IGNITION LOSS FOR TREATED AND UNTREATED BENTONITE

Components	Weight (%)	Type	Ignition loss (%)
SiO_2	70.6	Bentonite	8.5
Al_2O_3	16.4	Bentonite FA1	14.2
Fe_2O_3	2.5	Bentonite FA2	16.5
MgO	1.6	Bentonite FA3	28.0
CaO	1.8	Bentonite FA4	17.0
K_2O	2.4	–	–
Na_2O	0.3	–	–

The percentage of ignition loss for treated and untreated bentonite indicates that the amount of fatty acids adsorbed on the surface increases with respect to their amounts added during the treatment.

Table-3 indicated the characteristics IR bands of bentonite, modified bentonites, crystal violet dye and bentonites with dye after adsorption process. FTIR spectrum of treated and untreated bentonites (Table-3) showed significant change in position of peaks and appearance of new peaks. Presence of peaks at 3627 and 3403.8 cm^{-1} due to stretching vibration band of OH group and the peak at 1634.8 cm^{-1} assigned to OH deformation. The appearance of peaks at 2921.9 and 2850 cm^{-1} attributed to symmetric and asymmetric stretching vibrations of the methyl CH_3 and methylene CH_2 groups of fatty acid, this confirm the attachment of fatty acids to bentonites. Peaks appeared at 1001.9 cm^{-1} due to stretching band of Si-O group at 917 cm^{-1} due to stretching band of Al-OH group, at 883.7 cm^{-1} due to stretching band of Fe-O group and 796.52 cm^{-1} due to stretching band of Mg-OH group [1,16,28].

FTIR spectrum of bentonites and treated bentonites after adsorption process showed significant change in peaks position and disappearance of some peaks when compared with each other. The adsorption capacity depend on the ionization and the hydrogen bonding of functional groups present in the structure. The shift of peaks may be related to strong electrostatic interaction between the different functional groups of treated and untreated bentonites and dye.

TABLE-3
CHARACTERISTICS IR BANDS OF BENTONITES, TREATED BENTONITES, CRYSTAL VIOLET DYE AND BENTONITES WITH DYE AFTER ADSORPTION

Name	IR bands cm^{-1}
Bentonite	3627, 3403.8, 2921.9, 2850, 1634.8, 1467.8, 1116.2, 1001.9, 917, 883.7, 796.52, 721.8
Bentonite FA1	3627, 3403.8, 2921.9, 2850, 1634.8, 1467.8, 1116.2, 1001.9, 917, 883.7, 796.5, 721.8
Bentonite FA2	3627, 3412.6, 2920.1, 2850, 1639, 1467.9, 1114, 1002.8, 917, 884, 796.6, 721.3
Bentonite FA3	3626, 3393.6, 2955.5, 2916.5, 2849.7, 1710.8, 1541.2, 1469.9, 1114.7, 1001.9, 917, 884.3, 796.9, 719.9
Bentonite FA4	3625.5, 3402, 2918.4, 2849.7, 1711, 1632.2, 1538, 1468, 1114.6, 1003.7, 917, 883.8, 796.4, 721.6
Crystal violet dye	3380.7, 2923.3, 2854, 2358.5, 1582.3, 1520.2, 1478.5, 1443.2, 1360, 1299.6, 1227.4, 1189.67, 1170, 966.2, 941.5, 913.75, 829.7, 810, 794, 767.76, 758.8, 743.65, 723, 681 and 666.61
Crystal violet dye adsorbed on bentonite	3627.5, 3566, 3419.8, 2366, 2341.7, 1635.5, 1584.3, 1361.3, 1299.8, 1034.5, 916.6, 836.8, 797.8 and 724
Crystal violet dye adsorbed on bentonite FA1	3628, 2922.6, 2850.3, 2359.7, 2342, 1588.7, 1471, 1364, 1030, 916.4, 886.8, 797.7, 722.9
Crystal violet dye adsorbed on bentonite FA2	3627.2, 2921.1, 2850.2, 1589.4, 1467.9, 1367, 1021.5, 915.3, 886.5, 798.1, 722.7
Crystal violet dye adsorbed on bentonite FA3	3627.2, 2917, 2849.9, 1709.6, 1668.7, 1585.5, 1541, 1471.4, 1471.4, 1431.7, 1364.8, 1299, 1171.6, 1022.3, 914.7, 887.2, 833.5, 797, 721.7
Crystal violet dye adsorbed on bentonite FA4	3627.4, 2923.6, 2850.7, 1588.9, 1525, 1467.4, 1367.1, 1025.2, 917.4, 886.6, 796.3, 723.3, 701.5

Effect of pH on dye adsorption: The influence of solution pH (2 to 12) on dye adsorption capacity of bentonite and modified bentonites was carried out. The adsorption capacity of bentonite towards cationic dye slightly decreases on increasing pH of the solution, while the adsorption capacity of modified bentonites towards cationic dye increases on increasing pH of the solution (Fig. 1).

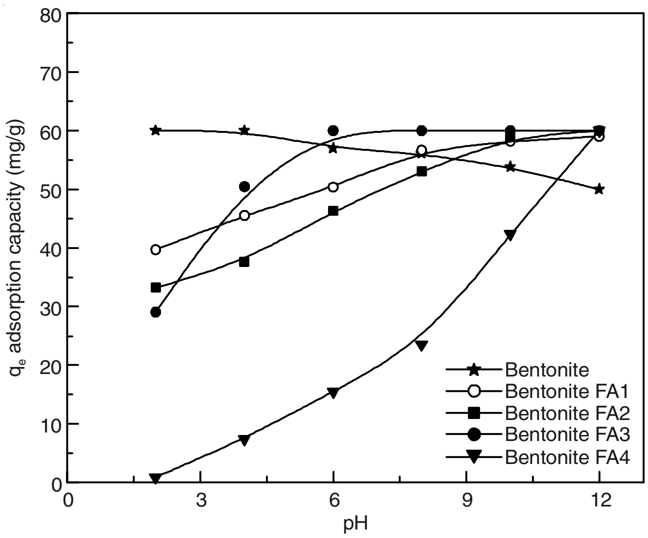

Fig. 1. Effect of pH on the adsorption of crystal violet cationic dye (basic dye) onto bentonite and modified bentonite samples

The pH of the dye solution is a significant factor in the adsorption process, which affect on the nature of dye structure, charge of the surface, ionization and dissociation of functional groups on the surface. At lower pH values, there is electrostatic repulsion of positively charged bentonites and cationic crystal violet dye and also the competition between hydrogen proton and cationic dye resulting in low adsorption of dye. When the pH increases the adsorption capacity of modified bentonites increased, according to domination of negatively charge on the surface of bentonites.

The adsorption capacity of bentonites increases due to the electrostatic attraction between negatively charged adsorbents existed by ion exchange or Si-O-Si structure and the positively charged dye, or due to hydrogen bonding between the nitrogen atoms of cationic dye and hydroxyl group on the surface by increasing pH values of solution [1].

Effect of contact time on adsorption process: The contact time is an important factor in determining the time required to reach the equilibrium for the adsorption process. The effect of contact time on the amount of crystal violet adsorbed onto bentonite FA1 and bentonite FA2 at different initial concentrations of dye were investigated in Figs. 2 and 3, respectively. It is clear that the adsorption capacity increases as the equilibrium time increases. The maximum adsorption capacity of bentonite FA1 was observed at 180 min, while the maximum adsorption capacity of bentonite FA3 was found at 100 min.

Adsorption isotherms: Five adsorbents from bentonite and modified bentonites were used to compare their adsorption capacity towards basic crystal violet dye. The adsorption isotherm of basic crystal violet dye on bentonite and modified bentonites was illustrated in Fig. 4. The examination of adsorption isotherm is required to establish a model for adsorption process design. The data obtained from the equilibrium adsor-

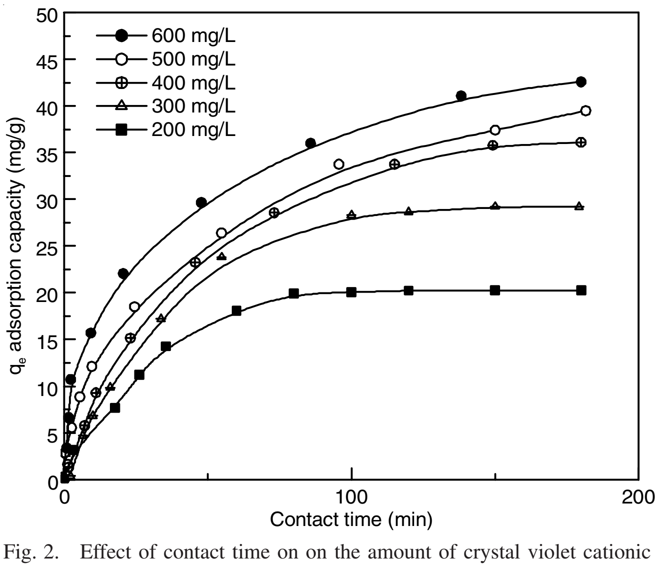

Fig. 2. Effect of contact time on on the amount of crystal violet cationic dye (basic dye) adsorbed onto bentonite FA1 at different initial concentrations of dye

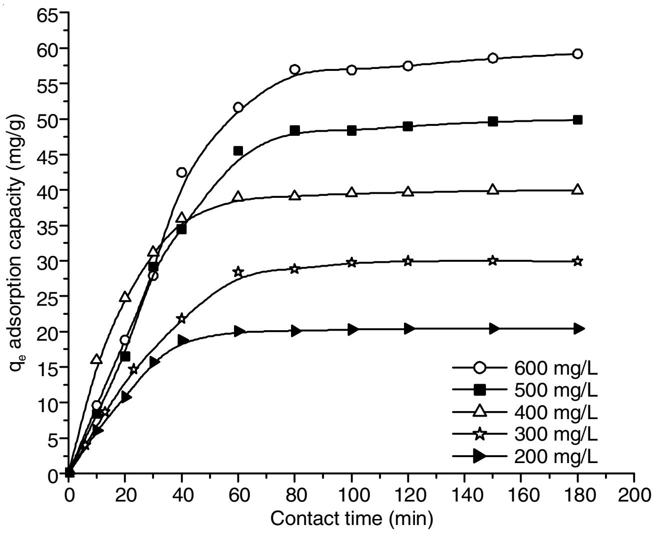

Fig. 3. Effect of contact time on the amount of crystal violet cationic dye (basic dye) adsorbed onto bentonite FA3 at different initial concentrations of dye

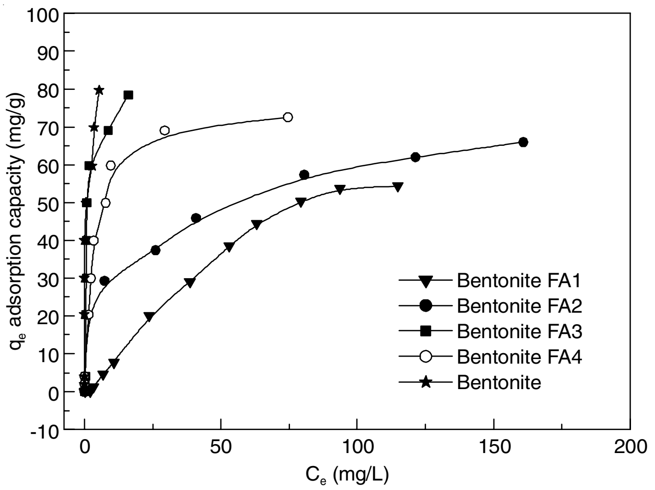

Fig. 4. Adsorption isotherm of basic crystal violet dye on bentonite and modified bentonites

ption at 298 K, at the solution pH and at different contact time were analyzed by using two models namely Langmuir and Freundlich isotherm equations [6,28].

Langmuir isotherm: The presence of monolayer Langmuir adsorption coverage at the external surface of adsorbent depends on intermolecular forces between adsorbent and adsorbate. The adsorption process occurs on homogenous surface sites of adsorbent, that means one molecule of dye for each site to form monolayer adsorption and no other molecules of dye can adsorbed. The sites of homogenous surface are the same and energetically equal. When the maximum dye adsorption capacity is attained, no other molecules of dye can be adsorbed.

Langmuir isotherm equation is:

$$q_e = (bK_LC_e)/(1 + K_LC_e)$$

The linear form of Langmuir isotherm equation is:

$$1/q_e = (1/bK_L)\ 1/C_e + 1/b$$

Multiplying both side of equation by C_e:

$$C_e/q_e = (1/bK_L) + C_e/b$$

where C_e is the adsorbate equilibrium concentration (mg/L), b is the maximum adsorption capacity monolayer coverage of adsorbate on adsorbent (mg/g), q_e is the equilibrium concentration of dye on the adsorbent (mg/g), K_L is constant Langmuir of adsorption (L/mg) and related to binding energy of adsorbents. The plot of C_e/q_e against C_e gets a straight line with slop 1/b and intercept $1/bK_L$. Langmuir isotherm constants for the adsorption of crystal violet are given in Table-4. R^2_L is the correlation coefficients for Langmuir isotherm.

TABLE-4
ADSORPTION ISOTHERM LANGMUIR CONSTANTS
FOR THE ADSORPTION OF CRYSTAL VIOLET

Adsorbent	K_L (L/mg)	R^2_L	b (mg/g)
Bentonite	0.011	0.986	105.26
Bentonite FA1	15.060	0.997	74.07
Bentonite FA2	0.072	0.996	69.45
Bentonite FA3	0.970	0.998	81.97
Bentonite FA4	0.559	0.997	73.80

Freundlich isotherm: The Freundlich adsorption isotherm is used to explain the heterogeneity surface (1/n) of adsorbents. Freundlich isotherm equation is $q_e = K_F\ C_e^{1/n}$ and the linear form of Freundlich equation is:

$$\ln q_e = \ln K_F + 1/n \ln C_e$$

where C_e is the adsorbate equilibrium concentration (mg/L), q_e is the amount of adsorbate equilibrium (mg/g), K_F is Freundlich constant (mg/g)(L/mg), referred to binding energy and defined as adsorption coefficient or distribution coefficient, n is Freundlich constant referred to adsorption intensity of the adsorbents or surface heterogeneity. The plot of ln q_e against ln C_e in Freundlich equation gives the slope 1/n and intercept ln K_F. Freundlich constant K_F implies for the adsorption capacity of bentonites and Freundlich constant n indicates the relationship linearity or deviation of the adsorption process. When the value of n equal to 1 the adsorption is a linear relationship, higher than 1 the adsorption is a physical process and lower than 1 the adsorption is a chemical process. Freundlich isotherm constants for the adsorption of crystal violet are given in Table-5. R^2_F is the correlation coefficients for Langmuir isotherm.

TABLE-5
ADSORPTION ISOTHERM FREUNDLICH CONSTANTS
FOR THE ADSORPTION OF CRYSTAL VIOLET

Adsorbent	K_F (L/mg)	n	R^2_F
Bentonite	24.66	12.658	0.912
Bentonite FA1	46.43	9.750	0.952
Bentonite FA2	28.50	15.748	0.885
Bentonite FA3	58.21	53.190	0.954
Bentonite FA4	21.65	9.011	0.925

Langmuir adsorption isotherms presume that the adsorption occurs on homogeneous sites within the bentonite adsorbents, while Freundlich adsorption isotherms assume that the adsorption occurs on heterogeneous sites within the bentonite adsorbents. Based on Langmuir correlation coefficients and Freundlich coefficients listed in Tables 4 and 5, it is clear that the surface of bentonite and modified bentonites is consisted of homogeneous sites for the adsorption process (R^2_L in the range of 0.999-0.986 and R^2_F in the range of 0.955-0.885).

The Freundlich constant K_F presented in Table-5 indicates the adsorption capacity of bentonites and modified bentonites. The Freundlich constant n refers to the relationship linearity or deviation of the adsorption process. The values of n are higher than 1 for the adsorption of crystal violet on all adsorbents. This indicates that the adsorption on all adsorbents is physical process than chemical process and that means the adsorption bond is weak van der Waals force.

Conclusion

The adsorption of basic dye on bentonite and modified bentonites revealed that the modification of natural bentonite using different fatty acids increases the adsorption capacity of bentonite. The adsorption potential are greatly affected by the features of surface bentonites. The amount of dye adsorbed was found to vary with the initial concentration of dye, contact time and pH of solution. The adsorption process is strongly dependent on the pH solution. The adsorption equilibrium was achieved within 180 min. The correlation coefficients of the two models indicate that the surface of bentonite and modified bentonites is consisted of homogeneous sites for the adsorption process and Langmuir model is more preferable for adsorption process than Freundlich model. From the values of n it is clear that the adsorption of crystal violet on modified bentonites is physical process than chemical process and the bond is weak van der Waals force.

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