Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2018.22704

124 (2018) 279–286
August

Removal of Methylene Blue dye from aqueous solutions by illite clay

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Received 28 February 2018; Accepted 23 June 2018

ABSTRACT

In this study, adsorption of methylene blue (MB) dye on illite from aqueous solutions was investigated as a function of pH, electrolyte concentration and temperature. Illite clay was characterized using FTIR-ATR, BET, SEM, XRF and XRD instruments. Adsorption studies showed that adsorption process attained to equilibrium about 3 h and adsorbed amount of MB on illite increased with increasing pH, electrolyte concentration and temperature. Experimental data were analysed with Temkin, Dubinin-Radushkevich (DR), Freundlich and Langmiur isotherms and correlated reasonably well by Langmiur adsorption isotherm with highest R^2 values. Then, Langmiur isotherm parameters (q_m and K) were calculated. The value of maximum adsorption capacity (q_m) was varied from $14.61\cdot10^{-5}$to $31.63.10^{-5}$ $mol\cdot g^{-1}$ for different experimental conditions. The adsoption heat was calculated as 14.38 $kJ\cdot mol^{-1}$ for isosteric conditions ($\theta = 0.5$). The positive and relatively low value of adsorption heat shows that adsorption process is an endothermic process and interaction between the dye and illite is a physical interaction. The values of R_L, calculated dimensionless separation factor, showed that illite can be used for removal of MB from aqueous solutions.

Keywords: Illite; Clay; Methylene blue; MB; Adsorption; Isotherm; Dye

1. Introduction

Today, dyestuffs originating from industrial wastes such as leather, textile, paper, printing, food, cosmetics, paint, pigments, etc. are important pollutants for soil, air and water. These polluted areas pose great threats to living organisms. Cleaning the polluted environments require quite expensive and complex facilities. For this reason, it is more important to try to prevent the pollution of water, soil and air. The most important of the areas mentioned above is water pollution because materials that cause pollution in soil and air also pass to water with factors such as rain and snow in time [1–4]. Many industries use dyes to color their products. All over the world, there are more than 10,000 various kinds of commercial dyes and are consumed above $7\cdot10^5$ tones annually. Approximately 12% of synthetic dyes are lost during production processes. 20% of these lost dyes are given to the environment as wastes of industrial enterprises and threat environment [5]. With the development of industry, factory wastes and some water-soluble dyestuffs form significant environmental pollution and it is necessary to remove these pollution from water [6]. Biological, physical and chemical methods are widely used in the removal of dyestuffs from wastewater. One of the most important physical methods is adsorption. Adsorption is an effective and economic method to remove dyes, pigments and other colorants and to control the bio-chemical oxygen demand. The most important criterion in the selection of adsorbent to be used in a process is that the adsorbent is cheap, abundant and reusable [7]. Adsorbents commonly used in the removal of industrial wastes are alumina, rutile, zirconia, perlite, manganese oxide, silica, goethite, hematite, amorphous iron oxide, bentonite, sepiolite, activated carbon, sphalerite, titanium oxide, red mud, mica, kaolinite, clays, volatile ash, lignite, oxides, various poly-

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mers, clays, resins, etc. [1]. There are many studies showing that these adsorbents are used in the removing of different pollutants. Özmetin et al. determined optimum process parameters for a real textile industry wastewater treatment using Bigadiç zeolite (clinoptilolite) by response surface methodology [8]. Özdemir et al. investigated the removal of the cationic dyes, methyl violet (MV) and MB from aqueous solutions using sepiolite as an adsorbent and found that the adsorbed amount of MV and MB dyes on sepiolite increased with increasing pH, electrolyte concentration and temperature. The isotherm data were reasonably well correlated by Langmuir isotherm [9]. Doğan et al. studied the adsorption behavior of MB from aqueous solutions onto unexpanded and expanded perlite samples activated by H_2SO_4 and NaCl solutions [10]. Rytwo et al. calculated the enthalpy of adsorption of MB and crystal violet on montmorillonite and found that the enthalpy of adsorption of MB is endothermic and the enthalpy of adsorption of crystal violet is exothermic. Despite the prolific uses in the water and wastewater industries, some of them remain as an expensive material, and the adsorption capacities are insufficient in the removal of dyes from wastewaters [11]. Another clay mineral, a low cost and abundantly available in nature, is illite. Illite is a non-expanding and 2:1 layered mineral, and possess potassium atoms bonded covalently with oxygen atoms on the interlayer of its lattice [12]. Illite is a convenient adsorbent for a variety of compounds due to its moderate cation exchange capacity (CEC) and specific surface area [13]. There are some studies on the removal of pollutants from aqueous solutions using illite as an adsorbent. However, these studies are rather limited. For example, Lee et al. investigated selective and irreversible adsorption mechanism of cesium on illite [14]; Chen et al. the adsorption behavior of hydrocarbons on illite [15]; Du et al. the adsorption of copper on illite from aqueous solutions [16]; Turan et al. the adsorption of copper and zinc ions on illite from aqueous solutions [17]; Chang et al. the adsorption of tetracycline on 2:1 layered non-swelling clay mineral of illite [13]; Omer et al. the adsorption thermodynamics of cationic dyes on a natural clay mineral from aqueous solution between 293.15 and 323.15 K [18]; Fil et al. the application of nonlinear regression analysis for MV dye adsorption from solutions onto illite clay [19].

The aim of this work is to investigate the adsorption behavior of MB on illite from aqueous solutions as a function of pH, temperature and electrolyte concentration.

2. Material and methods

2.1. Materials

The illite was obtained from Süd-Chemie Company in Turkey. The samples were treated as follows before being used in the experiments: The clay was firstly dried on air and then dried at 110°C for 2 h. The solid material was ground and then sieved by 100 µm ASTM sieve. In the further experiments, the fraction of the particles between 0 and 100 µm was used. Methylene blue (MB), being given molecular structure in Fig. 1 was selected as adsorbate material in the study.

Illite used in this study was characterized by FTIR-ATR, SEM, BET, XRD and XRF analyzes. Its chemical composition determined by XRF is given in Table 1. Its BET surface area was determined as 78 $m^2·g^{-1}$ by N_2 adsorption (at 77K) using a surface analyzer (Quantachrome Ins., Nova 2200e). Also, its some physicochemical properties are given in Table 2. All chemicals used were supplied from Merck and Aldrich, and were of analytical grade.

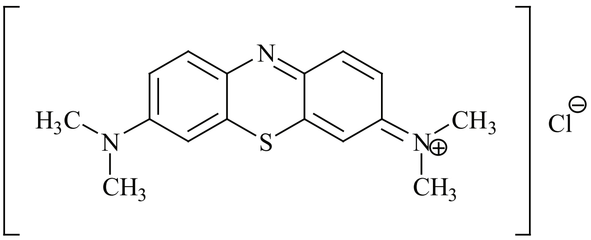

Fig. 1. The structure of MB

Table 1
The chemical composition of illite

Chemical compound	% (in weight)
SiO_2	45.67
Al_2O_3	36.88
K_2O	8.90
MnO	0.82
F	0.64
FeO	–
Na_2O	0.31
Fe_2O_3	–
H_2O	6.78

Table 2
Some physicochemical properties of illite

Characteristic	Value
Colour	White
Density, $g·cm^{-3}$	2.60–2.90
Transparency	Transparent
Form	Aggregates
Brightness	Earthy
Line colour	White
Surface area, $m^2·g^{-1}$	78

2.2. Methods

Adsorption experiments were carried out in 100 mL polyethylene flasks by shaking 50 mL aqueous solution having different initial MB concentrations with 0.15 g of illite sample at various pHs, electrolyte concentrations and temperatures. The adsorption time was selected as 3 h because the adsorption process attained to the equilibrium in 3 h. The initial concentrations of aqueous MB solutions were changed from 1.10^{-4} to 30.10^{-4} M. In the all experiments, the adsorption medium was shaken by using an incubator agitated at 150 rpm. Electrolyte solutions were prepared with NaCl. Except for experiments in which the effect of pH was examined, all adsorption experiments were carried out at natural pH (about 5.95) of the adsorbate solutions. The pH of the solution was adjusted with NaOH and HCl solutions using an Orion 920A pH-meter equipped with a combined electrode. The pH-meter was calibrated with NBS buffer before each measurement. At the end of adsorption period, the solution was centrifuged at 5,000 rpm for 15 min. The remaining MB solutions were then diluted at specific ratios and concentrations were determined by a Cadas 30S UV-Visible Spectroscopy. Measurements were carried out at wavelengths of 663 nm corresponding to the maximum absorbance for MB. A blind sample without MB solutions was used for measurements of each series of experiments. Quantities of adsorbed dye on illite surface at the equilibrium were calculated from the concentrations in solutions before and after adsorption using the following mass equations:

$$q_e = (C_0 - C_e)\frac{V}{W} \qquad (1)$$

Here, the C_0 and C_e are the concentrations (M) of MB in liquid phase at the initial and equilibrium, respectively; V is the volume of the MB solution (L); and W is the mass of the used illite sample (g). Each experimental point is the mean of two independent adsorption experiments [10].

3. Results and discussion

3.1. Characterization of illite

FTIR-ATR spectrum of illite sample is given in Fig. 2. The expected peaks for an illite clay was obtained by FTIR results of the sample: 3619 cm^{-1} assigned to ν(OH); 1634 cm^{-1}, δ(OH) of water; 914 cm^{-1}, δ(Al-Al-OH); 619 cm^{-1}, δ(OH) [20]. A broad peak centered at 3619 cm^{-1} is mainly due to the structural inner OH stretching modes of the octahedral sheet of the layer [21]. Fig. 3 shows the SEM photograph of illite. It is seen from the photograph that the illite is in the porous structure. The XRD pattern of illite is given in Fig. 4. The characteristic XRD peaks of illite are shown in Fig. 4. In this case, it can be said that the illite used in the study is quite pure.

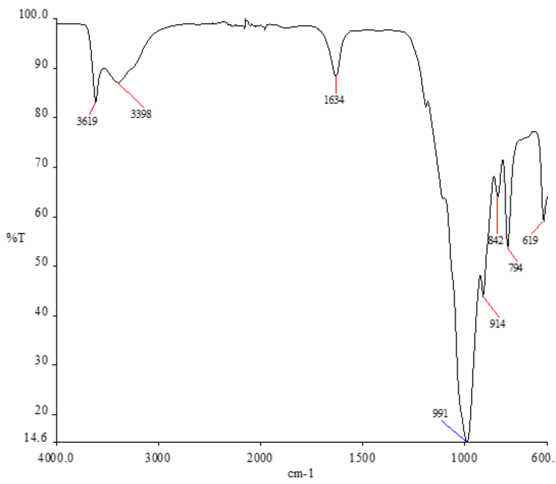

Fig. 2. FTIR-ATR spectra of illite.

3.2. Adsorption of MB on illite

Adsorption of MB on illite from aqueous solutions was investigated as a function of pH, electrolyte concentration and temperature, and the results obtained were given below.

3.2.1. Effect of pH

One of the most important factors controlling the degree of adsorption of dye substances on oxide surfaces is pH of solution [22]. The adsorption process is often dependent on the electrokinetic properties of the oxide surface, which are identified by the amount of H$^+$/OH$^-$ adsorbed. Electrokinetic behavior is defined by the net charge on the particle surface [23]. From electrokinetic studies, the isoelectric point of the illite was found to be 2.08 [24]. This result

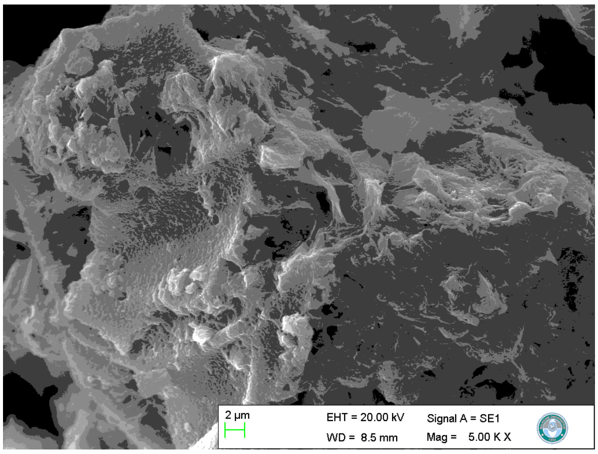

Fig. 3. SEM image of illite

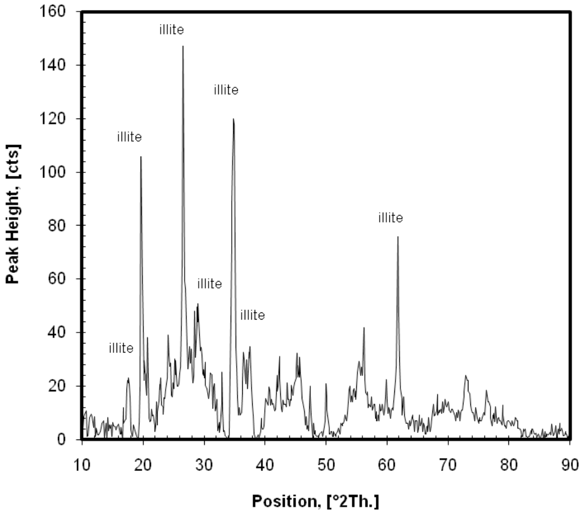

Fig. 4. XRD pattern of illite.

shows that the illite surface has a positive zeta potential at pH values below 2.08 and a negative zeta potential at pH values above 2.08.

The adsorption of MB on illite was studied at initial pH values in the range of pH = 3–9. The temperature and time in experiments were kept constant at 30°C for 3 h, respectively. The experimental results are plotted in Fig. 5. As can be seen from Fig. 5, the adsorbed amount of MB increased with increasing initial pHs of solutions.

For suspensions with higher pH values than isoelectric pH in the equilibrium, it can be said that the interaction of the cationic dye molecules with the negatively charged illite surface may be increased due to the increasing negative charge of the oxide-solution interface and the negative zeta potential. This demonstrates that more cationic MB dye is adsorbed on the illite surface. This can be illustrated by the following reaction.

$$-SOH + OH^- \rightleftharpoons -SO^- + H_2O \quad (2)$$

In addition, since hydroxyl (silanol and aluminol) groups on the surface show amphoteric properties at the mineral edges, specific adsorption of cations and anions on these surfaces is also possible [25].

3.2.2. The effect of electrolyte concentration

Numerous studies have shown that the extent of dye removal is significantly influenced by the concentration and nature of the various electrolyte species in dye medium [26]. In this work, sodium chloride was added into the suspensions in order to investigate the effect of electrolyte concentration in the adsorption of MB on illite. Fig. 6 shows the adsorption curves of MB on illite from aqueous solutions at different NaCl concentrations at 30°C and the natural solution pH value (5.95). As seen in Fig. 6, the increase in the electrolyte concentration of the solution causes an increase in the amount of adsorbed MB on illite. The presence of an electrolyte in adsorption medium may have different effects on the adsorption process, as follows: a. It may interfere with the electrostatic interaction between the adsorbate and the adsorbent by entering between the oppositely charged illite surface and the dye, thereby reducing adsorption. b. The increased electrolyte concentration decreases the solid-solution interface tension in solution and, therefore, causes to increase the surface interaction of the cationic dye material. c. The degree of dissociation of the dye molecules will increase by the increased electrolyte concentration and thus increase the adsorption [27–29].

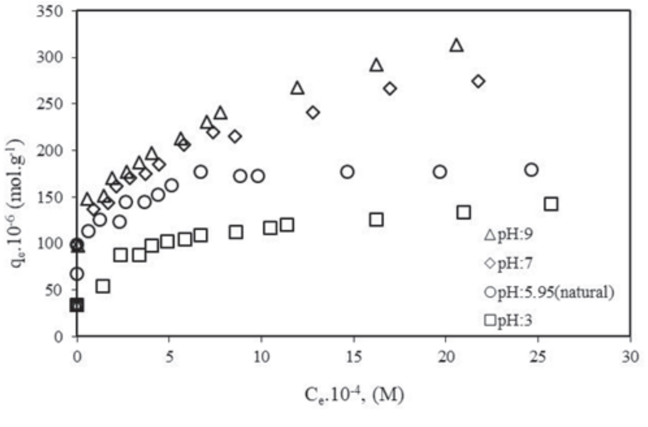

Fig. 5. The effect of pH of the solution on the adsorption of MB on illite (T: 303K, E: 0 M, S/L: 3 g·L^{-1}).

It can be said that the increasing ion intensity increased the adsorption of MB dye on the illite surface because of the b and c effects explained above [28,29]. Other hand, the higher adsorption capacity of dye under these conditions can be attributed to the aggregation of dye cations induced by the action of salt ions, i.e., salt ions force dye molecules to aggregate, increasing the extent of adsorption onto clay surface [30].

3.2.3. Effect of temperature

The effect of temperature to the adsorption of MB on illite was investigated at 30, 40, 50 and 60°C. The initial pH value of the solution and processing time were kept constant at 5.95 and for 3 h, respectively. The results are plotted in Fig. 7. As can be seen from Fig. 7, the adsorption of MB on illite increased with increasing temperature. This increase is more pronounced in the increasing initial solution concentration of the dye for the same amount of solids. In the case of higher molecular weight dye molecules, which are more

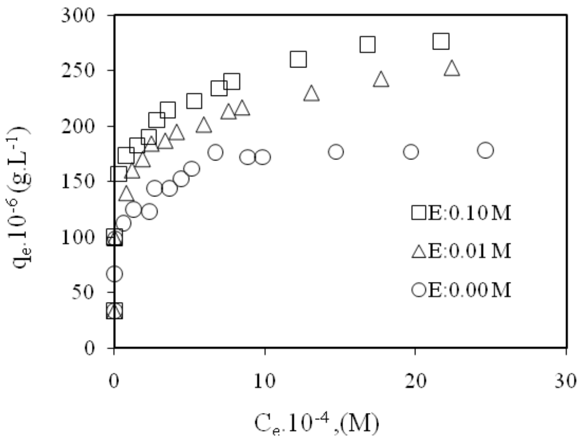

Fig. 6. The effect of electrolyte concentration of the solution on the adsorption of MB on illite (pH: 5.95 (natural), T: 303 K, S/L: 3 g·L^{-1}).

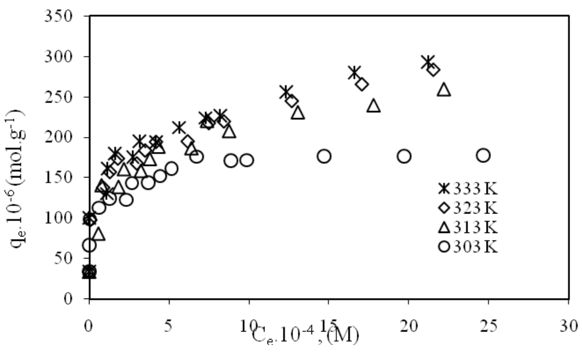

Fig. 7. The effect of temperature of the solution on the adsorption of MB on illite (pH: 5.95 (natural), E: 0 M, S/L: 3g·L^{-1}).

immobile at low temperatures, rates and thus kinetic energies will increase with increasing temperature. Also, a large number of dye molecules will interact with the active sites on illite with increasing temperature [4,31]. This is more pronounced on illite, which is more saturated in increasing initial dye concentrations. Increasing the adsorption capacity of illite with increasing temperature requires the enthalpy change to be positive. This shows that the adsorption process of MB on illite is an endothermic process. Similar results were found for the adsorption of methyl violet and MB on the sepiolite [9], montmorillonite [11], kaolinite [32], bentonite [33].

3.3. Adsorption Isotherms

Adsorption isotherms are referred to as relations or curves that show the relationship between the amount of adsorbate adsorbed on the surface of the adsorbent at a constant temperature and the concentration of the adsorbate in the solution phase. Adsorption isotherm is very important both theoretically and practically [22]. In this study, Temkin, Dubinin-Radushkevich (DR), Freundlich and Langmuir adsorption isotherms were used to analyze experimental data. Furthermore, the applicability of isotherm equations to experimental data was evaluated by using correlation coefficients.

3.3.1. Temkin isotherm

Temkin isotherm includes a factor considering of adsorbent–adsorbate interactions. By neglecting the extremely low and high concentration values, the model assumes that the heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmic with coverage. The model is defined by the following equation [32]

$$q_e = B \cdot \ln A_T + B \cdot \ln C_e \tag{3}$$

where A_T = Temkin isotherm equilibrium binding constant (L·g^{-1}), B = Constant related to heat of sorption (J·mol^{-1}). From the Temkin isotherm correlation, the relative low R^2 values ranging from 0.7272 to 0.9632 were obtained by plotting the quantity sorbed q_e against lnC_e (Table 3).

3.3.2. Dubinin–Radushkevich (D-R) isotherm

D-R isotherm model is generally applied to explain the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The model has often suitably fitted high solute activities and the moderate range of concentrations data well [34].

$$\ln q_e = \ln q_s - K_{ad} \cdot \varepsilon^2 \tag{4}$$

$$\varepsilon^2 = R \cdot T \cdot \ln\left[1 + \frac{1}{C_e}\right] \tag{5}$$

where q_e, q_s, K_{ad}, ε are amount of adsorbate in the adsorbent at equilibrium (mg·g^{-1}), theoretical isotherm saturation capacity (mg·g^{-1}), Dubinin–Radushkevich isotherm constant (mol^2·kJ^{-2}) and Dubinin–Radushkevich isotherm constant, respectively. The adsorption data are plotted as a function of logarithm of amount adsorbed (lnq_e) vs the square of potential energy (ε^2) and the constant such as q_s, and K_{ad} were determined from the suitable plot using equation above. From the linear plots of Dubinin-Radushkevich isotherm model, R^2 values were calculated as 0.7983–0.9823 (Table 3).

3.3.3. Freundlich isotherm

Freundlich isotherm is an experimental equation and gives well results for low concentrations. This equation is given in logarithmic form as follows [10]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

The Freundlich constant, *n*, is a measure of the adsorption density or surface heterogeneity. If the experimental data are in good agreement with the Freundlich isotherm,

Table 3
Isotherm constants and the values of the separation factor

Parameters			Langmuir Isotherm				Freundlich Isotherm	Temkin Isotherm	D-R Isotherm
T (°C)	pH	*E* (M)	q_m (mol·g^{-1})·10^{-5}	K (L·mol^{-1})·10^3	R^2	R_L	R^2	R^2	R^2
30	Natural	0	18.08	21.46	0.9981	1.000–0.019	0.9651	0.8395	0.8897
40	Natural	0	26.39	6.56	0.9879	0.999–0.064	0.9512	0.8178	0.9091
50	Natural	0	28.33	7.04	0.9810	0.997–0.062	0.9744	0.9191	0.9823
60	Natural	0	29.60	7.24	0.9825	0.997–0.061	0.6959	0.7272	0.8254
30	Natural	0	18.08	21.46	0.9981	1.000–0.019	0.9651	0.8395	0.8897
30	Natural	1·10^{-2}	25.35	11.66	0.9941	0.999–0.211	0.9528	0.9632	0.9739
30	Natural	1·10^{-1}	27.96	13.53	0.9947	0.991–0.033	0.8017	0.9197	0.7983
30	3	0	14.61	4.86	0.9898	0.999–0.074	0.8812	0.7697	0.8129
30	Natural	0	18.08	21.46	0.9981	1.000–0.019	0.9651	0.8356	0.8897
30	7	0	27.94	6.71	0.9833	0.999–0.064	0.9710	0.8766	0.9161
30	9	0	31.63	6.11	0.9766	0.996–0.007	0.9730	0.9025	0.9792

the 1/*n* values vary between 0 and 1, and the more this value approaches the zero, the greater the surface heterogeneity [10]. According to Eq. (6), the curve of lnq_e against lnC_e will give a straight line and the isotherm constants, K_F and *n*, from these lines can be determined. Table 3 shows the results of Freundlich isotherm analysis for the adsorption of MB on illite. The correlation coefficients for the Freundlich isotherm are in the range of 0.695–0.974 (Table 3) and are very small from 1, it can be said that this isotherm does not match well with the experimental data.

3.3.4. Langmuir isotherm

The Langmuir isotherm is an isotherm developed to describe single layer adsorption on a surface occurring from a number of similar sites. This model assumes that the energy of the adsorption process on the surface is constant and that adsorbate molecules on the adsorbent surface cannot be transported. The Langmuir isotherm can be given by the following Eq. (7) [10]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \tag{7}$$

The curve of C_e/q_e vs. C_e will give a straight line with a slope of $1/q_m$ and an extrapolation of $1/q_mK$. The straight lines were obtained by applying the experimental results to the Langmuir isotherms. The correlation coefficients and q_m values calculated from these lines are given in Table 3. As seen from Table 3, correlation coefficients vary between 0.976–0.998. This result shows that the experimental data are compatible very well with the Langmuir adsorption isotherm (Figs. 8–10). Since the Langmuir isotherm is assumed to be homogeneous of active sites on adsorbent [35,36], the experimental results are consistent with the Langmuir isotherm, indicating that the active sites on illite are homogeneously distributed. A comparison between the MB adsorption capacity of illite and other adsorbents under similar conditions is presented in Table 4. This comparison shows that the illite samples can adsorb MB as effectively as the other adsorbents listed.

The shape of the isotherm may also be considered in predicting if an adsorption system is ‘favourable’ or ‘unfavourable’. It is possible to express the features of a Langmuir isotherm in terms of a dimensionless separation factor or equilibrium parameter R_L [37], which is defined by

$$R_L = \frac{1}{1 + KC_e} \tag{8}$$

where R_L is a function of the Langmuir constant K. According to R_L values, the slope of isotherm can be explained as follow [38].

R_L value	Adsorption type
R_L >1.0	Inappropriate
R_L = 1.0	Linear
0 < R_L < 1.0	Appropriate
R_L = 0	Irreversible

The R_L values obtained were given in Table 3. The fact that these values are in the range of 0 to 1.0 shows that illite is a suitable adsorbent for the adsorption of MB.

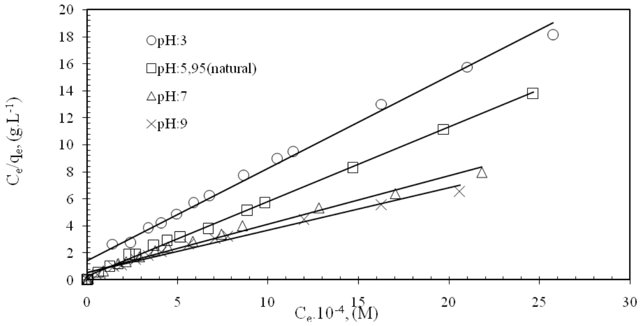

Fig. 8. Straight lines of Langmuir isotherm correlations of pH effect for MB adsorption on illite (T: 303 K, E: 0 M, S/L: 3 g·L^{-1}).

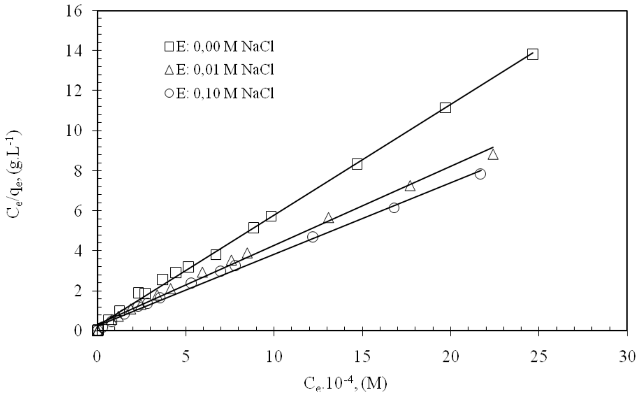

Fig. 9. Straight lines of Langmuir isotherm correlation of electrolyte concentration effects for MB adsorption on illite (T: 303 K, pH: 5.95 (natural), S/L: 3 g·L^{-1}).

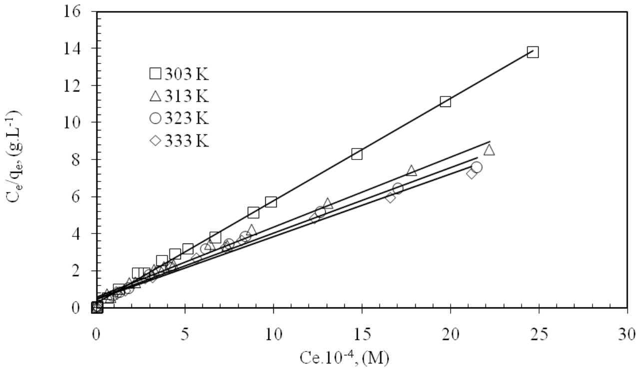

Fig. 10. Straight lines of Langmuir isotherm correlation of temperature effect for MB adsorption on illite (pH: 5.95 (natural), E: 0 M NaCl, S/L: 3 g·L^{-1}).

3.4. Heat of adsorption

From adsorption data at various temperatures, the adsorption heat (ΔH) as a function of the surface coverage fraction ($\theta = q_e/q_m$) can be determined from the following equation [36]:

$$\left[\frac{\partial \ln(C_e)}{\partial(1/T)}\right]_{\theta=0.5} = \frac{\Delta H^0}{R_g} \tag{9}$$

Table 4
Comparison of the MB adsorption capacity with other adsorbents

Adsorbents	q_m (mol·g^{-1})·10^{-5}	References
Expanded Perlite	4.65–8.21	[10]
Bentonite	11.20–22.70	[10]
Zeolite	14.20	[10]
Sepiolite	16.30–27.30	[9]
Illite	14.61–31.63	This study

From the Langmuir equation, the value of C_e is equal to 1/K at a surface coverage of 0.5. For 7·10^{-4} M MB concentration, the value of ΔH^0 from the graph of $-\ln C_e$ against 1/T was calculated as 14.38 kJ·mol^{-1} (Fig. 11). The result obtained shows that the adsorption process is an endothermic process and the interactions between dye and illite are physical interactions [39,40]. Similar results were found for the adsorption of methyl violet and MB on the sepiolite [9], montmorillonite [11], kaolinite [32], bentonite [33].

4. Conclusions

The results obtained in this study were given below:

- The amount of adsorbed methylene blue on illite increased with increasing suspension temperature, suspension pH and electrolyte concentration.
- The Langmuir adsorption isotherm showed good agreement with the experimental data.
- The isosteric adsorption heat for the adsorption process of methylene blue on illite was calculated as 14.38 kJ·mol^{-1}.
- The adsorption process is an endothermic process.
- Since the adsorption heat is low and the adsorption process is an endothermic process, the interactions between adsorbate and adsorbent are physical interactions.
- Illite can be used as an adsorbent in the removal of cationic dyestuffs from aqueous solutions due to its high adsorption capacity.

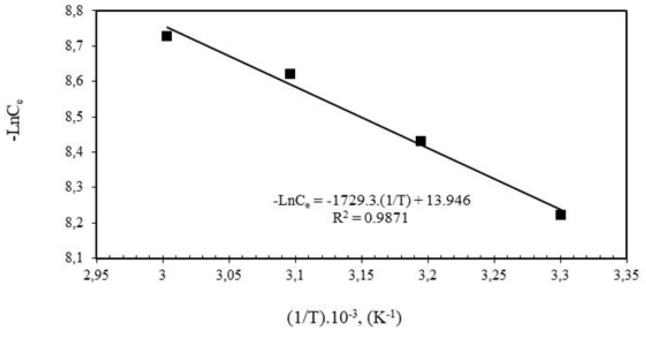

Fig. 11. The plot of $-\ln C_e$ vs. 1/T. (pH: 5.95 (natural), E: 0 M, S/L: 3g·L^{-1}, C_0: 7.10–4 M).

Symbols

FTIR-ATR — Fourier-transform infrared spectroscopy-Attenuated Total Reflection
BET — Brunauer–Emmett–Tellersurface area analysis
SEM — Scanning electron microscope
XRD — X-ray diffraction
XRF — X-ray fluorescence
R_L — The dimensionless separation factor
ASTM — American standard test sieve series
ΔH — Adsorption heat (kJ·mol^{-1})
S/L — Solid to liquid ratio (g·L^{-1})
M — Molarity (mol·L^{-1})
E — NaCl concentration (mol·L^{-1})
T — Temperature (K)

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