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Adsorption of CI Basic Blue 3 Dye Molecules from Aqueous Media by Sulfuric Acid-Activated Montmorillonite Mineral

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Abstract: Many industries (especially textile, paper, plastic) which use chemicals and colorants, generate considerable amount of waste water since they use excessive amounts of water in their operations. and they These waste waters form a significant reason of worldwide water pollution, and if they are released before being treated, they bring an important harm to these waters. Therefore, In this paper, adsorption kinetics and equilibrium of CI Basic Blue 3 (BB3) from aqueous media using sulfuric acid-activated montmorillonite mineral (SAM) was investigated. For this aim, firstly the natural montmorillonite mineral (NM) was activated by treating with a 6 M H_2SO_4 solution for 4 hours at 395 K. After sulfuric acid treatment the SAM samples were characterized using a BET surface analyzer and FTIR spectroscopy. The adsorption experiments in different conditions such as i.e., contact times (0-120 min), initial pH values (2-8), temperatures (298-318 K), and initial dye concentrations (100-350 mg/l) were performed in a thermostatic water bath at an agitation speed of 180 rpm. The experimental maximum adsorption capacity (q_e) was determined to be 277 mg/g at 60 min, 6 ± 0.02, 298 K and 350 ppm initial dye concentration. For adsorption of CI Basic Blue 3 (BB3) molecules from aqueous media by the sulfuric acid activated montmorillonite mineral (SAM) is determined that Lagergren's kinetic model (pseudo first order) simulated the kinetic data better than the Ho's kinetic model (pseudo second order) and the Freundlich isotherm is the best fitting isotherm model equation. Also, the thermodynamic parameters calculated using Van't Hoff equation show that the adsorption process is spontaneous and exothermic. The experimental results of the study indicated that, the acid activated mineral is suitable for adsorption of BB3 dye molecules from aqueous media.

Keywords: Adsorption, CI Basic Blue 3, sulfuric acid-activated montmorillonite mineral (SAM), thermodynamic and kinetic parameters

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INTRODUCTION

Color removal from wastewaters is an important environmental aspect in textile industry. which is one of the fastest-growing major industries in Turkey. The wastewaters released from this industry contain high amounts of dyes and pigments, which generally have been synthesized and contain complex aromatic molecules. They contain a lot of double bonds and various functional groups (1). Therefore these dyes and pigments are not biologically decomposed due to their stable structures, so they accumulate easily in natural bodies of water (2). When these wastewaters are discharged into aquatic media, serious environmental problems may be occurred such as impairment of the aesthetic nature, the reduction of the degree of penetration of light and decrease in the solubility of gases (3). These wastewaters can cause a variety of health problems such as skin irritations, allergic reactions and cancer on the living beings. (2–4). For these reasons, the removal of dye materials and pigments from waste water is important with respect to the protection of the health of the ecosystem and the living organisms that may be exposed to these wastewaters. Colored wastewater is known as one of the most difficult wastewater to be improved because of the present disadvantages expressed. Treatment difficulties are based on stability of recalcitrant dyes and their ability to bestow good coloring in very low concentrations. Many treatment techniques can be used for the removal of these pigments and dyes from colored wastewater before they are discharged to aquatic media. These techniques include adsorption (5–11), membrane processes (12), oxidation processes (13), ion exchange (7,8), reverse osmosis (14), electrocoagulation (2), and coagulation (15). Unlike other remediation techniques, because of simplicity, ease of use and high efficiency, adsorption process is considered one of the most attractive treatment options for the removal of the dye and pigments from the wastewater (16–18). It is known that the cost, sustainable resource, accessibility and adsorptive capacity of the adsorbent are very significant parameters that affect the efficiency, effectiveness, and costs of the process.

The aim of this research was to investigate the adsorption of CI Basic Blue 3 (BB3) from aqueous media by sulfuric acid-activated montmorillonite mineral (SAM). To do this, the SAM samples were firstly produced from natural montmorillonite mineral and characterized with FTIR and BET techniques. Secondly, the effects of the efficiency and rate of adsorption of BB3 on the SAM samples were studied in a batch system. Then the kinetic and thermodynamic parameters were calculated using experimental data and appropriate models equations.

MATERIAL AND METODS

Preparation and characterization of adsorbent

CI Basic Blue 3 dye molecules was provided from Sigma Aldrich and used in experiments without any purification. The molecule structure of BB3 and some specific properties were given Table 1 and Fig. 1.

The natural montmorillonite mineral (NAM) which was supplied by a local industry in Elazig/Turkey, The natural montmorillonite mineral was dried firstly under atmospheric condition, then at 105 ℃ in an oven and then divided into fractions based on the particle sizes. The fraction between 50 and 100 mesh was activated using 6 M H_2SO_4 solution at 97 ºC for 6 hr. And then sulphuric-activated montmorillonite mineral (SAM) which was washed with water until the sulphate ions were completely removed, were dried after the washing in an over same temperature and the samples stored in desiccators for subsequent use in the study.

BET Surface Area Analyzer (ASAP 2020, Micromeritics Inc., USA) and FTIR spectrometer (ATI Unicam Mattson 1000) were used to characterized of SAM samples. Besides, to the same aim, the pH of zero point of charge (pH_{zpc}) of the activated montmorillonite mineral was measured by using the pH drift methods (19,20).

Table 1: Computed properties of BB3.

Empirical Formula	**Molecular Weight**	**λ_{max}**	**composition**
$C_{20}H_{26}ClN_3O$	359.89	654 nm	Dye content, 25%

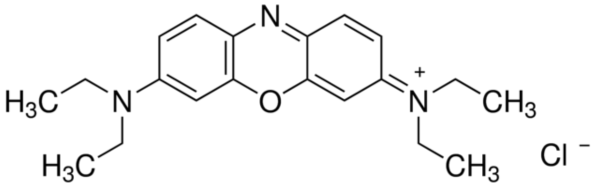

Figure 1: 2D structure of BB3.

Experimental Procedure

The dye stock solution of CI Basic Blue 3 (BB3) was prepared from 25 % dye content, Sigma Aldrich in a concentration of 1000 mg/L. During the experimental studies, all working dilute solutions were prepared using the stock solution and distilled water. The pH values of the dilute working solutions which were used in the experiment, were adjusted using 0.1 M solutions of NaOH and HCl especially in studies in which the effects of pH were investigated.

The experiments were performed in 14 parallel erlenmeyer flasks using a thermostatic water bath at an agitation speed of 180 rpm. The effect of various parameters such as initial pH (2-8), contact time (5-120 min), temperature (298-318 K), and initial concentration of BB3 (100-350 ppm) on adsorption yield was investigated in the study. All of the experiment series were conducted by mixing 50 mL of the BB3 solution with a certain amount of SAM in 100-mL erlenmeyer flasks which were prepared in the same conditions. At the end of the planned contact time of experiment each flask was removed from the water bath and the SAM particles were separated from the aqueous phase by centrifugation at 5000 rpm for three minutes. To calculate the adsorption yield and capacity of adsorption, the final concentration of BB3 in the filtrate was determined with analyzed by a UV-Vis spectrophotometer. All the experiments series were performed in duplicate, and the average results were reported. According to experimental results and working line, the adsorption efficiency and capacity of adsorption were calculated using Eqs. (1) and Eqs (2).

$$Adsorption\ efficiency(\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad \text{(Eq. 1)}$$

$$q_e = \frac{v \times (C_o - C_e)}{m}, \qquad \text{(Eq. 2)}$$

Where q_t (mg/g) is the amount of BB3 molecules per mass unit of SAM at t = t. C_0, C_t and C_e (mg/L) are the initial, at time t and final (equilibrium) concentration of BB3 molecules, respectively. m (g) is the mass of SAM and V is the volume of the BB3 solution (L)

RESULT AND DISCUSSION

Characterization Results of the Adsorbent

The average pore diameter and BET surface area were determined by the nitrogen adsorption method as 21.2 Å and 113.3 m^2/g for the sulfuric acid-activated montmorillonite mineral (SAM). Same quantities for the natural montmorillonite mineral (NM), were obtained as 65.4 Å and 73.6 m^2/g.

The functional groups on the surface of montmorillonite mineral before and after activation process were identified using the Fourier transform infrared (FTIR) spectroscopy. Wavenumber and vibration type of the significant peaks of the samples are given in Table 2. Liu *et al*. and Öztürk *et al*. in their researches (21,22) have reported similar peaks and assignment for other clay mineral.

Table 2: FTIR spectral data of the SAM and NM.

Frequency (cm^{-1})		**Assignment**
Acid-activated montmorillonite mineral (SAM)	**Natural Montmorillonite mineral (NAM)**	
433	-	Si–O deformation
469	469	Si–O–Si deformation
525	530	Al–O–Si deformation
690	690	Si–O perpendicular
794	-	Si–O
1013	-	In-plane Si–O stretching
1074	1043	Si–O stretching
-	1262	C-H bending
1415	1420	Aromatic methyl ($-CH_3$) group vibrations
-	1516	C=C stretching vibrations of aromatic ring
1639	1633	OH deformation of water
-	2930	Aliphatic C-H stretching
3435	3403	OH stretching of inner hydroxyl groups

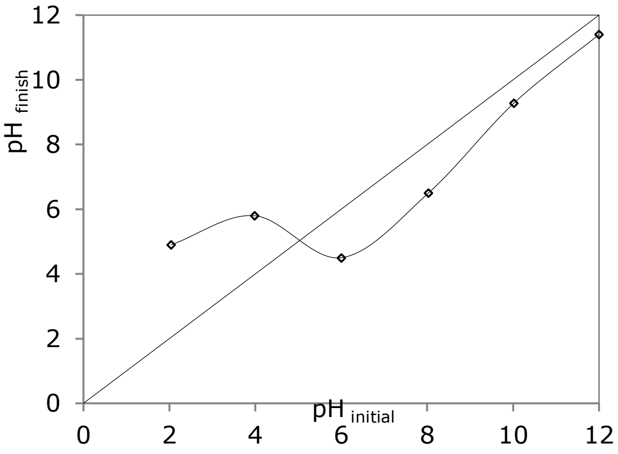

Figure 2: The point of zero charge of SAM.

It is well known that the point of zero charge (pH_{zpc}), which is indicative of the types of surface active centers and the adsorption mobility of surface, is an important factor in adsorption processes (23). Fig.2, which was drawn using the drift method, shows that the value of pH_{zpc} was 5.1. The experimental results indicated that, when the pH of the BB3 solution was less than 5.1, the surface of the SAM was positively charged and could attract anions from the solution.

When the pH of the solution was greater than 5.1, the surface of the SAM was negatively charged and attracted cations.

Effect of The Initial pH of The BB3 Dye Solution Depending on The Contact Time

Figure 3 shows the relationship between initial pH values of BB3 dye solutions and adsorption capacity, depending on the duration of contact. Figure 3 shows that the adsorption of the BB3 molecules was very high in the first 30 min. After that period, the adsorption efficiency declined because the active sites on the surface area available for adsorption was decreased. Also, the high adsorption efficiency during the initial stage have been due to the higher driving force's producing faster transfer of BB3 molecules to the surface of the SAM.

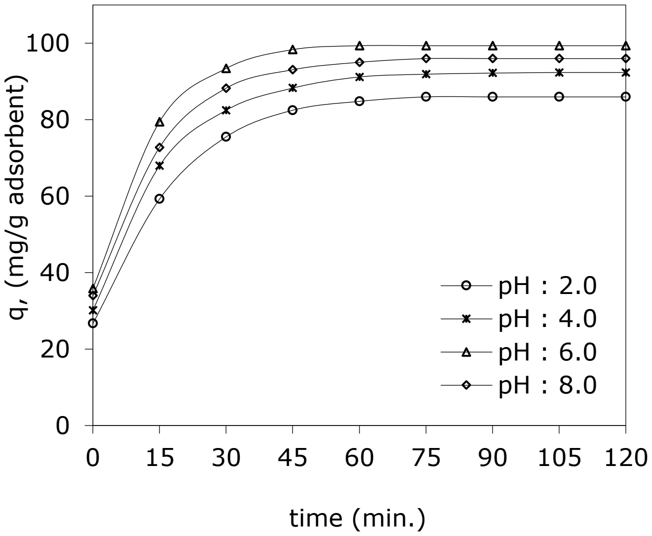

Figure 3: Effect of contact time on adsorption capacity of SAM (initial BB3 conc. 100 ppm; contact time: 120 min; SAM conc. 2 g/L; temperature: 298 K)

In addition, the adsorption capacity of the SAM increased with contact time and reached its maximum value in the range of 85-99 mg/g for different initial pH values after approximately 60 min. After this time, the adsorption capacity remained almost constant, for that reason contact time of 60 min was considered the equilibrium time for BB3 adsorption. It can be observed that the adsorption capacity of SAM increased linearly up to pH 6, reaching a maximum value (99 mg/g) at pH 6 (Figure 4). After that point, the adsorption capacity decreased. It was concluded that the results obtained were in accordance with previous studies and the result that the initial pH of the dye solution affected the concentration of counter ions in the functional groups of SAM, the surface charge of SAM and the degree of dissociation /ionization of SAM during adsorption process (24–26). These results are consistent with the pH_{zpc} value of the SAM samples (pH_{zpc} = 5.1). Vijayaraghavan *et al.* (27) have reported similar results in their research.

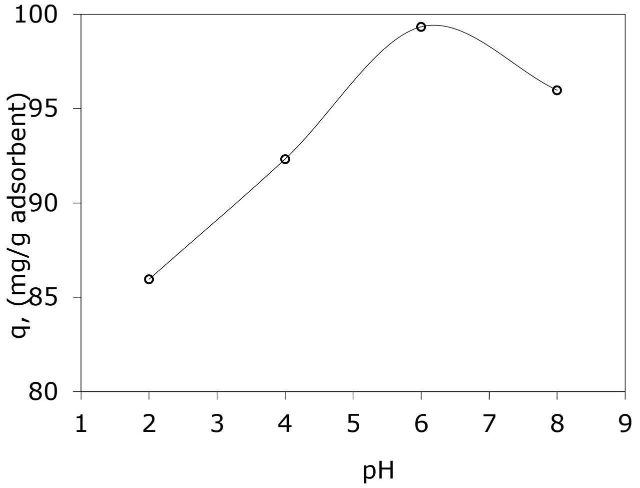

Figure 4: Effect of initial pH on adsorption capacity of SAM (initial BB3 con. 100 ppm; contact time: 120 min; SAM con: 2 g/L; temperature: 298 K)

The Kinetic Analysis of the Adsorption

The effect of the temperature on the adsorption of BB3 molecules by SAM in is shown in Figure 5. It was observed that the adsorptive capacity of the SAM was increased as the temperature decreased from 318 K to 298 K. The equilibrium adsorption capacity of the SAM was determined to be about 97 and 89 mg BB3/g at 298 and 318 K, respectively. The increase in the removal of BB3 with decrease in temperature of solution showed that the adsorption process was exothermic.

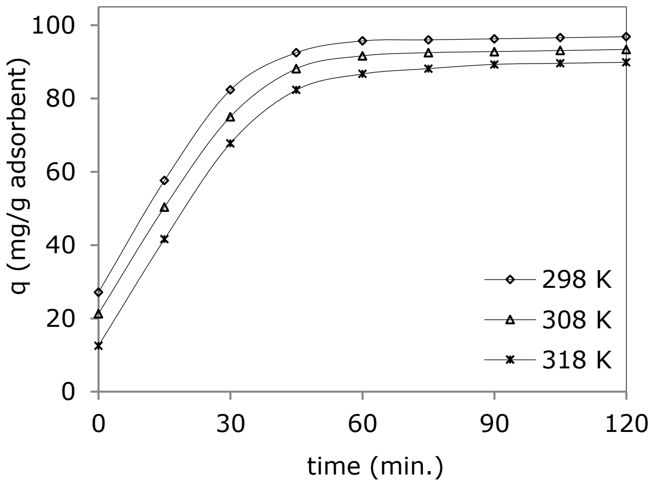

Figure 5: Effect of temperature on adsorption capacity of SAM (initial BB3 con. 100 ppm; contact time: 120 min; SAM con: 2 g/L; pH: 6±0.02)

Adsorption processes are time dependent; therefore, while designing the reactor for this process, the relationship between the adsorption rate and the contact time should be known. This relationship can be demonstrated by kinetic model equations. For that reason, the adsorption rate constants were calculated with pseudo first-order (Lagergren (28)) and pseudo second-order (Ho (29)) kinetic models, which can be used to describe the mechanism of the BB3 dye molecules adsorption.

The pseudo-first order equation of Lagergren is generally expressed in equation (3):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad \text{(Eq. 3)}$$

if equation 4 is integrated (t =0 to t =t and q_t =0 to q_t =q_t)

$$q_t = q_e(1 - e^{-k_1 t}) \qquad \text{(Eq. 4)}$$

if the equation(4) is transformed into a linear form to provide ease of use in kinetic data,

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad \text{(Eq. 5)}$$

The pseudo second-order model is given by Eq. (6):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad \text{(Eq. 6)}$$

If the Eq. (5) is integrated, then Eq (7) is obtained.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{t}{q_e}, \qquad \text{(Eq. 7)}$$

Where; t (min) is the contact time of adsorbate (BB3) and adsorbent (SAM); k_1 (min^{-1}), Lagergren adsorption rate constant, k_2 ($g/mg^{-1}.min^{-1}$) second order adsorption rate constant, q_e (mg/g)amount of dye absorbed in equilibrium, qt (mg/g) amount of dye absorbed at t=t time.

If the y values in equations are ln (q_e-q_t) or t/q_t plotted against x value t , k_1, k_2 and q_e values can be found, respectively. (Fig. 6 and 7).

The values of k_1, q_{ec1}, k_2, q_{ec2}, and the correlation coefficient (R^2) are given in Table 3. The correlation coefficient (R^2) and the difference between the calculated adsorption capacity (q_{ec}) and the experimental adsorption capacity (q_e) indicate that the Lagergren's kinetic model (pseudo first order) simulated the kinetic data better than the Ho's kinetic model (pseudo second order).

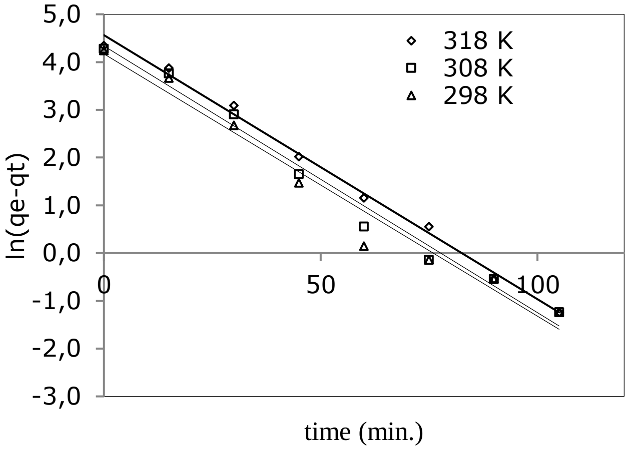

Figure 6: Pseudo first-order kinetic plots for the removal of BB3 molecules

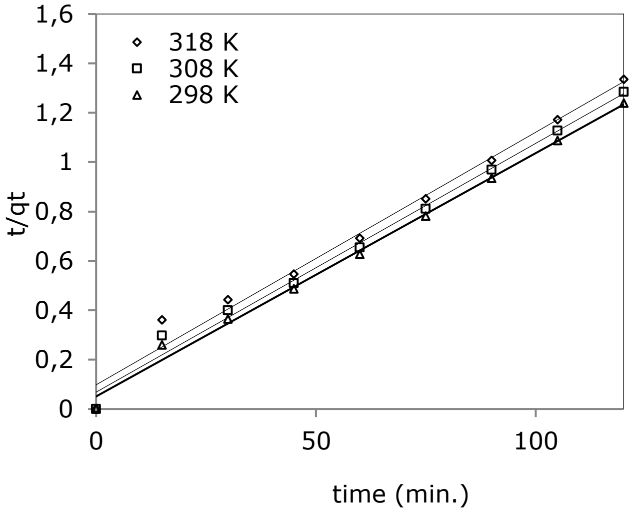

Figure 7: Pseudo second-order kinetic plots for the removal of BB3 molecules

Table 3: Kinetic constants of Lagergren and Ho models for the removal of BB3 by SAM

Temperature (K)	**q_e (mg/g)**	**Pseudo-first-order (Lagergren) kinetic model**		
		R^2	**k_1x10^3 (min^{-1})**	**q_{ec1} (mg/g)**
298	99.3	0.97	54.9	64.71
308	93.4	0.98	55.8	76.71
318	89.8	0.99	55.3	95.85
Temperature (K)	**q_e (mg/g)**	**Pseudo-second-order (Ho) kinetic model**		
		R^2	**k_2 x10^3 (g/mg min)**	**q_{ec2} (mg/g)**
298	99.3	0.99	1.1	101.0
308	93.4	0.99	1.5	99.00
318	89.8	0.98	1.9	98.04

Thus, the activation energy of the adsorption process of BB3 molecules by the SAM was calculated using the rate constants (k_2) and the Arrhenius equation (Eq. 8).

$$\ln k_2 = \ln A - \frac{E_a}{RT} \qquad \text{(Eq. 8)}$$

Where Ea (J/mol), A (g/mg min), R (8.314 J/mol K) and T (K) are the activation energy, the Arrhenius constant, the ideal gas constant and the temperature of the solution, respectively.

The activation energy value (E_a) was calculated as about 19 kJ/mol, and this value indicated that physical adsorption is a dominate mechanisms on the removal process. On the other hand, it was observed that the values of q_{ec2} increased and the values of k_2 decreased with decrease in temperature. These results indicated that the adsorption of BB3 by the SAM occurred more rapidly at higher temperatures.

Thermodynamic Analysis of Adsorption

According to experimental results, the adsorptive capacity of the SAM was a function of the initial concentration of BB3 molecules in the aqueous solution. It was observed that the the adsorption capacity of BB3 increased from 130 to 180 mg/g at the range of initial concentrations values between 100 to 350 mg/L due to the fact that the initial dye concentration is an important driving force to overcome mass transfer resistance. Özer *et al.* (30) have reported similar results their paper. When the temperature of the solution decreased from 318 to 298 K, the value of the maximum adsorption capacity increased from approximately 89.8 to 99.3 mg/g for 100 ppm and 210 to 280 mg/g for 350 ppm. The decrease of efficiency and capacity of adsorption with the temperature increases shows that the adsorption process is exothermic and the adsorption is applicable at low temperature efficiently. this result is the result of weak interaction forces such as van der Waals and hydrogen bonds between dye molecules and adsorbent. Vimoneses et al (31), Toor et al (32) have given similar results and comments for their work.

The equilibrium adsorption isotherm is fundamentally important in the design of an adsorption system. Therefore, an adsorption isotherm study was carried out on Langmuir (33) and Freundlich (34) isotherm models.

The Langmuir isotherm is given by Eq. (9):

$$\frac{C_e}{(x/m)} = \frac{1}{q_{max}K} + \frac{C_e}{q_{max}} \qquad \text{(Eq. 9)}$$

Where K (L/mg) is the Langmuir constant. C_e (mg/L) is the equilibrium concentration of BB3. q_e (x/m) (mg/g) and q_{max} are the adsorptive and maximum adsorption capacity of the SAM.

The Freundlich isotherm is given by Eq. (10):

$$x/m = K_f C_e^{1/n} \qquad \text{(Eq. 10)}$$

if the equation (10) is transformed into a linear form:

$$\ln(x/m) = \ln K_f + \frac{1}{n}\ln C_e \qquad \text{(Eq. 11)}$$

Where n is the intensity of adsorption, and K_f (mg/g) is the adsorptive capacity.

The adsorption data were analyzed with the Freundlich and Langmuir sorption models. Figs. 8 and 9 show the Langmuir and Freundlich isotherm plots, respectively. The parameters of isotherm models equations and constant are given in Table 4.

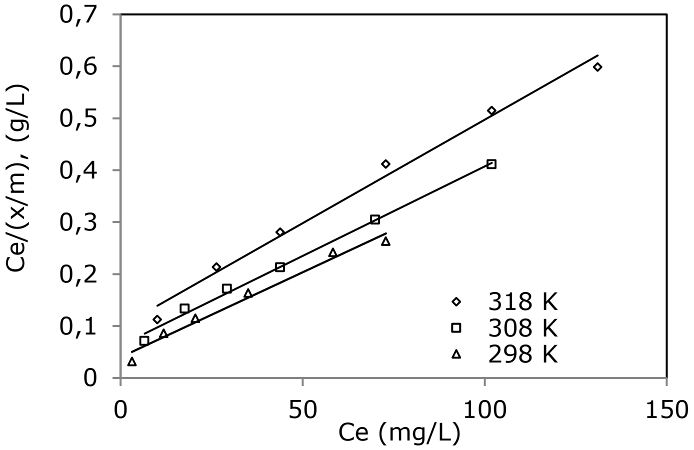

Figure 8: Langmuir isotherm.

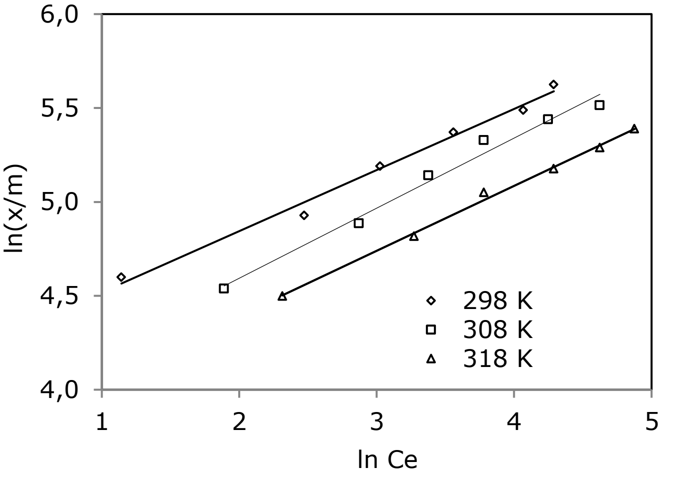

Figure 9: Freundlich isotherm.

Table 4: Parameters of investigated isotherms of BB3 molecules adsorption onto SAM.

Temperature K	Langmuir Constants		
	q_{max} (mg/g)	K (L/mg)	R^2
298	303.0	0.081	0.979
308	294.1	0.054	0.985
318	250.0	0.040	0.989
Temperature K	**Freundlich Constants**		
	K_f (mg/g)(L/mg)^n	n	R^2
298	64.53	3.00	0.991
308	46.86	2.68	0.984
318	40.56	2.89	0.996

It was found that the adsorption of BB3 onto SAM was described better by the Freundlich isotherm than Langmuir isotherm model. The relationship between temperature and the adsorption equilibrium constant, called van't Hoff equation, is given as:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^o}{RT^2} \quad \text{(Eq. 12)}$$

An integrated form of the van’t Hoff equation is presented in Eq. (13):

$$-\ln K = \frac{\Delta H^o}{R}\left(\frac{1}{T}\right) + C \quad \text{(Eq. 13)}$$

Eq. (14) is obtained when the constant is replaced by
(-∆Sº/R):

$$\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R}\left(\frac{1}{T}\right) \quad \text{(Eq. 14)}$$

If ∆Gº = -RTlnK is combined with Eq. (14) the following equation is obtained:

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad \text{(Eq. 15)}$$

Where ∆Sº, ∆Hº and ∆Gº, are changes in free entropy, changes in free enthalpy and changes in Gibbs free energy, respectively. K is the adsorption equilibrium constant; T (K) is absolute temperature. and R (8.314 J/mol K) is the universal gas constant. The intercept and the slope of the plots of lnK versus 1/T were used to determine the values of ΔSº and ΔHº.

The thermodynamic parameters were calculated for the process. The change of free energy (ΔGº) was calculated as -21.27 for 298 K, -21.05 for 308 K and -20.80 kJ/mol for, 318 K, respectively by using Eq.(14). The change in entropy (ΔSº) and enthalpy (Δ*H*º) were determined to be 21.86 J/mol K and -27.78 kJ/mol, respectively. The affinity of the SAM for BB3 is understand from the positive value of ΔSº. The negative values of ΔH° revealed that the adsorption is likely to be dominated by physical processes in nature involving weak forces of attraction (35,36). Also, the negative values of Δ*G*º indicate the feasibility the spontaneous of adsorption process.

DISCUSSION

The sulfuric acid-activated montmorillonite mineral (SAM) was prepared by natural montmorillonite mineral (NM), and it was used for the adsorption of BB3 from an aqueous media in a thermostatic water bath. The experimental results indicated that the adsorption of the BB3 depended on the initial pH of the solution, the initial concentration of the adsorbate (BB3), the temperature, and the contact time. The experimental result is summarized as follows:

1. It was observed that the value of pH_{zpc} was 5.1 for the acid activated montmorillonite mineral,
2. It was determined the adsorption capacity of the SAM increased with contact time and reached its maximum value in the range of 85-99 mg/g for different initial pH values after approximately 60 min,
3. It was obtained that the adsorption capacity of SAM increased linearly up to pH 6, reaching a maximum value (99 mg/g) at pH 6,
4. The equilibrium adsorption capacity of the SAM was determined to be about 97 and 89 mg BB3/g at 298 and 318 K,
5. It was determined that the adsorption capacity of BB3 increased from 130 to 180 mg/g at the range of initial concentrations values between 100 to 350 mg/L,
6. The optimum adsorption conditions were determined 298 K, 6 ± 0.02, 350 ppm, and 60 min,
7. The maximum efficiency and capacity of adsorption was obtained to be about 80% and 277 mg/g at the optimum experimental conditions,
8. Lagergren’s kinetic model (pseudo first order) simulated the kinetic data better than the Ho’s kinetic model (pseudo second order),
9. It was obtained that The Freundlich isotherm is the best fitting isotherm model equation.

As a result of the study, the acid-activated mineral is suitable for adsorption of BB3 dye molecules from aqueous media.

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