

## Adsorption from Aqueous Solution Onto Natural and Acid Activated Bentonite

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### ABSTRACT

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, paint, cosmetics and food industries. Nowadays, more than 100,000 commercial dyes are available with a total production of 700,000 tones manufactured all over the world annually. About 10-15% of dyes are being disposed off as a waste into the environment after dyeing process. This poses certain hazards and environmental problems. The objective of this study is to investigate the adsorption behavior of Methylene Blue (MB) from aqueous solution onto natural and acid activated Jordanian bentonite. Both bentonites are firstly characterized using XRD, FTIR and SEM techniques. Then batch adsorption experiments were conducted to investigate the effect of initial MB concentration, contact time, pH and temperature. It was found that the percentage of dye removal was improved from 75.8% for natural bentonite to reach 99.6% for acid treated bentonite. The rate of MB removal followed the pseudo second order model with a high correlation factor. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms. The Langmuir isotherm model was found more representative. The results indicate that bentonite could be employed as a low cost adsorbent in wastewater treatment for the removal of colour and dyes.

**Keywords:** Adsorption, Bentonite, Methylene Blue, Acid Activation

### 1. INTRODUCTION

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, paint, cosmetics and food industries (Chen and Zhao, 2009; Gupta and Suhas, 2009). Nowadays, more than 100,000 commercial dyes are available with a total production of 700,000 tones manufactured all over the world annually. About 10-15% of dyes are being disposed off as a waste into the environment after the completion of dyeing process (Gupta and Suhas, 2009). Coloured stuff discharged from these industries poses certain hazards and environmental problems. These compounds are not only aesthetically displeasing but also dyes interfere with the transmission of light and upset the biological metabolism processes which cause the destruction of aquatic

communities present in ecosystem (Ozcan and Ozcan, 2004). In addition, dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade. Furthermore, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities (Srinivasan and Viraraghavan, 2010).

Dyes also affect human and animal health. For example, when they come into contact with eyes, they result in eye burns and could lead to permanent injury to human or animals. In addition, inhalation of some dyes could result in rapid or difficult breathing. While ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia (Hameed *et al.*, 2001). In addition dyes can cause

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allergic dermatitis, skin irritation, cancer and mutations (Gupta and Suhas, 2009).

Hence treating wastewater with dyes is of a prime importance. There are several methods for dye removals, such as adsorption, oxidation-ozonation, coagulation, coagulation-flocculation and biological methods (Eren and Afsin, 2009; Turabik, 2008; Waranusantigul *et al.*, 2003; Juang *et al.*, 1997).

Adsorption process provides an attractive treatment of wastewater containing dyes over other conventional wastewater treatment techniques due to economic consideration, its availability and easy to operate as well as greater efficiency (Eren and Afsin, 2009; Gok *et al.*, 2010). Activated carbon is widely used as an adsorbent in gas and liquid phase separation. However, the activated carbon remains an expensive material. This depresses its large scale usage. In order to overcome this deficiency, many researchers investigated the development and preparation of low cost alternative adsorbents such as wood (Poots *et al.*, 1978), dead and pretreated (*A. niger*) fungus (Fu and Viraraghavan, 2000; 2001a; 2001b; 2002a; 2002b), zeolite (Armagan *et al.*, 2004; Wang *et al.*, 2006), Tripoli (ALzaydien, 2009) and bentonite (Ozcan and Ozcan, 2004; Hu *et al.*, 2006).

In the present study, the adsorption of Methylene Blue (MB) dye onto two adsorbents; natural and acid activated bentonite were studied. Various parameters affecting adsorption process, such as contact time, initial dye concentration, temperature and pH were investigated. In addition, kinetic parameters were also calculated to determine adsorption mechanism and rate constants. Experimental data at equilibrium was fitted into adsorption isotherms in order to give the best fit correlation.

## 2. MATERIALS AND METHODS

### 2.1. Bentonite

The bentonite used in this study was supplied by Jordanian Natural Resources Authority (NRA) from Al-Azraq Basin, northeastern Jordan. Clay sample was crushed, ground and sieved. The bentonite sample was stored in an air-tight container for further use.

### 2.2. Preparation of Acid-Activated Bentonite

For acid-activation bentonite, sample of 100 g of natural bentonite was soaked in 500 mL of 5M HCl acid for 24 h. at room temperature. The activated bentonite was washed several times with distilled water until the pH of the solution was 6. Then it was dried at 105°C until constant mass and grounded to pass 106  $\mu\text{m}$ . It is then stored for further use.

### 2.3. Adsorbate

The Adsorbate used in this study is the basic dye, Methylene Blue (MB). It was purchased from Sigma-Aldrich (molecular weight 319.87  $\text{g mol}^{-1}$ ) and used without further purification. Different concentrations of MB were prepared from a stock of 1000 ppm solution with distilled water. To determine the dye concentration, a calibration curve was first obtained from a series of predetermined concentration of dye solutions. The maximum absorbance of the dye was confirmed by scanning the dye aqueous solution over the spectral range of 550-660 nm by using UV-vis spectrophotometer (Model SPUV-19). The absorbance of those standard samples was then measured at the corresponding maximum wavelength. Absorbance of dye solution after adsorption experiment was then converted to concentration using the established calibration curve.

### 2.4. Adsorbents Characterization

The mineralogical composition of bentonite samples was determined using X-ray Diffraction (XRD) technique. X-ray analyses of the samples were made using (Shimadzu model XRD6000). The FTIR spectra of both natural and acid activated bentonite were obtained with KBr using Shimadzu model R-prestige Fourier Transform Infrared Spectrometer to observe the surface functional groups. FTIR spectra were recorded in the region of 4000-400  $\text{cm}^{-1}$ . The Scanning Electron Microscopy (SEM) analysis was carried out using a FEI Scanning Electron Microscope (Inspect F 50) equipped with a Silicon-drifted Energy Dispersive X-ray spectrometer (SEM-EDX). Operating conditions were 5 kV accelerating voltage at full vacuum.

### 2.5. Batch Adsorption Study

Adsorption experiments were carried out batch wise. A specific amount of adsorbent was added to dark amber glass bottles of 100 mL capacity containing 50 mL of MB solution of desired concentrations in the range 10 to 100  $\text{mg L}^{-1}$ . The bottles were subsequently capped and placed on a controlled temperature mechanical shaker at a speed of 250 rpm at desired temperature and time. After adsorption, the solution was centrifuged at 3000 rpm for 6 min. The residual dye concentrations of each solution were determined by measuring their characteristic absorbance using a single beam UV-Vis spectrophotometer (Model SPUV-19) at a wavelength of maximum absorbance (660 nm). The absorbance is then converted to concentration using the calibration curve.

The amount of adsorbed MB at any time,  $q_t$  (mg/g), was calculated using Eq. 1:

$$q_t = \frac{(C_0 - C_t) V}{m} \quad (1)$$

where,  $C_0$  and  $C_t$  are the initial and liquid-phase concentrations at any time  $t$  of dye solution (mg/L), respectively,  $V$  is the volume of dye solution (L) and  $m$  is the mass (g) of the adsorbent used.

The removal efficiency,  $R$  (%) of the system, is Eq. 2:

$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

## 2.6. Effect of Adsorption Parameters

To examine the effect of temperature, adsorption experiments were conducted at 25, 35 and 45°C, respectively. The influence of the initial pH was studied at values: 3, 5, 7 and 9. Dye solution pH was adjusted using 0.1M NaOH and 0.1M HCl solutions and measured using a Meter Lab, pH M210 meter. Adsorbent dosage used in this study was in the range 2 to 60 g L<sup>-1</sup>.

## 3. RESULTS

### 3.1. Characterization of the Adsorbents

Bentonite is considered one of the most promising natural materials available in Jordan that can be used for adsorption of some dyes found in wastewater. The chemical composition of natural bentonite is (in %): SiO<sub>2</sub>: 43.32, Al<sub>2</sub>O<sub>3</sub>: 12.59, K<sub>2</sub>O: 2.89, CaO: 9.59, MgO: 4.99, Fe<sub>2</sub>O<sub>3</sub>: 5.95, TiO<sub>2</sub>: 0.59, Na<sub>2</sub>O: 2.25 and loss of ignition: 17.41 (Khoury, 2002). This indicates the presence of silica, alumina, calcium oxide, iron oxide and magnesium oxide as major constituents. Traces of sodium, potassium and titanium oxides are found in the form of impurities.

The ratio SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is 3.44 which indicate that the bentonite is of montmorillonite nature. This is also confirmed by the XRD analysis. The mineral phases identified along with montmorillonite were quartz and minor levels of feldspar, dolomite and calcite.

In order to illustrate the effect of acid activation of bentonite, FTIR and SEM have been conducted. The FTIR spectra of natural bentonite and acid activated bentonite were taken in the range of 4000-400 cm<sup>-1</sup>. FTIR spectroscopy is very sensitive to modification of the clay structure upon acid treatment as illustrated in Fig. 1. In FTIR-spectrum of the acid activated bentonite, weakening of absorption band intensity at 3426 and 1639 cm<sup>-1</sup> is marked (Fig. 1b). It corresponds to the process of removal of interlayer water (Farmer, 1971; 1974; Wilson, 1994; Olphen, 1977; Hideomi, 1977; Loeb and

Schrader, 1992). Absorption peaks between 3426 and 3626 cm<sup>-1</sup> are due to stretching bands of the OH groups. While the band at 1639 cm<sup>-1</sup> corresponds to the OH deformation of water to observe natural bentonite and acid-activated bentonite, but the peak intensities of acid-activated bentonite are lower than that of natural bentonite. Absorption band reduction at 3626 cm<sup>-1</sup> indicates development of dehydroxylation process. This is believed to occur as a result of acid activation of bentonite (Ozcan and Ozcan, 2004; Vlasova *et al.*, 2003).

In addition, the transformation of the tetrahedral sheet was found at 781 cm<sup>-1</sup>. The acid activation leads to the formation of amorphous silica, indicated by the increased intensity of the peak, which may expose more adsorption sites (Komandel *et al.*, 1990).

Natural and acid activated bentonite samples were analyzed to detect the change in surface morphology after acid activation using SEM. Clumps of uneven surface can be seen for acid activated bentonite with distribution of pores (Fig. 2b) compared with flat flakes of low porosity for natural bentonite (Fig. 2a). The leaching of cations by acid activation creates voids in the bentonite leading to increase its surface porosity.

### 3.2. Effect of Contact Time and Initial (MB) Concentration on Adsorption

The effect of contact time on the percentage of color removal using various initial dye concentrations range from 10 to 100 mg L<sup>-1</sup> was examined at different time as shown in Fig. 3. The results showed that the rate of adsorbed MB onto both natural and acid activated-bentonite was initially rapid and then it slowed down gradually until equilibrium was attained.

As Fig. 3 illustrates, uptake attained equilibrium at 60 min for acid activated bentonite while it needed 180 min using natural bentonite at the same conditions.

The results also indicated that the amount of retained dye increased with the increase of initial dye concentration. Although the rate behavior of both bentonite and acid activated bentonite was similar, but it has been found that under identical conditions the acid activated bentonite presented higher adsorption capacity.

### 3.3. Effect of pH on Adsorption

The effect of pH on MB adsorption onto natural and acid activated bentonite was studied through tests carried out on solutions of various pH as shown in Fig. 4. It showed that the adsorption of MB dye onto natural bentonite increased with increasing solution pH.

However, the adsorption of MB dye on acid activated bentonite was controlled by a pH-independent adsorption mechanism as indicated in Fig. 4.

### 3.4. Effect of Temperature

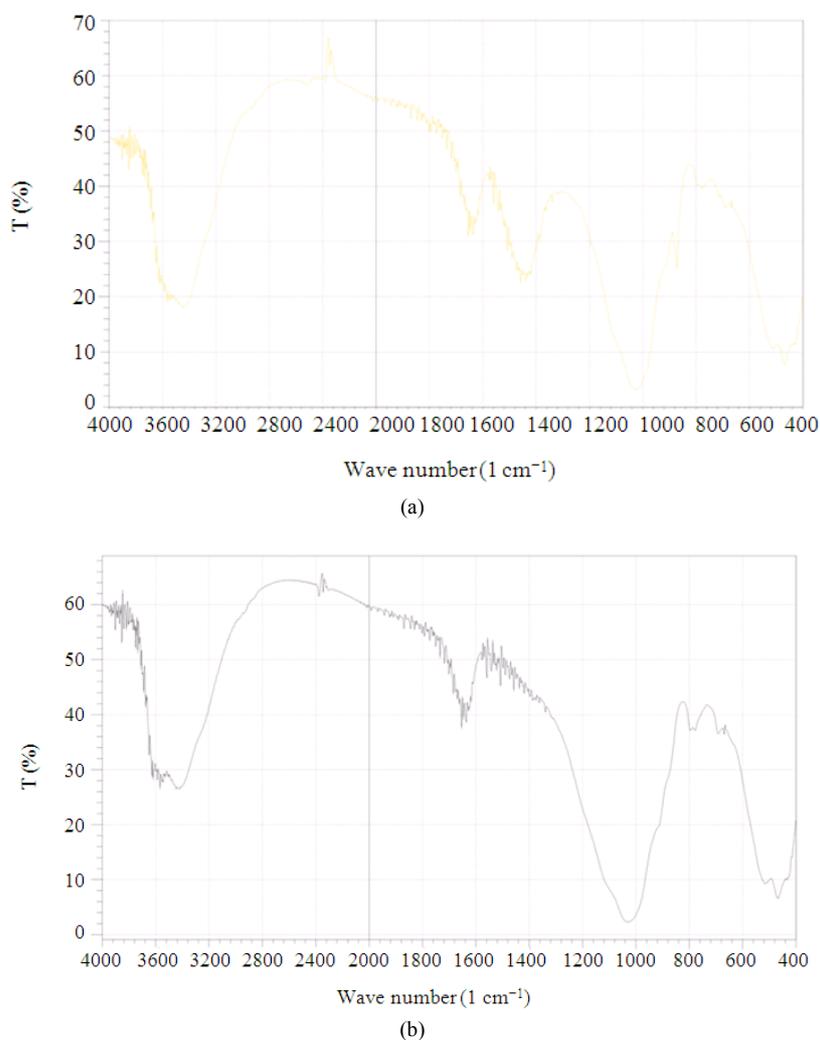
The effect of temperature on the equilibrium adsorption capacity of MB onto both bentonite and acid activated bentonite was investigated at a concentration of  $100 \text{ mg L}^{-1}$  at 25, 35 and  $45^\circ\text{C}$ . The results were presented in **Fig. 5**. It can be seen that with the increase of temperature, the adsorption capacity of MB onto natural bentonite was slightly increased (about 3%). This observation revealed that the adsorption process is slightly endothermic.

On the other hand, the adsorption capacity of MB onto acid activated bentonite has a negligible effect, suggesting the adsorption behavior was insensitive to the changes of temperature in the range investigated.

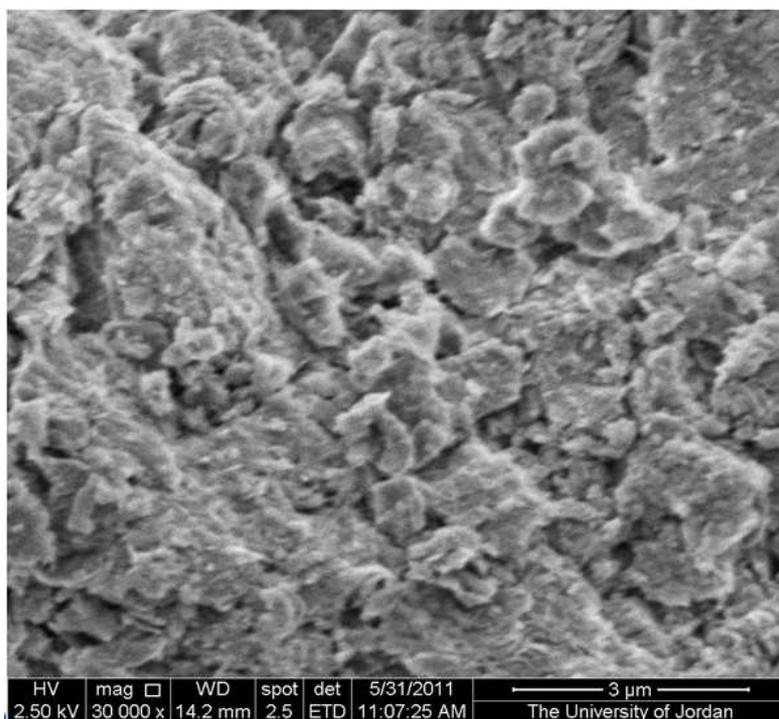
### 3.5. Effect of Adsorbent Dosage

The effect of adsorbent concentration on the percentage removal of MB dye using an initial dye concentration of 100 ppm is examined. The studied adsorbent dosages were 2, 10, 40 and  $60 \text{ g L}^{-1}$  as shown in **Fig. 6**. It can be noticed that increasing the natural bentonite dosage gradually increase the percentage removal of MB. It was also noted that increasing the dosage of acid activated bentonite from  $2\text{-}10 \text{ g L}^{-1}$  increase the percentage removal of MB dye.

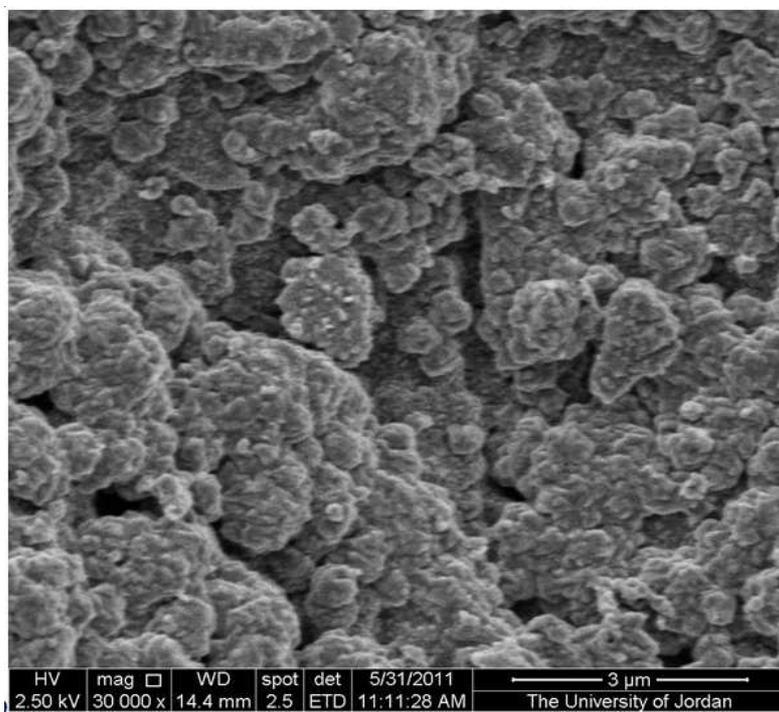
However, when the dosage of acid- activated bentonite increased from 10 to  $60 \text{ g L}^{-1}$  the removal of MB was constant.



**Fig. 1.** FTIR spectra of natural bentonite (a) and acid-activated bentonite (b)

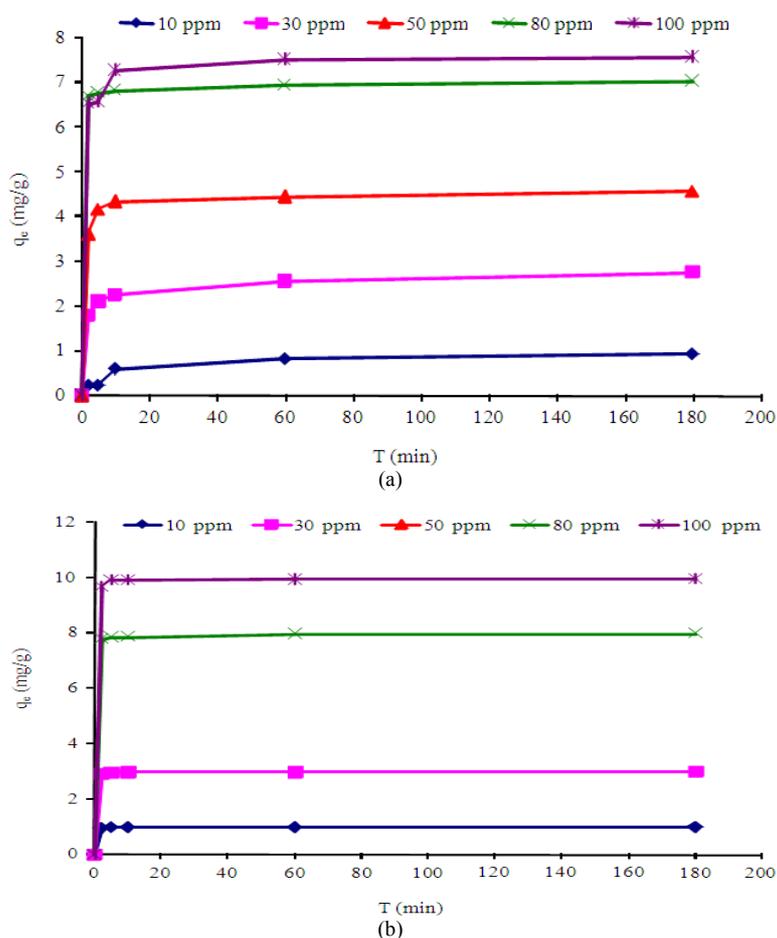


(a)

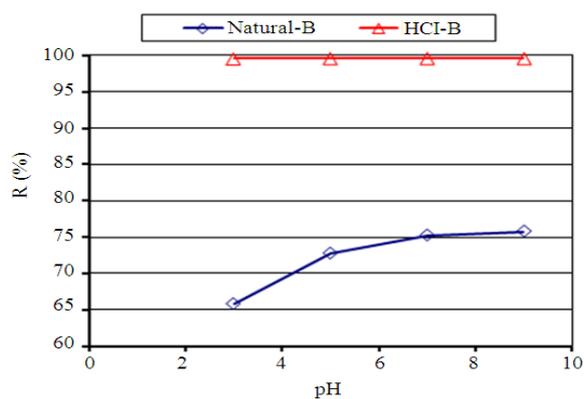


(b)

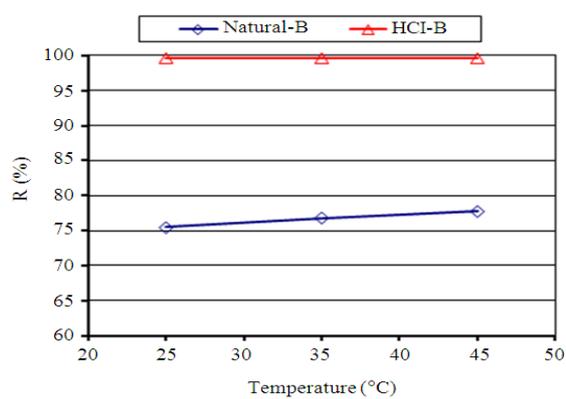
**Fig. 2.** SEM surface morphology of natural bentonite (a) and acid-activated bentonite (b)



**Fig. 3.** Effect of contact time on MB adsorption on natural bentonite (a) and acid activated bentonite (b) at different initial concentrations (temperature = 20 ± 2°C, pH = 9, dosage = 10 g L<sup>-1</sup>)



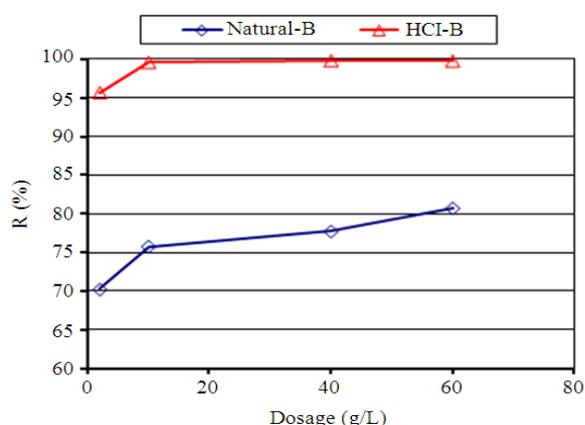
**Fig. 4.** Effect of pH on MB removal by natural bentonite (diamonds) and acid-activated bentonite (triangles) at initial concentration = 100 ppm, temperature = 20 ± 2°C and dosage = 10 g L<sup>-1</sup>



**Fig. 5.** Effect of temperature on MB removal by natural bentonite (diamonds) and acid-activated bentonite (triangles) at initial concentration = 100 ppm, pH = 9 and dosage = 10 g L<sup>-1</sup>

**Table 1.** Kinetic models' parameters for natural and acid-activated bentonite

First order kinetic model parameters							Second order kinetic model parameters					
Natural bentonite				Acid-activated bentonite			Natural bentonite			Acid-activated bentonite		
$C_0$ (mg/L)	$q_e$ (mg/g)	$K_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ (mg/g)	$K_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ (mg/g)	$K_2$ (g/mg min)	$R^2$	$q_e$ (mg/g)	$K_2$ (g/mg min)	$R^2$
10	1.14	0.031	0.670	0.07	0.034	0.220	0.94	0.174	0.999	1.00	5.258	1
30	0.74	0.033	0.910	0.13	0.052	0.314	2.76	0.221	1.000	2.99	6.052	1
50	1.00	0.039	0.488	0.76	0.470	0.594	4.57	0.392	1.000	4.99	0.359	1
80	0.75	0.040	0.368	0.54	0.061	0.474	7.03	0.622	1.000	7.98	1.764	1
100	1.70	0.061	0.718	0.33	0.067	0.718	7.58	0.392	1.000	9.96	3.600	1



**Fig. 6.** Effect of dosage on MB removal by natural bentonite (diamonds) and acid- activated bentonite (triangles) at initial concentration = 100 ppm and temperature = 20 ±2°C, pH = 9

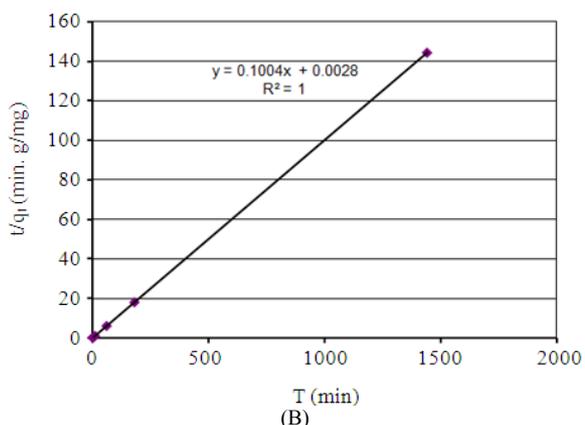
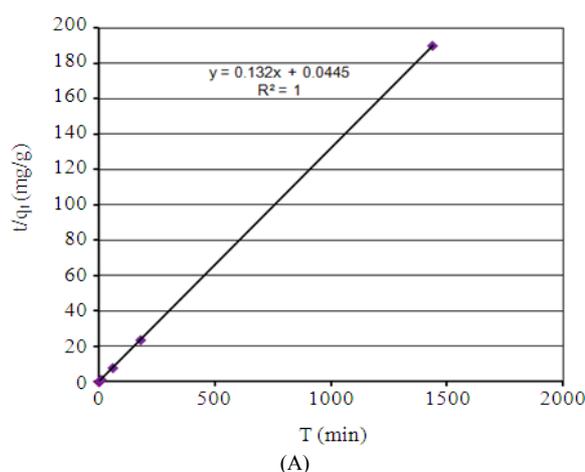
### 3.6. Adsorption Kinetics

In order to examine the adsorption kinetics, two popular kinetic models: pseudo-first order and pseudo-second order were applied. The linear forms of these models can be expressed as follows Eq. 3 and 4 (Lagergren, 1898; Ho and McKay, 1998):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where,  $q_e$  and  $q_t$  are the amount of dye adsorbed on adsorbent at equilibrium and time  $t$ , respectively (mg/g) and  $k_1$  is the rate constant of first order adsorption ( $\text{min}^{-1}$ ).  $k_2$  is the pseudo-second order rate constant of adsorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ).



**Fig. 7.** Pseudo-second order adsorption kinetic model for MB adsorbed on natural bentonite (A) and acid-activated bentonite (B) (initial concentration = 100 ppm, temperature = 20±2°C, pH = 9 and dosage = 10g L<sup>-1</sup>)

The parameters  $q_e$  and  $k_1$  obtained from pseudo-first order adsorption kinetic model were calculated and summarized in **Table 1**. The regression correlation

factors were generally low; therefore, the adsorption kinetics of MB dye on natural and acid activated bentonite did not show good compliance with pseudo-first order adsorption kinetic model.

Further investigation has been carried out to gauge the compliance of the adsorption kinetics with the pseudo-second order kinetic model. **Figure 7** shows the application of the pseudo-second order kinetic model for the adsorption systems of both adsorbents and for initial dye concentration = 100 ppm. The regression coefficients obtained are almost 1, which indicates a good compliance of this model with experimental data.

With increasing initial dye concentration from 10 to 100 mg L<sup>-1</sup>, the adsorption capacity increases from 0.94 to 7.58 mg g<sup>-1</sup> and from 1.0 to 9.96 mg g<sup>-1</sup> for natural and acid activated bentonite, respectively as summarized in **Table 1**. This indicates that dye removal content depends on the initial dye concentration when the adsorbent amount is constant.

### 3.7. Adsorption Isotherms

Adsorption isotherm models are very useful for predicting adsorption capacities and also for incorporating into mass transfer relationships in the design of contacting equipment. So, in order to optimize the design of an adsorption system to remove MB dye from effluents, it is important to establish the most appropriate correlation for the equilibrium curves. In this respect, the equilibrium experimental data for adsorbed MB onto natural and acid activated bentonite were compared using two isotherm models: Langmuir and Freundlich.

### 3.8. Langmuir Isotherm Model

The Langmuir adsorption model depends on the assumption that the intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent (Langmuir, 1918). In addition, the isotherm model assumes that adsorption occurs at specific homogeneous sites within the adsorbent. It is assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Furthermore, the Langmuir equation is based on the assumption of a structurally homogeneous adsorbent, where all sorption sites are identical and energetically equivalent.

Theoretically, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further sorption can occur. The saturated or monolayer capacity can be represented as the known Langmuir (1918) Eq. 5:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left( \frac{1}{q_{\max} K_L} \right) \frac{1}{C_e} \quad (5)$$

where,  $q_{\max}$  (mg/g) and  $K_L$  (L/mg) are the Langmuir constants and  $C_e$  (mg/L) is the equilibrium dye concentration in the solution.

The Langmuir adsorption equilibrium isotherm of MB dye onto both clays at 20°C is presented in **Fig. 8**. Regression analysis reveals that the Langmuir model fits the experimental data well with correlation factor higher than 0.98 for both adsorbents.

An essential characteristic of Langmuir isotherm can be expressed by a dimensionless constant called separation factor,  $R_L$  (Hall *et al.*, 1966) given by:

$$R_L = \frac{1}{1 + K_L C_m}$$

where,  $C_m$  is the highest initial dye concentration (here 100 ppm). The value of  $R_L$  indicates the type of the isotherm to be either unfavorable when  $R_L > 1$ , linear if  $R_L = 1$ , favourable if  $0 < R_L < 1$  or irreversible when  $R_L = 0$ .

The  $R_L$  values are 0.056 for natural bentonite and 0.005 for acid activated bentonite as shown in **Table 2** indicating that the adsorption of this dye on both adsorbents was a favorable process.

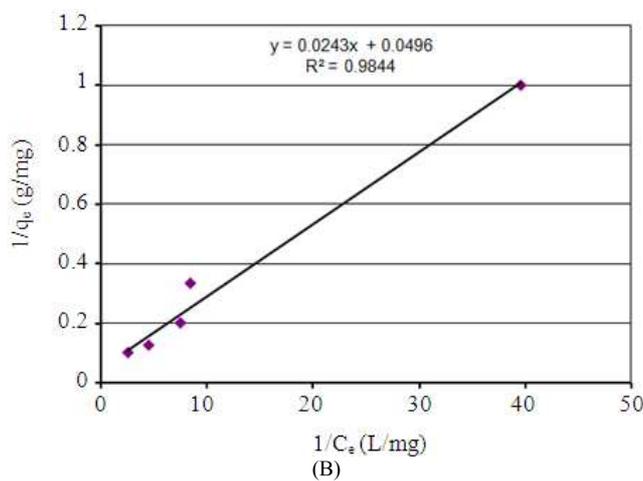
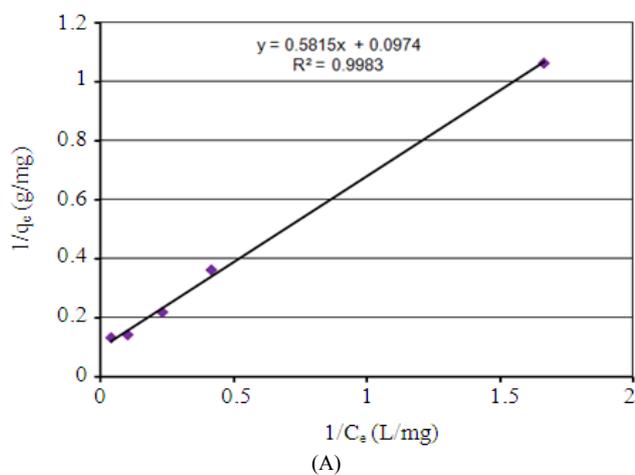
### 3.9. Freundlich Isotherm Model

This model describes heterogeneous adsorption systems (Freundlich, 1906). The model is given in its linear form as Eq. 6:

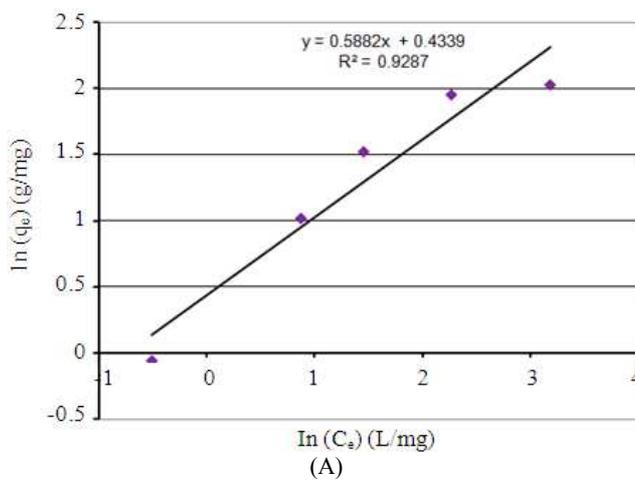
$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

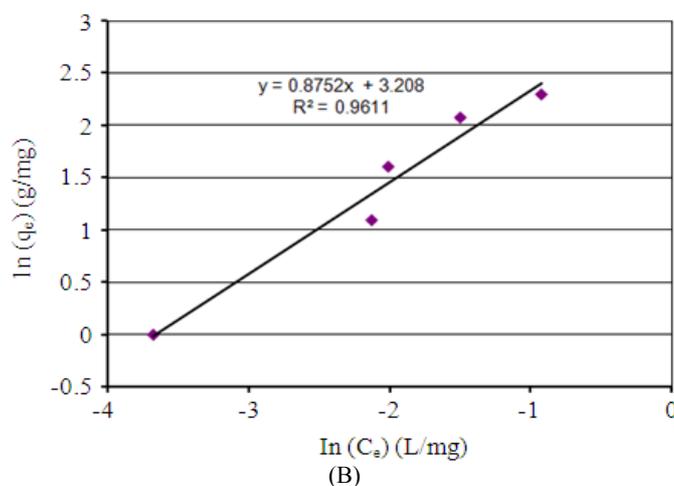
where,  $K_F$  is the Freundlich constant related to overall adsorption capacity (mg/g); and  $1/n$  is a dimensionless constant related to the intensity of adsorption, or the heterogeneity factor describes reversible adsorption and is not restricted to the formation of the monolayer.

**Figure 9** shows plots of  $\ln q_e$  versus  $\ln C_e$  for the adsorption of MB dye on natural and acid activated bentonite. Values of  $K_F$  and  $n$  are obtained from intercept and slope, respectively. These are 1.54 and 1.7 for natural bentonite and 24.73 and 1.14 for acid activated bentonite. This indicates that both adsorption systems were favorable and the acid activated bentonite had a higher adsorption capacity.



**Fig. 8.** Langmuir adsorption isotherm for MB adsorbed on natural bentonite (A) and acid-activated bentonite (B) (initial concentration = 100 ppm, temperature =  $20 \pm 2^\circ\text{C}$ , pH = 9 and dosage =  $10 \text{ g L}^{-1}$ )





**Fig. 9.** Freundlich adsorption isotherm for MB adsorbed on natural bentonite (A) and acid-activated bentonite (B) (initial concentration = 100 ppm, temperature =  $20\pm 2^\circ\text{C}$ , pH = and dosage =  $10\text{ g L}^{-1}$ )

**Table 2.** Isotherm models parameters for natural and acid-activated bentonite.

Isotherm model	Parameter	Natural bentonite	Acid-activated bentonite
Langmuir	$q_{\text{max}}$ (mg/g)	10.27	20.16
	$K_L$ (L/mg)	0.167	2.041
	$R_L$	0.056	0.005
	$R^2$	0.998	0.984
Freundlich	$K_F$ (L/mg)	1.543	24.73
	$n$	1.700	1.143
	$R^2$	0.929	0.961

Both the Langmuir and Freundlich isotherms parameters for the adsorption of MB onto natural and acid-activated bentonite and the correlation coefficients are summarized in **Table 2**. The correlation coefficients of the Langmuir model were higher than that of Freundlich model suggesting a more like monolayer adsorption process.

## 4. DISCUSSION

### 4.1. Effect of Contact time and Initial (MB) Concentration on Adsorption

The rate of adsorbed MB onto both natural and acid activated-bentonite was initially rapid and then it slowed down gradually until equilibrium was attained. It would be for that a large number of vacant surface sites were available for adsorption during the initial stage of the treatment time and after a lapse of time, less remaining vacant surface sites were available.

The amount of retained dye showed an increasing trend with the increase of initial dye concentration. Although the rate behavior of both bentonite and acid

activated bentonite was similar, but it had been found that under identical conditions the acid activated bentonite presented higher adsorption capacity.

This increase in the adsorption capacity of activated bentonite may be attributed to many factors. HCl dissolved impurities such as calcite and leached cations from bentonite sheets. In addition, it replaced the exchangeable cations with hydrogen ions (Diaz and Santos, 2001). Furthermore, acid opened the edges of the platelets and produced a more porous structure which implied a greater surface area as illustrated by SEM images.

### 4.2. Effect of pH on Adsorption

The adsorption of MB dye onto natural bentonite increased with increasing solution pH. This might be attributed to the surface charge of the natural bentonite. Bentonite is positively charged at low pH values and negatively charged at higher pH (Tahir and Rauf, 2006). Therefore the electrostatic interactions between the positively charged alkylamino groups in the dye molecule and the negatively charged adsorbent increased. As a result, the amount of dye molecules onto the natural bentonite increased at higher pH values.

However, the adsorption of MB dye on acid activated bentonite was controlled by a pH-independent adsorption mechanism as indicated in **Fig. 4**. It is believed that the adsorption mechanism occurred partly by ion exchange releasing exchangeable cations in the interlayer and basal plane surfaces and partly via non-coulombic interactions between an adsorbed cation and a neutralized site. Similar behavior was observed by Eren and Afsin (2008) and Turabik (2008).

#### 4.3. Effect of Temperature

A slight increase in adsorption capacity of MB onto natural bentonite was observed with increasing temperature. This observation revealed that the adsorption process was slightly endothermic. This may be caused by the increased tendency of adsorbate ions mobility with temperature which slightly enhances the adsorption of MB from the solution into the clay (Hameed *et al.*, 2007; Alkan and Dogan, 2003).

On the other hand, the adsorption capacity of MB onto acid activated bentonite has a negligible effect, suggesting the adsorption behavior is insensitive to the changes of temperature in this range. The weak influence of temperature for the adsorption of MB probably indicated the low activation energy in the predominantly ionic system (Hu *et al.*, 2006).

#### 4.4. Effect of Adsorbent Dosage

The increase in the adsorption efficiency of natural and acid activated bentonite by increasing the dosage can be explained by increasing surface area of the clay where the adsorption takes place.

However, when the dosage of acid- activated bentonite increased from 10 to 60 g L<sup>-1</sup> the removal of MB is constant. This may be attributed to the attainment of equilibrium between adsorbate and adsorbent under the operating conditions. The adsorption process reached a saturation point after which no further MB adsorption took place.

#### 4.5. Adsorption Kinetics

The regression coefficients obtained for pseudo-second order adsorption kinetic model for both bentonite were almost 1, which indicated a good compliance of this model with experimental data. Consequently, the dye adsorption on natural and acid activated bentonite was assumed to be due to chemisorption.

With increasing initial dye concentration, the adsorption capacity increased for natural bentonite and acid activated bentonite. This indicated that dye removal

content depends on the initial dye concentration when the adsorbent amount is constant.

#### 4.6. Adsorption Isotherms

Regression analysis reveals that the Langmuir model fits the experimental data well with correlation factor higher than 0.98 for both adsorbents. This indicates that the adsorption mechanism of MB onto bentonite can be assumed as monolayer coverage and the adsorption is homogeneous, where the adsorption of each adsorbate molecule onto the surface has equal sorption activation energy.

The  $R_L$  values were 0.056 for natural bentonite and 0.005 for acid activated bentonite as shown in **Table 2** indicating that the adsorption of this dye on both adsorbents was a favorable process.

### 5. CONCLUSION

Bentonite deposits have been reported in different parts of Jordan. In the present study, bentonite clay was selected as a local, cheap and readily available adsorbent for the removal of MB from the aqueous solutions. Natural and acid activated bentonites were characterized using XRD, FTIR and SEM. Adsorption of the dye was studied by batch adsorption experiments.

Natural bentonite used is of montmorillonite nature as confirmed by the XRD analysis and chemical composition found in literature. FTIR and SEM analyses confirmed modification of bentonite treated with acid. This led to increase adsorption capacity of activated bentonite. It was observed that the percentage of dye removal was improved from 75.8% for natural bentonite to reach 99.6% for acid treated bentonite.

The results revealed that the adsorption of the dye increases with increasing the pH using natural bentonite. However, there was no effect of solution pH on the removal percentage of MB dye by acid activated bentonite.

In addition, they indicated a gradual increase in the percentage removal of MB dye with temperature for natural bentonite. However, no effect was observed when acid activated bentonite was used. An optimum dosage of both natural and acid activated bentonite is 10g L<sup>-1</sup>.

The adsorption kinetic studies showed that the removal of MB is a rapid process and the adsorption process obeys the pseudo-second order model, indicating cationic dye has a very strong affinity on the bentonite surface. It was found that the experimental isotherm data can be fitted well to the Langmuir equilibrium isotherm model.

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## 6. REFERENCES

- Alkan, M. and M. Dogan, 2003. Adsorption kinetics of victoria blue onto perlite. *Fresen. Environ. Bull.*, 12: 418-425.
- ALzaydien, A.S., 2009. Adsorption of methylene blue from aqueous solution onto a low-cost natural jordanian Tripoli. *Am. J. Environ. Sci.*, 5: 197-208. DOI: 10.3844/ajessp.2009.197.208
- Armagan, B., M. Turan and M.S. Elik, 2004. Equilibrium studies on the adsorption of reactive azo dyes into zeolite. *Desalination*, 170: 33-39. DOI: 10.1016/j.desal.2004.02.091
- Chen, H. and J. Zhao, 2009. Adsorption study for removal of Congo red anionic dye using organo-attapulgite. *Adsorption*, 15: 381-389. DOI: 10.1007/s10450-009-9155-z
- Diaz, F.R.V. and P.D.S. Santos, 2001. Studies on the acid activation of Brazilian Smectitic clays. *Química Nova*, 24: 345-353. DOI: 10.1590/S0100-40422001000300011
- Eren, E. and B. Afsin, 2008. Investigation of a basic dye adsorption from aqueous solution onto raw and pre-treated bentonite surfaces. *Dyes Pigments*, 76: 220-225. DOI: 10.1016/j.dyepig.2006.08.019
- Eren, E. and B. Afsin, 2009. Removal of basic dye using raw and acid activated bentonite samples. *J. Hazard. Mater.*, 166: 830-835. PMID: 19188017
- Farmer, V.C., 1971. The characterization of adsorption bonds in clays by infrared spectroscopy. *Soil Sci.*, 112: 62-68.
- Farmer, V.C., 1974. The layer silicates-the infrared spectra of minarlas.
- Freundlich, H., 1906. Adsorption solution. *Z. Phys. Chem.*, 57: 384-470.
- Fu, Y. and T. Viraraghavan, 2000. Removal of a dye from an aqueous solution by the fungus *Aspergillus niger*. *Water Qual. Res. J. Can.*, 35: 95-111.
- Fu, Y. and T. Viraraghavan, 2001a. Fungal decolorization of dye wastewaters: A review. *Bioresour. Technol.*, 79: 251-262. PMID: 11499579
- Fu, Y. and T. Viraraghavan, 2001b. removal of C.I. acid blue 29 from an aqueous solution by *Aspergillus niger*. *Am. Assoc. Text. Chem. Color. Rev.*, 1: 36-40.
- Fu, Y. and T. Viraraghavan, 2002a. Removal of Congo Red from an aqueous solution by fungus *Aspergillus niger*. *Adv. Environ. Res.*, 7: 239-247. DOI: 10.1016/S1093-0191(01)00123-X
- Fu, Y. and T. Viraraghavan, 2002b. Dye biosorption sites in *Aspergillus niger*. *Bioresour. Technol.*, 82: 139-145. PMID: 12003314
- Gok, O., A.S. Ozcan and A. Ozcan, 2010. Adsorption behavior of a textile dye of Reactive Blue 19 from aqueous solutions onto modified bentonite. *Applied Surf. Sci.*, 256: 5439-5443. DOI: 10.1016/j.apsusc.2009.12.134
- Gupta, V.K. and Suhas, 2009. Application of low-cost adsorbents for dye removal--a review. *J. Environ. Manage.*, 90: 2313-2342. PMID: 19264388
- Hall, K.R., L.C. Eagleton, A. Acrivos and T. Vermeulen, 1966. Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Ind. Eng. Chem. Fundamen.*, 5: 212-223. DOI: 10.1021/i160018a011
- Hameed, B.H., A.A. Ahmad and N. Aziz, 2007. Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash. *Chem. Eng. J.*, 133: 195-203. DOI: 10.1016/j.cej.2007.01.032
- Hameed, B.H., A.T. Din and A.L. Ahmad, 2001. Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies. *J. Hazard. Mater.*, 141: 819-825. PMID: 16956720
- Hideomi, K., 1977. Clay for our future. Proceedings of the 11th International Clay Conference (ICC' 97), Ottawa, Canada, June 15-21.
- Ho, Y.S. and G. McKay, 1998. Sorption of dye from aqueous solution by peat. *Chem. Eng. J.*, 70: 115-124. DOI: 10.1016/S0923-0467(98)00076-1
- Hu, H., S.Z. Qiao, F. Haghseresht, M.A. Wilson and G.Q. Lu, 2006. Adsorption study for removal of basic red dye using bentonite. *Ind. Eng. Chem. Res.*, 45: 733-738. DOI: 10.1021/ie050889y
- Juang, R.S., F.C. Wu and R.L. Tseng, 1997. The ability of activated clay for the adsorption of dyes from aqueous solutions. *Environ. Technol.*, 18: 525-531. DOI: 10.1080/09593331808616568

- Khoury, H.N., 2002. Clays and Clay Minerals in Jordan. 1st Edn., University Jordan Publ., Amman, p: 116.
- Komandel, P., D. Schmidt, J. Madejova and B. Cicel, 1990. Alteration of smectites by treatments with hydrochloric acid and sodium carbonate solutions. *Applied Clay Sci.*, 5: 113-122. DOI: 10.1016/0169-1317(90)90017-J
- Lagergren, S., 1898. About the theory of so-called adsorption of soluble substances. *Kongliga Svenska Vetenskaps Academiens Handlingar*, 24: 1-39.
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.*, 40: 1361-1403. DOI: 10.1021/ja02242a004
- Loeb, G.I. and M.E. Schrader, 1992. *Modern Approaches to Wettability: Theory and Applications*. 1st Edn., Springer, New York, ISBN-10: 0306439859, pp: 484.
- Olphen, H.V., 1977. *An Introduction to Clay Colloid Chemistry*. 2nd Edn., Wiley, New York, ISBN-10: 047101463X, pp: 318.
- Ozcan, A.S. and A. Ozcan, 2004. Adsorption of acid dyes from aqueous solutions onto acid-activated bentonite. *J. Colloid Interface Sci.*, 276: 39-46. PMID: 15219427
- Poots, V.J.P., G. McKay and J.J. Healy, 1978. Removal of basic dye from effluent using wood as an adsorbent. *J. Water. Pollut. Control Fed.*, 50: 926-935.
- Srinivasan, A. and T. Viraraghavan, 2010. Decolorization of dye wastewaters by biosorbents: A review. *J. Environ. Manage.*, 91: 1915-1929. PMID: 20627542
- Tahir, S.S. and N. Rauf, 2006. Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay. *Chemosphere*, 63: 1842-1848. PMID: 16380152
- Turabik, M., 2008. Adsorption of basic dyes from single and binary component systems onto bentonite: Simultaneous analysis of Basic Red 46 and Basic Yellow 28 by first order derivative spectrophotometric analysis method. *J. Hazard. Mater.*, 158: 52-64. PMID: 18289779
- Vlasova, M., G. Dominguez-Patino, N. Kakazey, M. Dominguez-Patino and D. Juarez-Romero *et al.*, 2003. Structural-phase transformations in bentonite after acid treatment. *Sci. Sinter.*, 35: 155-166.
- Wang, S., H. Li and L. Xu, 2006. Application of zeolite MCM-22 for basic dye removal from wastewater. *J. Colloid Interface Sci.*, 295: 71-78. PMID: 16143340
- Waranusantigul, P., P. Pokethitiyook, M. Kruatrachue and E.S. Upatham, 2003. Kinetics of basic dye (methylene blue) biosorption by giant duckweed (*Spirodela polyrrhiza*). *Environ. Pollut.*, 125: 385-392. DOI: 10.1016/S0269-7491(03)00107-6
- Wilson, M.J., 1994. *Clay Mineralogy: Spectroscopic and Chemical Determinative Methods*. 1st Edn., Chapman and Hall, London, ISBN-10: 0412533804, pp: 367.