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# ADSORPTION OF METHYLENE BLUE ON IMINE MODIFIED SEPIOLITE FROM AQUEOUS SOLUTIONS

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## ABSTRACT

In this study, a modified sepiolite for methylene blue (MB) adsorption was designed. Modification of sepiolite was performed using N,N-dimethyl-4-(((3-(triethoxysilyl)propyl)imino)methyl)aniline (MESPIA) in the presence of ethanol solution. The modified sepiolite (SP-MESPIA) was characterized by using Fourier-transform infrared spectroscopy-attenuated total reflectance, scanning electron microscopy, thermal gravimetric analysis and Brunauer-Emmett-Teller instruments. The amount of adsorbed MB was measured by UV-Vis spectroscopy. The effects of concentration, temperature, ionic strength and pH to the adsorption capacity of SP-MESPIA were investigated. It was determined that chemical bonding took place between the hydroxyl groups and/or oxygen atoms within the structure of sepiolite and the silane group of MESPIA by releasing the ethoxy groups to the solvent. Sepiolite degraded in four steps, while modified sepiolite degraded in three steps and at higher temperatures. The adsorption capacity of modified sepiolite increased with increasing pH, temperature, ionic strength. The experimental data were analyzed using the Langmuir and Freundlich adsorption models. The experimental data fitted very well with Langmuir isotherm equation. The Langmuir monolayer capacity changed in the range of 32.9 $10^{-5}$-56.7 $10^{-5}$mol/g. The adsorption of MB was endothermic in nature (ΔH: 120 kJ/mol) and accompanied by an increase in entropy (ΔS: 513 J/molK) and a decrease in Gibbs energy (ΔG: 35.53 to 45.79 kJ/mol in the temperature range of 30-50$^o$C).

**KEYWORDS:**
Sepiolite, organo-modification, adsorption, characterization, methylene blue.

## INTRODUCTION

The disposal of wastewater to the environment without treatment is one of the main environmental problems. The presence of dyestuffs, especially in wastewaters, is carcinogenic and poses a serious danger to both aquatic organisms and human and environmental health. Therefore, the removal of organic and inorganic substances and dyestuffs that are not biodegradable in wastewater has been an important subject of study [1]. Removal of dyestuffs from wastewater is very difficult, as they are stable against light, heat and oxidizing agents and cannot be biodegradable. In addition, all conventional biological and chemical processes are inadequate to remove these pollutants. Therefore, in general, successful results are obtained by using adsorption technique in removing of dyestuffs from wastewater [2,3]. Activated carbons are generally used as adsorbents since they have high surface area and high adsorption capacity. However, since the obtaining activated carbons requires high cost, cheap adsorbents that can be an alternative to activated carbons have been investigated and clay minerals can be considered as a good example in this sense [4]. Increasing world population causes an increase in consumption and resource shortage. Therefore, the use of natural resources is of great importance. Clay is a good example of natural resources with different usage areas in terms of natural availability, abundance and cheapness [5]. Adsorption of dyestuff on clay minerals is of great importance due to the widespread use of these compounds in both domestic and industrial applications.

Sepiolite is a natural clay mineral composed of magnesium silicate with a micro fibrous morphology and unit cell formula of $Si_{12}O_{30}Mg_8(OH)_4(H_2O)_4.8H_2O$ [6,7]. The fibrous structure of sepiolite is formed by stacking the silicon-tetrahedral and magnesium-octahedral layers. The blocks in its structure consist of two tetrahedral silica layers surrounding a central magnesium layer, while tunnels are formed by reversing the silica layers. Unit sheet pores of sepiolite can be expanded. In addition, sepiolite has a high cation exchange. All these properties of sepiolite clay give it an excellent adsorbent property for the removal of organic or inorganic substances [8-11]. Adsorption on sepiolite surface occurs through oxygen atoms in the tetrahedral layer, water molecules coordinated with $Mg^{2+}$ ions at the edge of the structure, and silanol groups resulting from the breakdown of Si-O-Si bonds [12,13]. There are a lot of studies related to the removing of MB on different adsorbents from aqueous solutions in literature. Kul and Aldemir studied the adsorption performance of MB on natural, thermal and acid modified kaoline from aqueous solutions at three different temperature [14]; Dai et al the effect of contact time, solution pH, dosage of adsorbent, ionic strength and regeneration on adsorption behavior of MB on spent coffee grounds [15]; Dogan et al the removal of MB on micro- and nano-sized egg shell from aqueous solutions[16]; Pehlivan et al the effect of pH and temperature on the removal efficiency with PMMA/GF composites of MB from aqueous solutions[17]; Turkyilmaz et al the removal of MB on activated carbon, prepared from olive stones by chemical activation under different $H_3PO_4$ concentrations, from aqueous solutions[18]; Dogan et al the adsorption of MB onto hazelnut shell and perlite [19,20].

Sepiolite can be calcined or modified with organic or inorganic materials to further increase the adsorption capacity [21]. In the literature, there are limited numbers of studies on the removal of MB on sepiolite and/or modified sepiolite from the aqueous solutions. Cheng et al investigated the adsorption behaviors of MB dye onto modified sepiolite from its aqueous solutions [22]; Han et al the adsorption kinetics and thermodynamics of acid blue 25 and MB dye solutions on natural sepiolite [23]; Kuncek and Senerthe adsorption of MB onto sonicated sepiolite from aqueous solutions [24]; Dogan et al the adsorption kinetics and mechanism of cationic methyl violet and MB dyes onto sepiolite [4]. As seen from the literature summary above, there are limited number of studies on the modification of sepiolite with different organo-modifying compounds and removal of MB from wastewater. Therefore, the aim of this study was to investigate the adsorption of MB, a cationic dyestuff, on organo-modified sepiolite from aqueous solutions. The natural sepiolite was modified with N,N-dimethyl-4-(((3-(triethoxysilyl)propyl)imino)methyl)aniline. The sepiolite and modified sepiolite were characterized by using Fourier-transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR), scanning electron microscopy (SEM/EDX), thermal gravimetric analysis (DTA/TG) and Brunauer-Emmett-Teller (BET) instruments. The MB adsorption on the organo-modified sepiolite from the aqueous solutions was examined as a function of pH, temperature and ionic strength. Experimental values were analyzed according to Langmuir and Freundlich isotherms, and thermodynamic data were also calculated.

## MATERIALS AND METHODS

**Materials.** 4-(dimethylamino)benzaldehyde (DMAB), 3-aminopropyltriethoxysilane (3-APTS), MB, acetic acid, ethanol, toluene and sepiolite (SP) were obtained from Merck. The ethylalcohol ($C_2H_5OH$) used for washing processes of modified sepiolite was obtained from Sigma-Aldrich. All other chemicals were analytical grade. The structural form of MB was given in Figure 1.

**Method. Synthesis of modifier MESPIA.** 4-(dimethylamino)benzaldehyde (0.01 mol) and 3-aminopropyltriethoxysilane (0.01 mol) were reacted in 50 mL ethanol at about ~70 ºC for 24 hours. A few drops of acetic acid was used to catalyze the reaction. After cooling the reaction mixture, ethanol was removed on a rotary evaporator and a jelly dark yellow product (MESPIA) was obtained. Structure of the product was examined by FTIR-ATR spectroscopy. Figure 2a shows a schematic illustration of MESPIA production process [25,26].

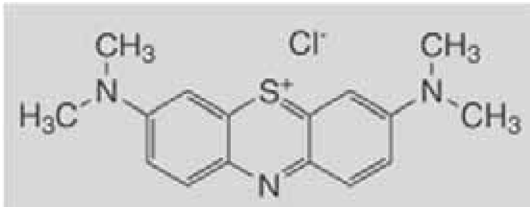



**FIGURE 1**
**The structure of MB dye**

**Modification of Sepiolite.** 5 g sepiolite and 2.5 mL modifier MESPIA were reacted in 100 mL of toluene at 110 °C for 24 hours. After 24 hours, the reaction mixture was cooled, filtered, and then washed twice with 30 mL toluene and ethanol. Finally modified yellowish sepiolite was dried in an oven at 100 ºC for 24 hours [25,26]. Figure 2b shows a schematic illustration of modified sepiolite process.

**Characterization.** Sepiolite and modified sepiolite clay samples were characterized by using BET, FTIR-ATR, DTA/TG and SEM/EDX devices. Specific surface areas of SP and SP-MESPIA clay samples were measured by using BET surface analyzer (Quantachrome Nova 2200e) by $N_2$ adsorption at 77 K. Before performing BET surface area analyses, samples were degassed at 200 ºC for 24 hours. FTIR-ATR spectroscopy was used for structural analysis of SP-MESPIA. Infrared spectra of SP and SP-MESPIA were obtained by using a FTIR-ATR (PerkinElmer Spectrum 65) spectrophotometer in the transmition mode in the wavenumber range of 4000-600 $cm^{-1}$ with ATR apparatus. The thermogravimetric analysis was performed by PerkinElmer Diamond simultaneous DTA/TG device in temperature scan rate of 10 ºC per minute in the temperature range of 30-1200 ºC under $N_2$ atmosphere. In order to investigate the morphological properties, scanning electron microscope (SEM/EDX) was used (Zeiss EVO LS 10).

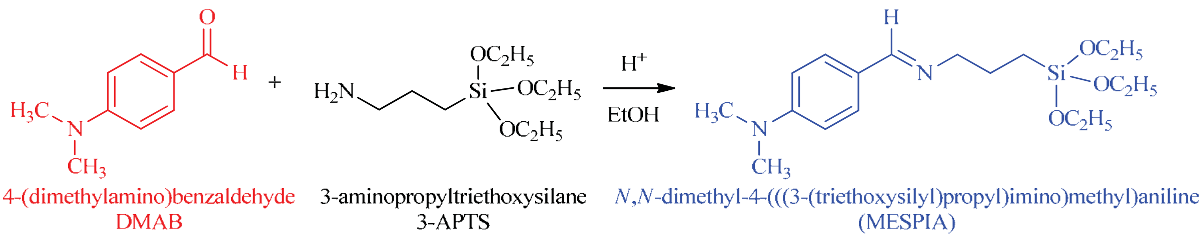



**FIGURE 2A**
**Schematic illustration of MESPIA production process**

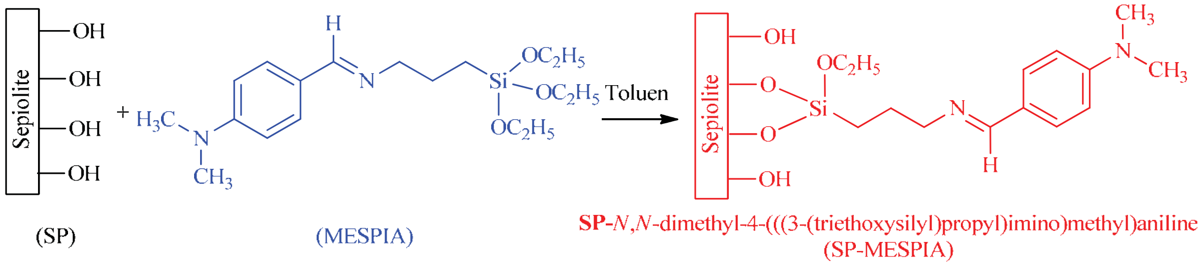



**FIGURE 2B**
**Schematic illustration of modification process**

**Adsorption Studies.** Adsorption studies of MB were carried out by using SP-MESPIA adsorbent. 50 mL aqueous solutions of MB at different initial dye concentrations (1-12.$10^{-5}$ M), pHs (3, 5, 7 and 9), ionic strengths (1.$10^{-1}$, 1.$10^{-2}$ and 1.$10^{-3}$ M NaCl) and temperatures (30, 40 and 50 °C) were shaken mechanically with 0.01 g SP-MESPIA for 24 hours. Stock solution was prepared in deionized water for MB and further experimental solutions were prepared from the stock solution by successive dilution. The pH of the solution was adjusted with diluted NaOH or HCl solution by using an Orion 920A pH-meter. The pH meter was calibrated with NBS buffers before each measurement. To keep the temperature constant an agitator incubator was used for the adsorption experiments. At the end of adsorption period, solutions were centrifuged at 5000 rpm for 15 minute and then, diluted. The MB concentration in solution after adsorption process was determined by UV-Vis spectrometer. The amounts of the adsorbed MB were calculated from the concentrations in solutions before and after adsorption according to Equation (1)

$$q_e = (C_o - C_e)\frac{V}{W} \quad (1)$$

where $C_o$ and $C_e$ are the initial and equilibrium liquid-phase concentrations of MB solution (mg/L), respectively; $q_e$ is equilibrium MB concentration on adsorbent (mg/g), V is the volume of MB dye solution (L), and W is the mass of adsorbent (g) [25,26].

## RESULTS AND DISCUSSION

**Characterization of Adsorbent. BET Analysis.** The surface area of sepiolite was measured as 118 $m^2$/g. As a result of modification of sepiolite with MESPIA, the surface area has decreased to 41 $m^2$/g. The decrease in the surface area may be due to the decomposition of the crystal structure of the sepiolite and the reduction of micropores by modification process [27].

**FTIR-ATR Analysis.** The modification of the sepiolite and the synthesis of the modifier has been proven by FTIR-ATR spectroscopy. Comparison of the spectra in Figure 3 shows that the MESPIA is synthesized. In the spectrum of 3-APTS, peaks at 2973-2884 $cm^{-1}$ belong to aliphatic C-H stretching vibrations and that at 1070 $cm^{-1}$ Si-O vibrations. Again, in the spectrum of DMAB, peak at 2904 $cm^{-1}$ is related to aliphatic C-H vibration, those at 2795-2714 $cm^{-1}$ aldehyde C-H vibrations and that at 1657 $cm^{-1}$ aldehyde C=O vibration. In the spectrum of MESPIA, the C=N vibration band of the imine structure appears. But the stretching vibration at 1657 $cm^{-1}$ of the carbonyl group of DMAB has disappeared. The FTIR-ATR spectra of sepiolite and modified sepiolite are shown in Figure 4. After modification, the bands of -OH deformation at 973 $cm^{-1}$ and Si-O stretching at 999 $cm^{-1}$ shift to 972 $cm^{-1}$ and 1004 $cm^{-1}$, respectively [28]. In addition, the wide -OH band at 3563 $cm^{-1}$ shifted to 3553 $cm^{-1}$ and its intensity decreased. Most importantly, the vibrations of MESPIA at 1605, 1538 and 1380 $cm^{-1}$ were also observed on the spectrum of the modified sepiolite.

**TG Analysis.** TG termograms of SP and SP-MESPIA under inert environment in the range of 30-1200 °C are shown in Figure 5. Thermogram of sepiolite has four parts that have different slopes.

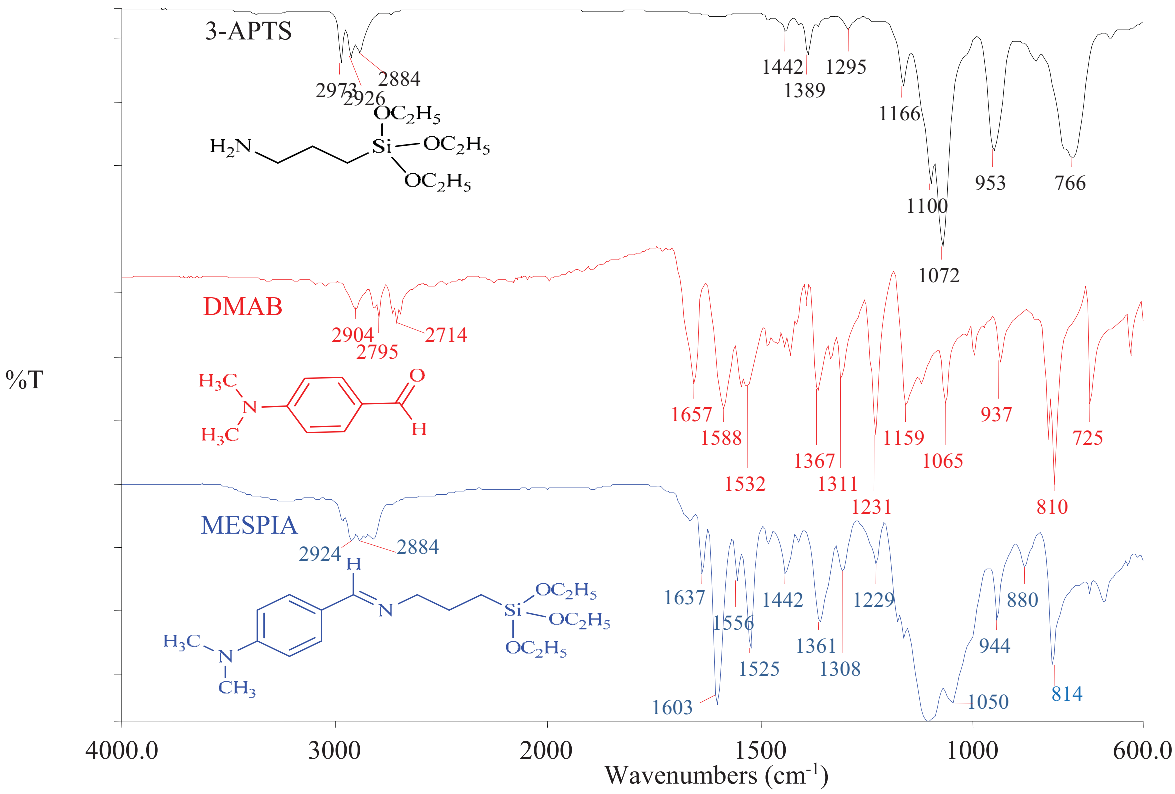



**FIGURE 3**
**FTIR-ATR spectra of 3-APTS, DMAB, and MESPIA**

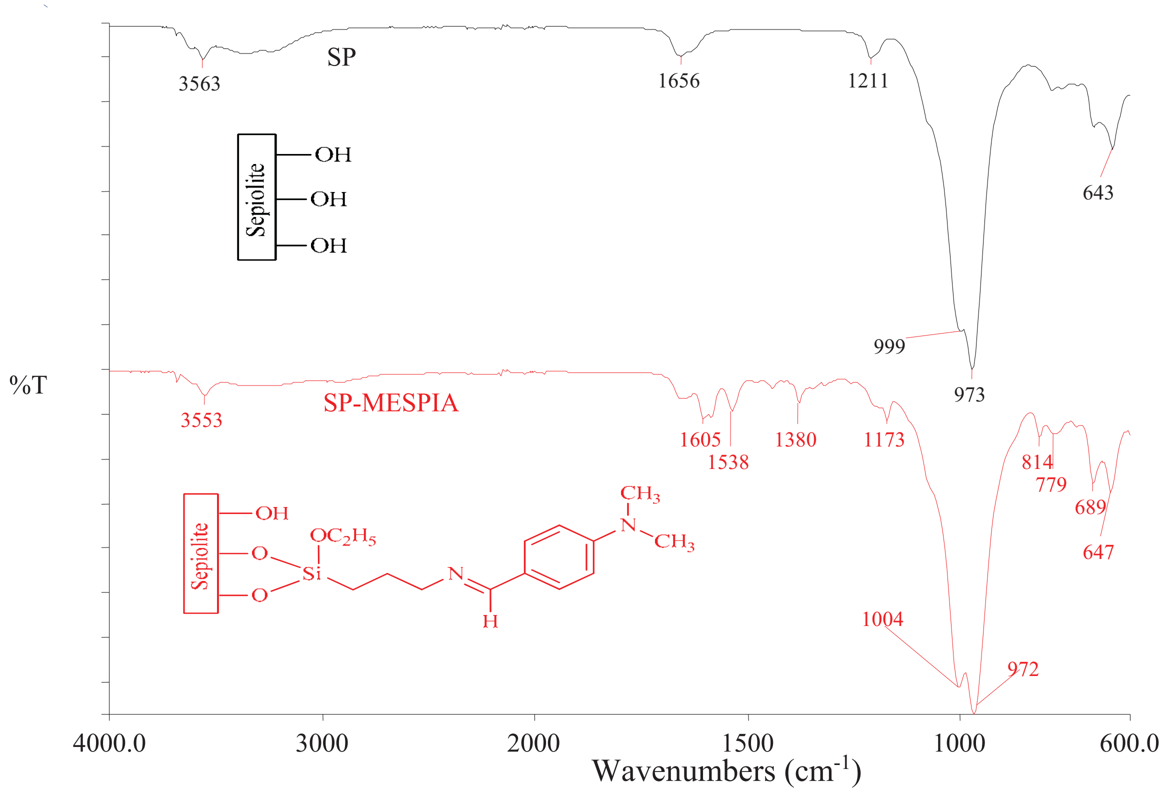



**FIGURE 4**
**FTIR-ATR spectra of sepiolite and modified sepiolite**

Step I $Mg_8Si_{12}O_{30}(OH)_4 \cdot (H_2O)_4 \cdot 8H_2O \leftrightarrow Mg_8Si_{12}O_{30}(OH)_4 \cdot (H_2O)_4 + 8H_2O$ (2)

Step II $Mg_8Si_{12}O_{30}(OH)_4 \cdot (H_2O)_4 \leftrightarrow Mg_8Si_{12}O_{30}(OH)_4 \cdot (H_2O)_2 + 2H_2O$ (3)

Step III $Mg_8Si_{12}O_{30}(OH)_4 \cdot (H_2O)_2 \rightarrow Mg_8Si_{12}O_{30}(OH)_4 + 2H_2O$ (4)

Step IV $Mg_8Si_{12}O_{30}(OH)_4 \rightarrow Mg_8Si_{12} + 2H_2O$ (5)

Frost and Ding stated that up to 200 $^0$C bothhygroscopic and zeolitic water were lost [29]. Between 250 and 450°C bound water were lost; more strongly bound water (coordinated water) and the hydroxyl units were lost in the temperature range 450-610°C. In this study, sepiolite also degrades in four steps. The first step occurs before 100 °C and is attributed to the loss of adsorbed water. The second, third and final steps were observed at 287, 520 and 799 °C, respectively. Nagata et al proposed a set of reaction steps for the dehydration and dehydroxylation of sepiolite [30]. These steps correspond to the loss of adsorbed water, the loss of hydration water, the loss of coordination water and the loss of water through dehydroxylation. Such a scheme is represented by the following chemical equations (2-3-4-5):

In TG thermograms, the degradation steps of the modified sepiolite are different from those of the sepiolite. Because the modifier used in this modification is an organic substance. Modified sepiolite degrades in 3 steps and higher temperatures. While the residual amount of sepiolite is 83.86 wt%, the residual amount of the modified sepiolite is 77.54 wt%. This result shows that sepiolite is thermally more stable than modified sepiolite. This may be due to the hydrophobic character of the silanized sepiolite [31]. Thermal data obtained from TG analyzes also summarized in Table 1.

**SEM/EDX Analysis.** Figure 6 shows the SEM micrograph of the sepiolite and modified sepiolite. The clay samples exhibits fibrous morphology, and a number of sepiolite fibers congregate into bundles with modification. This is an important result in explaining the decrease in surface area with the modification process. Energy diffuser X-ray spectroscopy (EDX) analysis together with SEM images was performed to describe the chemical composition of the sepiolite and to explain the change in the structure of the organo-modified sepiolite. Figure 6 also shows EDX mapping images of sepiolite and modified sepiolite samples. The percent elemental contents calculated from EDX analysis of the sepiolite and modified sepiolite samples were given in Table 2. In the EDX patterns of sepiolite, peaks corresponding to the elements such as O, Si and Mg were observed, and the percent of these elements were determined as 52.37, 30.99 and 16.64 wt%, respectively. These results are compatible with the literature [32]. When the elemental compositions of natural and organo-modified sepiolite samples were compared, C and N elements were also appeared in the structure of the modified sepiolite, and the percent of these elements in structure were approximately 15 and 2.5 wt%, respectively. This was proof that the natural sepiolite surface was modified with MESPIA. The appearance of nitrogen and carbon atoms in addition to Si and O atoms in EDX pattern of the modified sepiolite confirmed the modification.

**Adsorption equilibrium.** The adsorption of MB dye on modified sepiolite from aqueous solutions was investigated as a function of pH, ionic strength and temperature.

**Effect of pH.** pH is one of the most important factors which controls the adsorption extent of dyes on oxide surfaces. Adsorption process usually depends on the electrokinetic properties of oxide which determines with $H^+/OH^-$ amount [33]. The adsorption behavior of MB on modified sepiolite was studied over a wide pH range of 3–9. Figure 7 indicates the effect of pH to the removal of MB on modified sepiolite from aqueous solutions. It is seen that the higher the pH, the higher the adsorbed amount of MB on modified sepiolite. Maximum MB removal was observed at pH 9. The increase in adsorption can be explained by considering the surface charge of adsorbent. In our previous study, we investigated the zeta potential of sepiolite suspensions as a function of pH, and found that sepiolite had an isoelectrical point at pH 6.6. According to this result, it can be said that sepiolite

**TABLE 1**
**The thermal data obtained from TG analysis of samples**

| Adsorbent | First step | | Second step | | Third step | | Fourth step | | Residue % |
|---|---|---|---|---|---|---|---|---|---|
| | $T_{max1}$ ºC | Weight loss % | $T_{max2}$ ºC | Weight loss % | $T_{max3}$º C | Weight loss % | $T_{max4}$ ºC | Weight loss % | |
| Sepiolite | 77.2 | 7.97 | 287.1 | 3.05 | 520.4 | 2.71 | 798.5 | 2.24 | 83.86 |
| Modified sepiolite | --- | --- | 129.4 | 2.519 | 355 | 14.15 | 1031.9 | 5.76 | 77.542 |

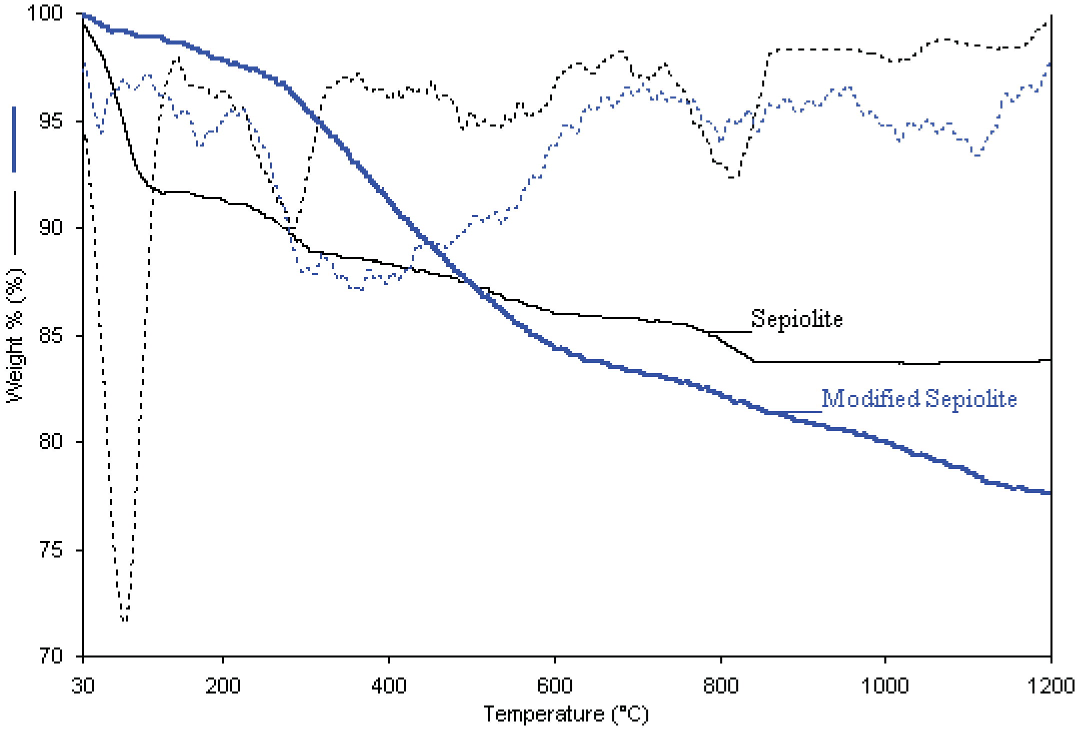
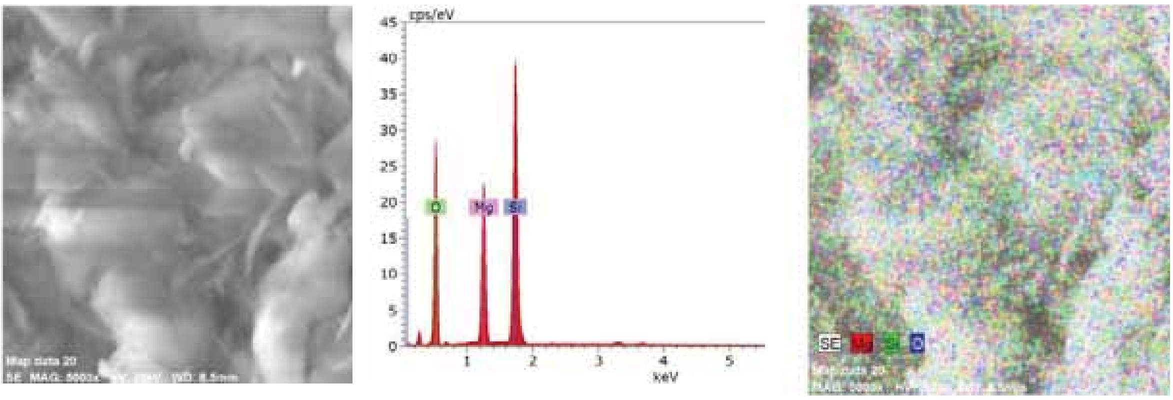
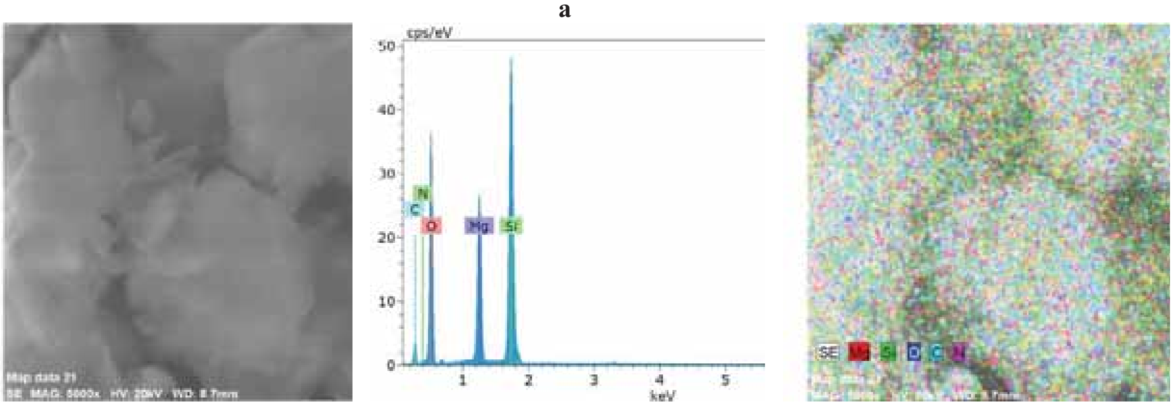



**FIGURE 5**
**TG and d[TG] curves of sepiolite and modified sepiolite**




**a**

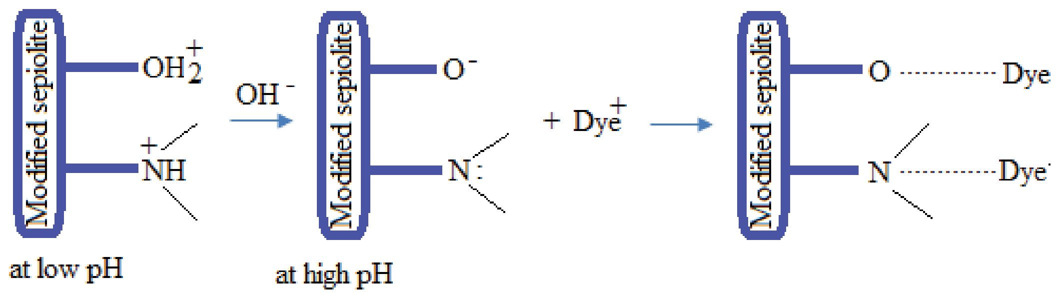



**b**

**FIGURE 6**
**SEM images, EDX pattern and Mapping images of a. sepiolite and b. modified sepiolite, respectively.**

**TABLE 2**
**Percent elemental contents obtained from SEM/EDX analysis**

| Samples | O wt% | Si wt% | Mg wt% | C wt% | N wt% |
|---|---|---|---|---|---|
| Sepiolite | 64.68 | 21.80 | 13.52 | --- | --- |
| SP-MESPIA | 55.06 | 13.29 | 7.76 | 20.74 | 3.15 |




(6)

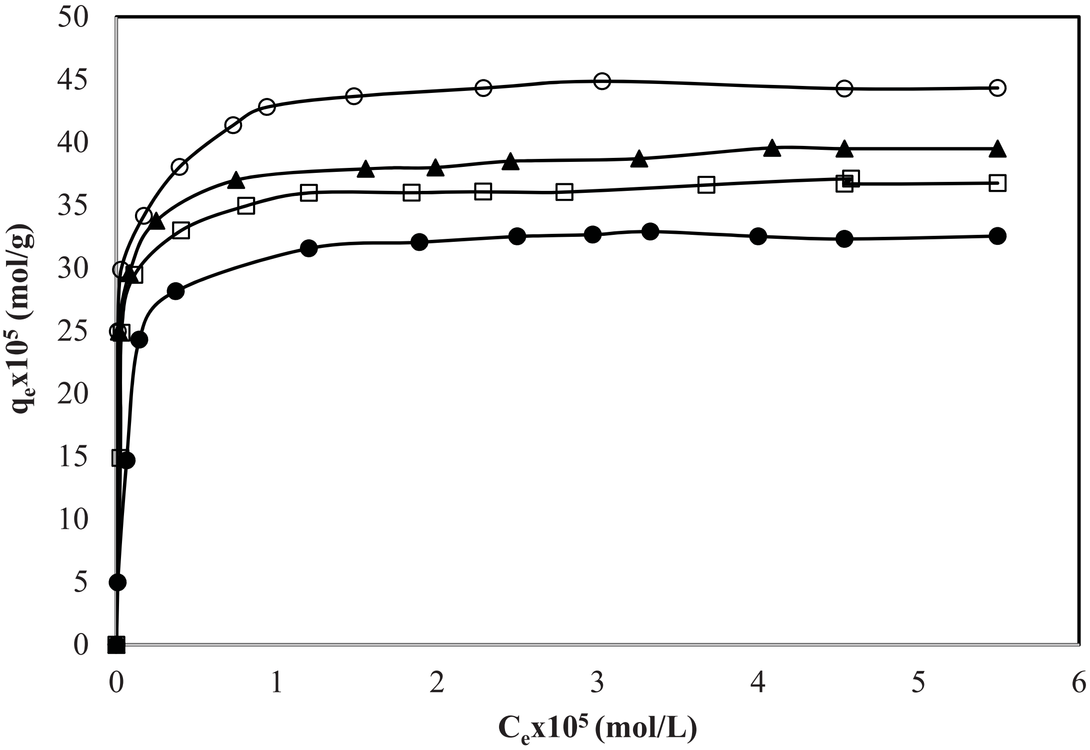



**FIGURE 7**
**The effect of pH to the adsorption of MB onto modified sepiolite**

surface exhibits positive zeta potential values at the lower pH values from pH 6.6, and negative zeta potential values at the higher pH values from pH 6.6 [34]. As the pH of the dye solution becomes higher, the association of dye cations with more negatively charged modified sepiolite surface can more easily take place eq. (6) above [20]:

A similar effect was previously reported by Mall and Upadhyay [35] for MB adsorption on fly ash particles and Dogan and Alkan [36] for methyl violet adsorption on perlite.

**Effect of Ionic Strength.** Different parameters can affect the adsorption of MB on modified sepiolite. Figure 8 shows the adsorption isotherms of MB on modified sepiolite at different NaCl ($1x10^{-3}$, $1x10^{-2}$ and $1x10^{-1}$ mol/L) concentrations. The amount of adsorbed MB on modified sepiolite increases and then reaches saturation. The presence of NaCl in the solution may have two opposite effects. On the one hand, since the salt screens the electrostatic interaction of opposite charges of the surface and the dye molecules, the adsorbed amount should decrease with increase of NaCl concentration. On the other hand, the salt causes an increase in the degree of dissociation of the dye molecules by facilitating

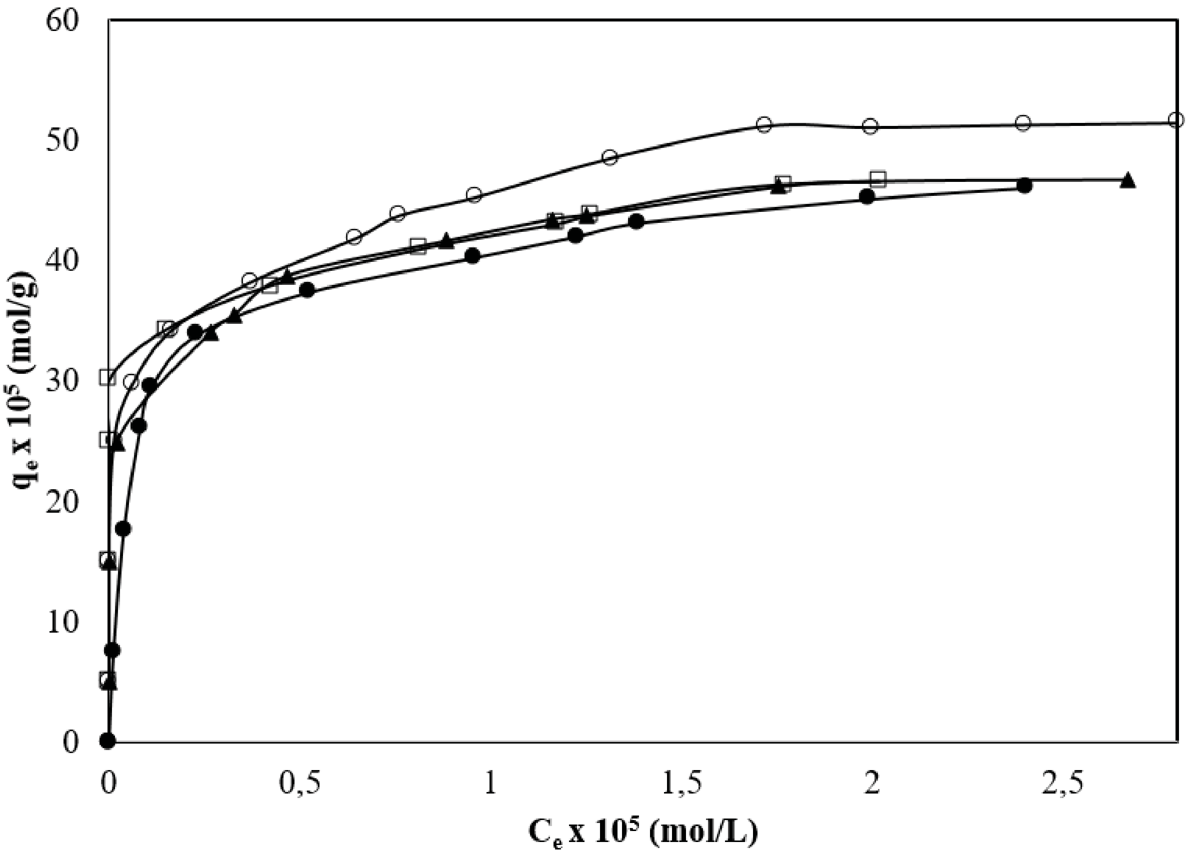



**FIGURE 8**
**The effect of ionic strength to the adsorption of MB onto modified sepiolite**

the protonation. Since the dissociated free dye ions for electrostatically binding onto oppositely charged solid surface increase, the amount adsorbed also increase [37]. The latter effect seems to be dominant on the adsorption capacity of the surface. For the adsorption of BBF by soils and malachite green by husk-based activated carbon, the adsorption was also found to increase with increasing ionic strength [38,39].

**Effect of Temperature and Thermodynamic Parameters.** Figure 9 shows the effect of temperature to adsorption of MB on modified sepiolite. The adsorption was carried out at three different temperatures from 298 to 318 K with an interval of 10 K. The adsorption of MB improved steadily with an increase in adsorption temperature. This may be a result of increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution, and change the equilibrium capacity of the adsorbent for a particular adsorbate. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the modified sepiolite enabling large dyes to penetrate further as found by As four et al [40]. Increase in raising temperature of the adsorption capacity of modified sepiolite implies that the enthalpy change has positive values, indicating that the adsorption process of MB on modified sepiolite was endothermic.

The change in standard free energy, enthalpy and entropy of adsorption were calculated using the following equations [41]:

$$lnK = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (7)$$
$$\Delta G = \Delta H^o - T\Delta S^o \quad (8)$$

where R is the ideal gas constant (8.314 J/mol K) and T is the temperature (K). In this study, the thermodynamic parameters, $\Delta G^o$, $\Delta S^o$ and $\Delta H^o$, for the adsorption process were computed from the plots of lnK versus 1/T (Figure10), and given in Table 3. This curve has a high regression coefficient (0,99). According to Van't Hoff equation, positive values of $\Delta H^o$ (120 kJ/mol) show the endothermic nature of adsorption. The negative values of $\Delta G^o$ (35.5, 40.7 and 45.8 kj/mol) indicate the spontaneous nature of adsorption. The positive values of $\Delta S^o$ (513 J/mol K) suggest the increasing randomness at the solid/solution interface during the adsorption of MB onto modified sepiolite.

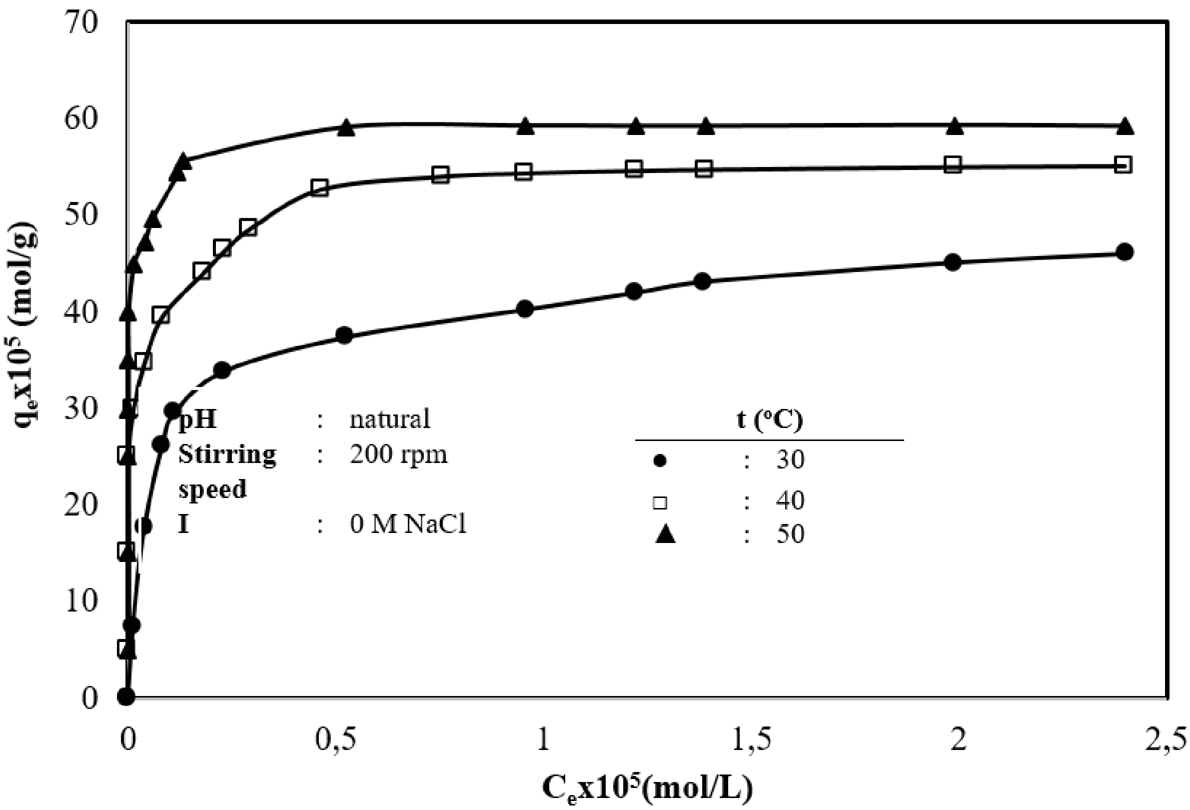



**FIGURE 9**
**The effect of temperature to the adsorption of MB on modified sepiolite**

**TABLE 3**
**Thermodynamic parameters calculated for MB adsorption on modified sepiolite**

| Adsorbate | Adsorbent | Parameters | | ΔH | ΔS | ΔG |
|---|---|---|---|---|---|---|
| | | t °C) | pH | (kJ/mol) | (J/mol K) | (kJ/mol) |
| MB | SP-MESPIA | 30 | natural | 120 | 513 | -35.6 |
| | | 40 | natural | | | -40.7 |
| | | 50 | natural | | | -45.8 |

**Isotherm Analysis.** The properties of adsorption process are generally determined through adsorption isotherms. The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [42]. Among several isotherm equations, two important isotherms, the Langmuir and Freundlich isotherms, were selected in this study. The Langmuir theory assumes that sorption takes place at specific sites within the adsorbent, which means that once a dye molecule occupies a site, no further adsorption can take place at that site [43]. The linearized Langmuir equation can be represented as follows [44];

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K} + \frac{C_e}{q_{max}} \quad (9)$$

where $q_{max}$ is the maximum amount of adsorption (mol/g), K is the affinity constant (L/mol) and $C_e$ is the solution concentration at equilibrium (mol/L). According to the Equation (9), a plot of $C_e/q_e$ versus $C_e$ should be a straight line with a slope $1/q_{max}$ and intercept $1/q_{max}K$ when adsorption follows the Langmuir equation.

The Freundlich model assumes that the sorption takes place on heterogeneous surfaces and adsorption capacity depends on the concentration of dyes at equilibrium. The well-known logarithmic form of Freundlich model is given by the following equation [45]:

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \quad (10)$$

where $K_F$ and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. If $1/n<1$, it indicates a favorable adsorption. So, the plot of $lnq_e$ against $lnC_e$ according to Eq. (10) should give a linear relationship, from which 1/n and $K_F$ can be determined from the slope and the intercept, respectively.

Adsorption isotherms were obtained using Eqs. (9) and (10) (Figures not shown). The parameters of the isotherm models calculated from the experimental data and the values of correlation coefficient ($R^2$) were presented in Table 4. All values of 1/n are smaller than 1. The correlation coefficients for Freundlich isotherm are in the range of 0.992-0.149, indicating that the isotherm is not compatible with the experimental results. $R^2$ values for the Langmuir isotherm are higher than those for Freundlich isotherm. It is clear that the equilibrium adsorption data compatible with Langmuir isotherm model, which suggests that the adsorption is a process which occurs in a homogeneous surface. Additionally, these results also explain no interaction and transmigration of dyes in the plane of the neighboring surface [46]. As can be seen from Table 4, the value of K (Langmuir constant) increased with increasing temperature, which show that high temperature favored the adsorption process.

The shape of the isotherm may also be considered with a view to predicting if an adsorption system is ‘favourable’ or ‘unfavourable’. The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter [47].

$$R_L = \frac{1}{1+KC_e} \quad (11)$$

where $R_L$ indicates the shape of the isotherm to be either unfavorable ($R_L$>1), linear ($R_L$=1), favorable (0< $R_L$<1), or irreversible ($R_L$=0). It can be observed from Table 4 that all values of $R_L$ are between 0 and 1 indicating the adsorption process was favorable. The values of $R_L$ at low temperatures are smaller than those at high temperatures, from which it can be deduced that the adsorption behavior is more effective at low temperature.

Table 5 lists the maximum monolayer adsorption values ($q_{max}$) of MB on different adsorbents. Based on the data in Table 5, it was found that modified sepiolite displayed a quite high adsorption capacity for MB. Additionaly, in the previous study related to MB adsorption onto raw sepiolite [33], the $q_{max}$ values were in the range of 16.3x10$^{-5}$-27.3x10$^{-5}$ mol/g. In this study, the $q_{max}$ values were in the range of 32.9x10$^{-5}$-56.7x10$^{-5}$mol/g.

## CONCLUSIONS

In this study, firstly, MESPIA was synthesized by condensation reaction of 4-(dimethylamino)benzaldehyde and 3-aminopropyltriethoxysilane. Then, sepiolite surface was modified by MESPIA. SP-MESPIA was characterized by FTIR-ATR, BET, DTA/TG and SEM/EDX. The removal of MB on modified sepiolite was systematically investigated under various conditions. FTIR-ATR analysis confirmed the modification. BET surface area analysis showed that surface area of SP-MESPIA decreased with modification. Sepiolite degraded in four steps, while

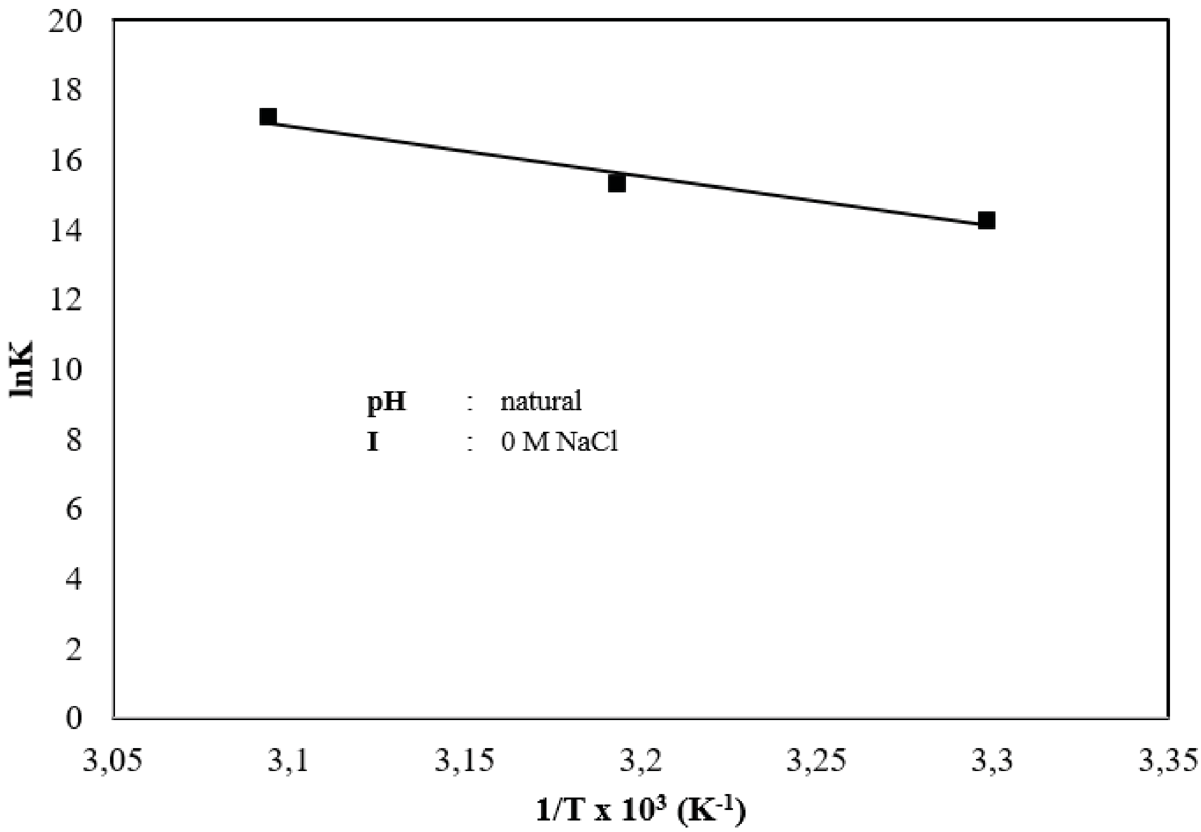



**FIGURE 10**
**Plot of lnK versus 1/T for adsorption of MB on modified sepiolite.**

**TABLE 4**
**Isotherm parameters calculated for MB adsorption onto modified sepiolite**

| Parameters | | [I] (mol/L) | Langmuir isotherm | | | | $R_L$ | Freundlich isotherm $R^2$ |
|---|---|---|---|---|---|---|---|---|
| Temperature (°C) | pH | | $q_{max(cal)}$ (mol/g)x10$^5$ | $q_{max(exp)}$ (mol/g)x10$^5$ | K (L/mol) x10$^{-5}$ | $R^2$ | | |
| 30 | - | - | 46.7 | 48.0 | 15.30 | 0.994 | 0.874-0.0265 | 0.7211 |
| 40 | - | - | 55.6 | 55.1 | 44.99 | 0.999 | 0.360-0.0092 | 0.9011 |
| 50 | - | - | 56.7 | 56.6 | 294.10 | 0.999 | 0.199-0.00141 | 0.6791 |
| 30 | - | 0.001 | 47.3 | 49.9 | 23.50 | 0.998 | 0.220-0.02070 | 0.9925 |
| 30 | | 0.010 | 47.2 | 46.6 | 11.76 | 0.994 | 0.801-0.0309 | 0.9798 |
| 30 | | 0.100 | 50.4 | 51.4 | 18.05 | 0.995 | 0.787-0.0194 | 0.9898 |
| 30 | 3 | - | 32.9 | 32.5 | 18.97 | 0.998 | 0.862-0.00951 | 0.7689 |
| 30 | 5 | - | 37.0 | 36.8 | 30.05 | 0.999 | 0.568-0.00602 | 0.1485 |
| 30 | 7 | - | 39.1 | 39.5 | 28.40 | 0.999 | 0.686-0.00637 | 0.1612 |
| 30 | 9 | - | 44.6 | 44.3 | 32.05 | 0.999 | 0.772-0.00565 | 0.9587 |

**TABLE 5**
**The maximum monolayer adsorption capacities calculated for the adsorption of MB onto different adsorbent**

| Adsorbents | $q_{max}$ x10$^5$(mol/g) | References |
|---|---|---|
| Pyrophyllite | 22.02 | [48] |
| Zeolite | 17.81 | [49] |
| Sonicated sepiolite | 32.90-43.42 | [24] |
| Modified chitosan | 3.41 | [50] |
| Chitosan modified zeolite | 11.58 | [51] |
| Natural sepiolite | 24.51-27.87 | [52] |
| Clay/biochar composite | 3.73 | [53] |
| Chitosan/sepiolite composite 50:50 wt.% | 12.81 | [54] |
| CuO-acid modified sepiolite | 12.07-20.16 | [55] |
| Pal-APTES-Sep-APTES | 15.47-18.76 | [27] |
| Natural clay | 19.54-31-26 | [56] |
| Algerian palygorskite | 17.97 | [57] |
| Sepiolite | 16.3-27.3 | [33] |
| SP-MESPIA | 32.9-56.7 | In this study |

modified sepiolite degraded in three steps and at higher temperatures. The adsorbed amount of MB dye on modified sepiolite increased with increasing pH, ionic strength and temperature. The adsorption data were evaluated by Langmuir and Freundlich isotherm equations and Langmuir adsorption isotherm was in good agreement with the experimental data. The negative values of ΔG° and the positive value of ΔH° indicate the spontaneous nature of adsorption and that the adsorption reaction is endothermic. The positive value of ΔS° suggests increasing randomness at the solid/ liquid interface during the adsorption of MB onto modified sepiolite in the aqueous solution. It is understood from the thermodynamic investigation that the removal of MB was spontaneous with increasing temperature and endothermic process. The dimensionless separation factor ($R_L$) values indicated favorable adsorption.

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