World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:3, No:7, 2009

Removal of Methylene Blue from Aqueous Solution by Using Gypsum as a Low Cost Adsorbent

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***Abstract*—**Removal of Methylene Blue (MB) from aqueous solution by adsorbing it on Gypsum was investigated by batch method. The studies were conducted at 25°C and included the effects of pH and initial concentration of Methylene Blue. The adsorption data was analyzed by using the Langmuir, Freundlich and Tempkin isotherm models. The maximum monolayer adsorption capacity was found to be 36 mg of the dye per gram of gypsum. The data were also analyzed in terms of their kinetic behavior and was found to obey the pseudo second order equation.

***Keywords*—**Adsorption, Dye, Gypsum, Kinetics, Methylene Blue.

I. Introduction

THE use of dyes by many industries, such as textile, paper and plastics to color their products is a common activity. Since these industries also use substantial amount of water in their processes, this results in highly colored effluent of these industries which is generally colored due to the presence of these organic chemicals. Color in water is not only the first detectable contaminant in water, it also blocks sunlight which is essential for many photo-initiated chemical reactions which are necessary for aquatic life [1,2]. Since synthetic dyes have good solubility in water, they may frequently be found in trace quantities in industrial wastewater. Water contamination becomes a serious issue due to the fact that that two per cent of dyes that are produced are discharged directly in aqueous effluent [3]. Increased environmental awareness and the relevant EPA restrictions on the organic content of industrial effluents makes it necessary to eliminate dyes from wastewater before it is discharged in the mainstreams. Aquatic living organisms pose a serious threat due to the toxicity and even carcinogenic properties of these organic chemicals [4].

Effluents containing dyes are difficult to treat because most of these chemicals are not prone to aerobic digestion [5]. There are several reported methods for the removal of pollutants from effluents; however, there is no single process which is capable of treating these effluents because of the complexity of the matrix [6]. Practically, a combination of different processes is often used to achieve the desired water quality in the most economical way. Liquid-phase adsorption is one of the most studied methods for the removal of pollutants from wastewater since it generally will produce a high-quality treated effluent [7-9]. The treatment of wastewaters by adsorption process is an excellent choice especially if the sorbent is inexpensive and does not require any additional pre-treatment step before its application.

Adsorption has been found to be superior to other techniques for water re-use in terms of its initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [10-12]. The process also does not result in the formation of harmful substances like in many other cases. The main sorbents used to remove dyes in wastewater employs activated carbon because of its good adsorption ability [13-14]. The use of activated carbon, however, is restricted due to its high cost. An attempt to develop cheaper and effective adsorbents and many non-conventional low-cost adsorbents such as clay materials, zeolites, siliceous material, agricultural wastes and industrial waste products have also been suggested [15-17]. This study is an aim in the same direction in exploring the use of a commonly available commodity namely gypsum for treating industrial effluents. The abundance of gypsum in nature besides its cheap cost was the main factor to study the potentials of this material as an adsorbent. Moreover no pretreatment of this material is required as compared to other adsorbents such as activated coal or inorganic substances. In this paper the attention is focused on the use of gypsum as an alternative low cost adsorbent for the removal of Methylene Blue (MB) from aqueous solutions due to the reason that many textile manufacturers use this and it releases aromatic amines (e.g., benzidine, methylene) and is a potential carcinogen [4]. No literature studies or citations are available in using gypsum as an adsorbent and the study thus becomes novel. The data shall be used to evaluate the adsorption parameters with the help of model equations and also find out the adsorption kinetics.

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II. Experimental

A. Preparation and Instrumention

Methylene Blue (MB) with a labeled purity of more than 98 % was procured from Aldrich. The characteristics and molecular structure of this dye is given in Table I. Dye solutions of desired concentrations were made in deionized water. Preliminary experiments were carried out on this dye solution to ascertain the working concentration range in the Lambert-Beer region. The dye solution is highly colored and shows an intense absorption peak in the visible region at 668 nm. A change in intensity of an absorption peak of the dye solution in an adsorption process can thus be targeted to characterize the removal of dye from the solution. In the present studies, commercially obtained gypsum powder (unbranded) was used as an adsorbent material because of its enormous availability, low price and its readiness to use without any prior treatment. The surface area of the gypsum sample was found by the nitrogen adsorption method [18] using the Quantasorb Autosorb Automated gas sorption system (Quantochrome corporation). Table II summarizes the physical characteristics of the gypsum sample used in this work. SEM images were registered by using a SEM (EDX, Jeol Model JSM-5600). The SEM images of gypsum show the porosity and surface structure. After dye adsorption, a significant change is observed in structure of this adsorbent (Fig. 1). The adsorbent appears to have a rough surface and pores containing a new shiny and bulky particle.

B. Adsorption Measurements

Adsorption experiments were carried out by adding a fixed amount of gypsum (0.25 g) to a series of 250 mL conical flasks filled with 100 mL diluted solutions (5– 25mg/L) of Methylene Blue dye. The conical flasks were then sealed and placed in a water-bath shaker and shaken at 100 rpm with a required time at 298 K. After regular time intervals, the flasks were then removed from the shaker, and the final concentration of dye in the solution was measured at maximum wavelength of the dye solution (668 nm) by a CARY 50 UV/VIS spectrophotometer, using a 1 cm quartz cell. The amount of dye adsorption at equilibrium q_e (mg/g) was calculated from the following equation:

$$q_e = (C_o - C_e)V/W \quad (1)$$

where, C_o and C_e (mg/L) are the liquid phase concentrations of dye at initial and equilibrium, respectively, V (L) the volume of the solution and W (g) is the mass of adsorbent used. The procedure of kinetic tests was basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals and the concentration of dye solution was similarly measured. The amount of adsorption at time t, q_t (mg/g), was calculated by

$$q_t = (C_o - C_t)V/W \quad (2)$$

Since the solution pH has a considerable effect on dye removal, the pH of the solution was also changed to monitor the adsorption behavior of dyes on gypsum samples. The pH was changed by adding incremental amounts of either dilute HCl or NaOH (0.1 M each) to the solution. Changes in absorption was then used to calculate the concentration and adsorption for the dye used in this study.

III. Results and Discussion

A. Effect of Initial Concentration and Contact Time

A 0.25 g sample of gypsum was added to each 50 mL volume of MB solution. The initial concentrations of dye solution tested were 5, 10, 15, 20 and 25 mg/L and the experiments were carried out at 298 K for 90 min.

B. Effects of Initial Dye Concentration and Contact Time

The amount of dye adsorbed (mg/g) increased with increase in time and then reached equilibrium. The initial dye concentration provides the necessary driving force to overcome the resistances to the mass transfer of MB between the aqueous and solid phases [19]. A similar phenomenon was observed for the adsorption of Methylene Blue (MB) dye onto banana stalk waste [20], pomelo (*C. grandis*) peel [12] and castor seed shell [21].

The adsorption of MB on gypsum was also studied as a function of contact time in order to find out the equilibrium time for maximum adsorption. The results showed that equilibrium time required for the adsorption of MB on gypsum ranged from 20 to 40 minutes. However the samples were left for 40 minutes to ensure complete equilibrium. An equilibrium adsorption time of 135 min was reported for the adsorption of Methylene Blue onto wheat shells [22] and 150 min for the adsorption of Methylene Blue on fallen phoenix tree's leaves [23].

C. Effect of Solution pH on Dye Adsorption

The pH of dye solution plays an important role in the adsorption process, particularly on adsorption capacity. The q_e was found to be maximum at the natural pH of the dye solution (pH = 7.5). The adsorption amount was less in acidic media but remained almost constant in basic conditions as shown in Fig.2. The observed low adsorption rate of MB on the gypsum at pH < 7.5 may be because the surface charge becomes positively charged, thus making (H^+) ions compete effectively with dye cations causing a decrease in the amount of dye adsorbed. A similar behavior was observed for Methylene Blue adsorption on other adsorbents [24-26].

D. Analysis of Data using Various Adsorption Models

Adsorption isotherms can be used to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface at equilibrium. In this regard the adsorption data were analyzed by fitting them to different equations. These included the Langmuir, Freundlich and Tempkin equations.
The Langmuir isotherm is represented by the following linear equation [27]:

$$C_e/q_e = 1/Q_o + (b/Q_o)C_e \quad (3)$$

where C_e (mg/L) is the equilibrium concentration, q_e (mg/g) the amount of adsorbate adsorbed per unit mass of adsorbate, and Q_o and b are the Langmuir constants related to adsorption capacity and rate of adsorption, respectively. When C_e/q_e was plotted against C_e, a straight line with a slope of b/Q_o was obtained (Fig. 3), indicating that the adsorption of MB on gypsum follows the Langmuir isotherm. The Langmuir constants b and Q_o were calculated from this isotherm and their values are listed in Table III.

The linear form of the Freundlich equation is given by [28]:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (4)$$

where q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration of the dye. K_F and n are Freundlich constants, n giving an indication of how favorable the adsorption process is, and K_F (mg/g $(L/mg)^{1/n}$) is the adsorption capacity of the adsorbent. The slope $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to 0 [29]. The plot of ln q_e versus ln C_e (Fig. 3) gives a straight lines with a slope of $1/n$. Fig. 4 shows that the adsorption of MB also follows the Freundlich isotherm. The Freundlich constants (K_F and n) calculated in this case are listed in Table III.

Tempkin isotherm is represented by the following equation [30]:

$$q_e = (RT/b) \ln(K_t C_e) \quad (5)$$

This equation in its linear form can also be written as:

$$q_e = B \ln K_t + B \ln C_e \quad (6)$$

where

$$B = RT/b \quad (7)$$

The adsorption data were analyzed with the help of equation (6). A plot of q_e versus ln C_e (Fig. 5) enables the determination of the isotherm constants K_t and B. K_t is the equilibrium binding constant (L/mg) and corresponds to the maximum binding energy, whereas, constant B is related to the heat of adsorption. The values of the various parameters used in this study are listed in Table III. A comparison of maximum monolayer adsorption capacity of MB on various adsorbents is shown in Table IV. One can see that gypsum used in this work had a suitable adsorption capacity of 36 mg/g as compared to other adsorbents found in the literature.

E. Adsorption Kinetics

Kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In the present study, the kinetics of the dye removal was carried out to understand the behavior of this low cost adsorbent. The rate constant of adsorption was determined from the pseudo-first- order rate expression given by Lagergren [33]:

$$\mathrm{Ln}(q_e - q_t) = \mathrm{Ln}\, q_e - k_1 t \quad (8)$$

where q_e and q_t (mg/g) are the amounts of dye adsorbed at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the rate constant of adsorption. In many cases the above equation does not fully describes the adsorption kinetics. In such cases, a pseudo-second-order equation can be used, which is given by [33].

$$t/q_t = 1/(k_2 q^2_e) + (1/q_e)\, t \quad (9)$$

where, the equilibrium adsorption capacity (q_e), and the pseudo-second- order constants k_2 (g/(mg/min)) can be determined experimentally from the slope and intercept of plot t/q_t versus t. The data did not fit well to the first order equation in the entire region of dye concentration used in this work, however, the data fits very well to the pseudo second order kinetic equation with $R^2 = 0.9638$ as shown in Fig.6. This suggests that the adsorption of MB on gypsum may be best described by the pseudo-second-order kinetic model.

Weber and Morris plot was also used to investigate the intra-particle diffusion mechanism [34]: The equation used in this case is as follows:

$$q_t = k_i t^{1/2} + C \quad (10)$$

where, k_i (mg/g $min^{1/2}$) is intra-particle diffusion rate constant. If intra-particle diffusion is rate-limited, then plots of adsorbate uptake q_t versus the square root of time ($t^{1/2}$) would result in a linear relationship. The value of k_i was found to be 7.38 mg/g $min^{1/2}$ with a R^2 value of 0.9862 (Fig. 7). If the plot of q_t versus $t^{1/2}$ is linear and passes through the origin, then intra-particle diffusion is the sole rate-limiting step [35]. However, the linear plot in our study did not pass through the origin. This indicates some degree of boundary layer control and also that the intra-particle diffusion was not the only rate controlling step.

IV. Conclusion

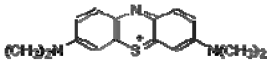
The maximum adsorption capacity of Methylene Blue(MB) on gypsum was found to be 36 mg/g from aqueous solution and the adsorption kinetics followed the pseudo second order equation.

Acknowledgment

The authors would like to thank the UAE University Scientific Research Affairs Unit for supporting this work through research project number 01-03-2-11/08.

TABLE I
PHYSICAL CHARACTERISTICS AND MOLECULAR STRUCTURE OF METHYLENE BLUE

Dye name	Methylene Blue
Suggested name	Methylene Blue
Abbreviation	MB
C.I name	Basic Blue 9
C.I number	52015
Class	Thiazin
λ_{max}	668 nm
Color	Blue

Empirical Formula	$C_{16}H_{18}N_3SCl$
Formula Weight	319.9 g /mol
Molecular volume (cm^3/mol)	241.9
Molecular diameter	0.80
Molecular structure	

* http://stainsfile.info/StainsFile/dyes/dyes.htm

TABLE II
PHYSICAL CHARACTERISTICS OF GYPSUM

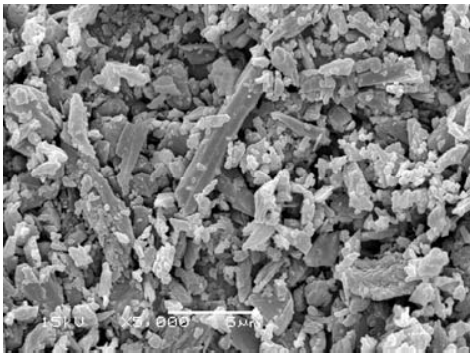
Sample name	Gypsum
Chemical Occurrence	$CaSO_4.2H_2O$
Gypsum content	> 97 %
Bulk density	0.87 g/cm^3
Particle density	2.5 g/cm^3
Moisture content	3 %
BET surface area	5.67 m^2/g
Average pore diameter	10.79 Å
Micropore volume	$3.59x10^{-3}$ cm^3/g
Mesh size	< 90 microns

TABLE III
LANGMUIR, FREUNDLICH AND TEMPKIN ISOTHERM MODEL CONSTANTS AND CORRELATION COEFFICIENTS FOR THE ADSORPTION OF METHYLENE BLUE ON GYPSUM

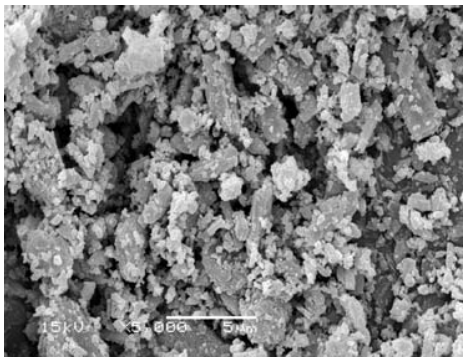
Isotherm Parameters	Parameters
Langmuir	
Q_0 (mg/g)	38.0
b (L/mg)	0.125
R^2	0.9251
Freundlich	
A	4.85
n	2.1
R^2	0.9547
Tempkin	
k	0.4286
R^2	0.9788

TABLE IV
COMPARISON OF ADSORPTION CAPACITIES OF VARIOUS ADSORBENTS FOR METHYLENE BLUE (MB)

Adsorbent	q_{max} (mg/g)	Reference
Gypsum	36	This work
Palygorskite	50.8	[31]
Yellow passion fruit waste	44.7	[26]
Coffee husks	90	[32]



(a)



(b)

Fig. 1 SEM images of gypsum (magnification: 5,000), (a) before dye adsorption (b) after dye adsorption (Dye concentration = $3x10^{-5}$ M)

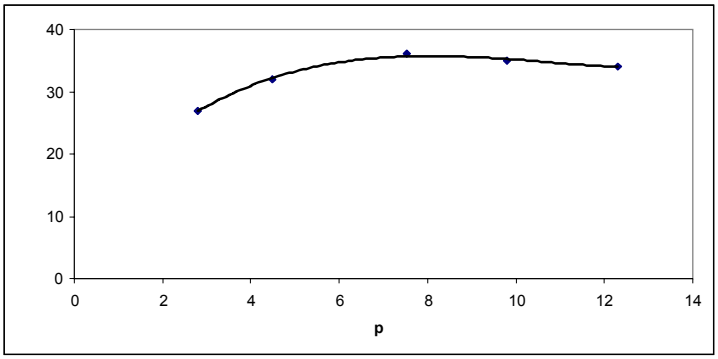


Fig. 2 Effect of pH on MB adsorption on gypsum (Dye=$1x10^{-4}$ M, gypsum= 0.25 gram, temperature = 25°C)

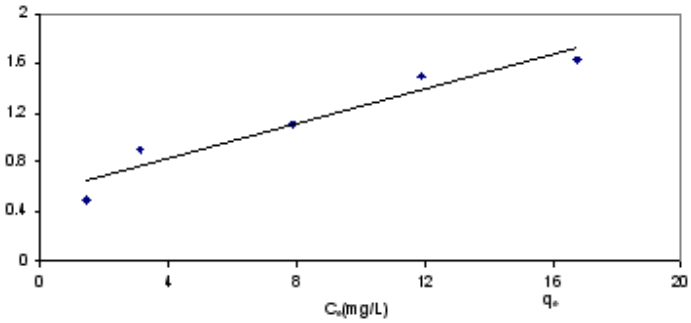


Fig. 3 Langmuir isotherm of the adsorption of Methylene Blue on gypsum

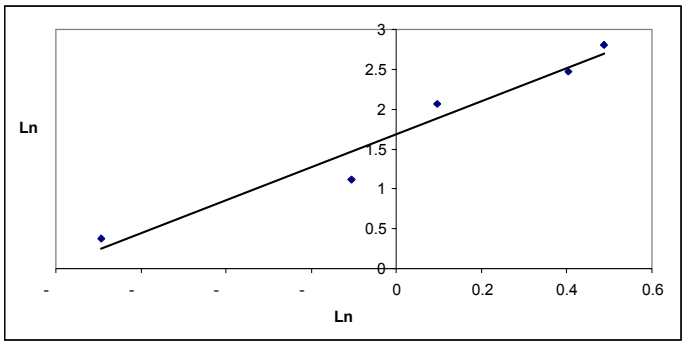


Fig. 4 Freundlich isotherm of the adsorption of Methylene Blue on gypsum

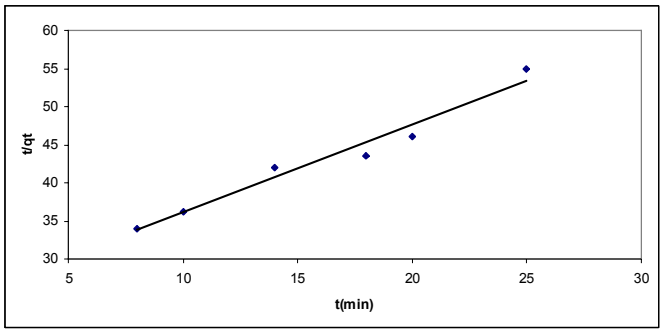


Fig. 6 Pseudo-second-order kinetics of MB adsorption on gypsum (Dye concentration = $3x10^{-5}$ M, gypsum = 0.25 gram, pH = 7.5, temperature = 25°C)

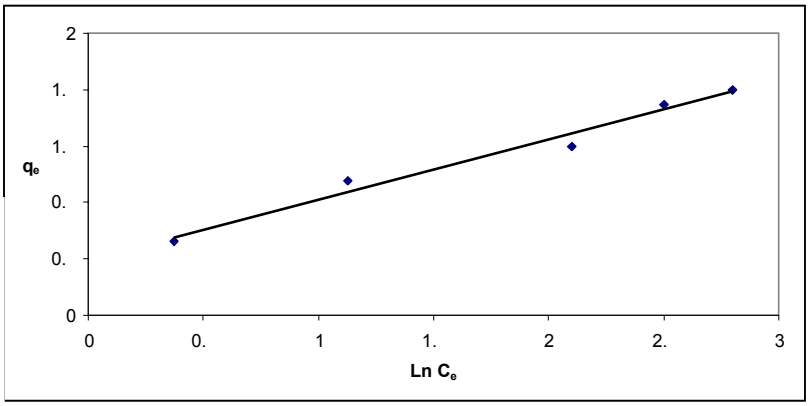


Fig. 5 Tempkin isotherm for Methylene Blue adsorption on gypsum

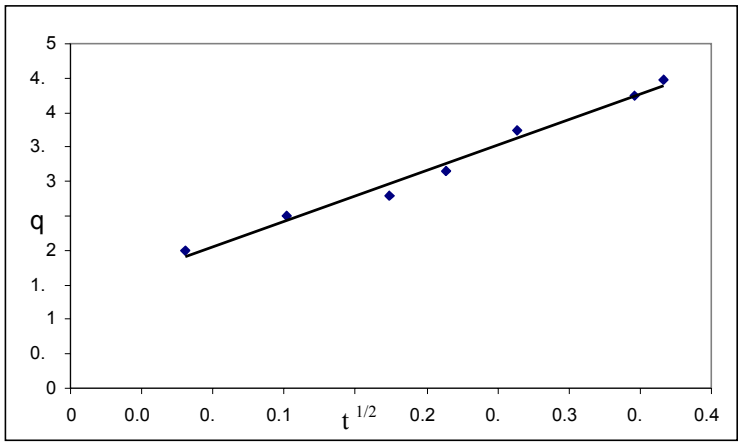


Fig. 7 Plot for evaluating the intraparticle diffusion rate constant for the adsorption of MB on gypsum (Dye concentration = $3x10^{-5}$ M, gypsum = 0.25 gram, pH = 7.5, temperature = 25°C)

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