



Adsorption studies of Toluidine Blue from aqueous solutions onto gypsum

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ARTICLE INFO

Article history:

Received 13 August 2008

Received in revised form

27 November 2008

Accepted 4 December 2008

Keywords:

Adsorption

Dye

Gypsum

Kinetics

Toluidine Blue

ABSTRACT

Gypsum was investigated as an inexpensive and efficient adsorbent to remove Toluidine Blue from aqueous solution. The adsorption studies were carried out at room temperature. Batch mode experiments were conducted at 25 °C to study the effects of pH and initial concentration of Toluidine Blue. The adsorption data was analyzed by using the Langmuir, Freundlich and Tempkin isotherm models and was found to give better results with respect to Langmuir equation. The maximum monolayer adsorption capacity was found to be 28 mg of the dye per gram of gypsum. The data were also studied in terms of their kinetic behavior and was found to obey the pseudo second order equation.

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1. Introduction

Dyes are used by many industries, such as textile, paper and plastics to color their products. These industries also use substantial amount of water in their processes. As a result of this, the effluent of these industries is generally colored due to the presence of these organic chemicals. Colored water is not only esthetically undesirable but also blocks sunlight which is essential for many photoinitiated chemical reactions which are necessary for aquatic life [1,2]. Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. The contamination of water bodies becomes serious due to the fact that 2% of dyes that are produced are discharged directly in aqueous effluent [3]. Due to increasing environmental awareness and the relevant EPA restrictions on the organic content of industrial effluents, it is necessary to eliminate dyes from wastewater before it is discharged. Many of these dyes are also toxic and even carcinogenic and thus poses a serious threat to aquatic living organisms [4].

Industrial wastewater containing dyes is very difficult to treat, since the dyes are generally resistant to aerobic digestion [5]. Several physical, chemical and biological decoloration methods have been reported to tackle the removal of dyes from aqueous solution, however, few have drawn the potential attention by the paper and textile industries. There are several reported methods for the removal of pollutants from effluents, however there is no single

process capable of adequate treatment, mainly due to the complex nature of the effluents [6]. In practice, a combination of different processes is often used to achieve the desired water quality in the most economical way. Literature data reveals that liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent [7–9]. This process is an excellent alternative for the treatment of wastewaters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application.

Adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [10–12]. Adsorption also does not result in the formation of harmful substances like in many other cases. Activated carbon is one of the main sorbents used to remove dyes in wastewater because of its good adsorption ability [13,14]. However, its widespread use is restricted due to its high cost. Numerous approaches have been studied for the development of 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 been suggested [15–17]. This study is an extension in the same direction in exploring the use of a commonly available commodity namely gypsum for treating industrial effluents. Gypsum was chosen as it is found abundantly in nature, is cheap as compared to other adsorbents such as activated coal or inorganic substances used for adsorption, and its readiness to use without any prior treatment. This paper focuses our attention on

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the use of gypsum as an alternative low-cost adsorbent for the removal of Toluidine Blue from aqueous solutions due to the reason that many textile manufacturers use dyes that release aromatic amines (e.g., benzidine, toluidine) and are potential carcinogens [4]. This study is novel in a way as no literature citations are available where gypsum has been used for removing dyes from aqueous solution. The data shall be used to evaluate the conditions of maximum adsorption along with the relevant kinetic studies with the help of model equations.

2. Experimental

Toluidine Blue with a labeled purity of more than 98% was procured from Aldrich. The characteristics and molecular structure of this dye is given in Table 1. 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. 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. Commercially available gypsum powder (unbranded) was purchased from the local market.

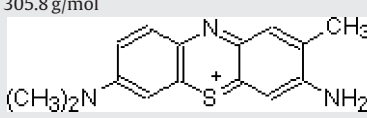
Initially, dye stock solution of 1×10^{-3} M was prepared in 100 mL of deionized water in a flask followed by necessary dilutions of this stock solution. A 0.1 g of gypsum sample was then added to a given amount of the diluted solution. The contents of the dye solution were then agitated for a given time period using a magnetic stirrer operated at a constant speed. The contents were then centrifuged and the supernatant solution was taken out with a pipette and monitored instantaneously on a spectrophotometer for absorption. The change in absorbance of the dye solution was then used to calculate the dye concentration in solution and the percentage adsorption of the dye on gypsum.

$$\text{Dye adsorption (\%)} = \left[\frac{C_0 - C_t}{C_0} \right] \times 100 \quad (1)$$

In the above equation, C_0 and C_t (both in mg/L) are the liquid-phase concentrations of initial dye and at any time t respectively. The adsorption was carried out at room temperature (25 ± 1 °C) and the findings were an average of three replicate measurements.

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.

Table 1
Physical characteristics and molecular structure of Toluidine Blue^a.

Dye name	Toluidine Blue
Suggested name	Toluidine Blue O
Abbreviation	TB
C.I. name	Basic Blue 17
C.I. number	52040
Class	Thiazin
λ_{max}	625 nm (Aldrich)
Color	Blue
Empirical formula	$C_{15}H_{16}N_3S$
Formula weight	305.8 g/mol
Molecular structure	

^a <http://stainsfile.info/StainsFile/dyes/dyes.htm>.

Table 2
Physical characteristics of gypsum.

Sample name	Gypsum
Chemical occurrence	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
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	3.59×10^{-3} cm ³ /g
Mesh size	<75 μm

In the present studies, commercially obtained gypsum powder 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 2 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). Fourier Transform Infrared (FTIR) (FTIR-2000, Perkin Elmer) analysis was applied on gypsum and dye adsorbed gypsum to determine the surface functional groups, where the spectra were recorded from 4000 to 400 cm⁻¹.

Removal of dye from aqueous solutions on gypsum surface was calculated by monitoring the changes in absorption values and hence the concentrations of the dye solutions. The absorption intensity changes corresponding to λ_{max} of the dye solution (625 nm) were monitored on a CARY 50 UV/VIS spectrophotometer, using a 1 cm quartz cell.

3. Results and discussion

3.1. Characterization of sorbent

The FTIR analysis of TB showed peaks at 3313 cm⁻¹ (N–H stretch), 1644 cm⁻¹ (C=N stretch), 1241 cm⁻¹ (C=S stretch) and 1023.6 cm⁻¹ (C–N stretch). These peaks shifted when the dye is adsorbed on gypsum surface, e.g., the C=N peak appears at 1621.85 cm⁻¹, C–N stretch peak appears at 1029.4 cm⁻¹ and N–H stretch appears at 3402 cm⁻¹. This shows the change in spectral behavior after dye adsorption. These changes observed in the spectrum indicate the possible involvement of the various functional groups on the surface of the gypsum in the sorption process.

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.

3.2. Effect of contact time and dye concentration

Conditions for maximum removal of the dye from aqueous solution by adsorbing it on gypsum were initially optimized as shown in Fig. 2(a). From this graph, an optimum time period of 60 min was chosen for further studies. The amount of dye adsorbed on gypsum increases with time and later becomes constant. The rapid adsorption observed during the first 20–30 min is probably due to the abundant availability of active sites on the gypsum surface with a gradual decrease of these sites with time and therefore adsorption becomes less with time and finally becomes constant [19]. Changing the concentration of dye solution also caused a change in adsorption of dye. This behavior is shown in Fig. 2(b) and indicates that the

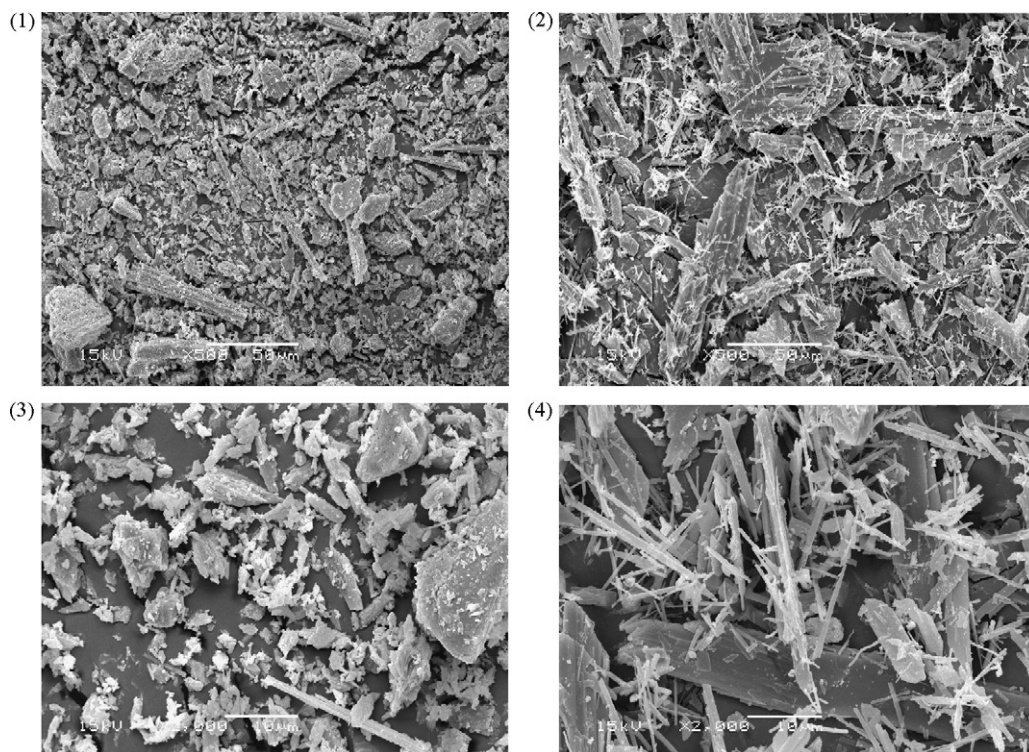


Fig. 1. SEM images of gypsum (magnification: 500 \times): (1) before dye adsorption, (2) after dye adsorption (magnification: 2000 \times), (3) before dye adsorption and (4) after dye adsorption (dye concentration = 1×10^{-4} M).

percentage adsorption decreases with increasing amount of dye. This is because that at low concentrations, the adsorption sites can be occupied by dye molecules, but when concentration of dye is increased in solution, the active sites on the adsorbent surface are already occupied, thereby causing less removal of dye from solution. Also the steric repulsion between the dye molecules can slow down the adsorption process. A similar behavior has been reported for other dyes on activated carbon [19].

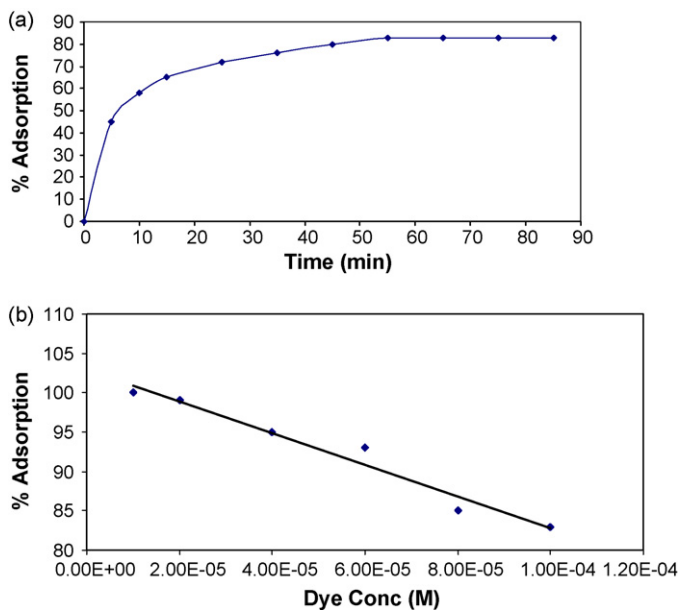


Fig. 2. (a) Change in adsorption of Toluidine Blue on gypsum with time (dye = 1×10^{-4} M, gypsum = 0.1 g, temperature = 25 $^{\circ}$ C). (b) Change in adsorption of Toluidine Blue with its concentration (amount of gypsum = 0.1 g, time = 60 min, temperature = 25 $^{\circ}$ C).

3.3. Effect of pH

Fig. 3 shows the effect of pH on percentage adsorption of Toluidine Blue on gypsum. The adsorption of this dye was found to decrease at low pH values. This may be due to the fact that at low pH values, the H^+ ions may compete with dye molecules for the adsorption sites of the adsorbent, thereby inhibiting the adsorption of dye [20]. The adsorption percentage is maximum at the natural pH value of the dye solution (pH 6.5). On increasing the pH values, the adsorption value goes down. This could be due to the reason that at higher pH levels, excess OH^- ions compete with dye ions for adsorption sites on the adsorbent surface resulting in less adsorption [20]. A similar behavior has been observed for other systems as well [21,22].

3.4. Analysis of data using various adsorption models

The adsorption of an adsorbate on a given surface can most probably arise by both the physical or chemical processes and the

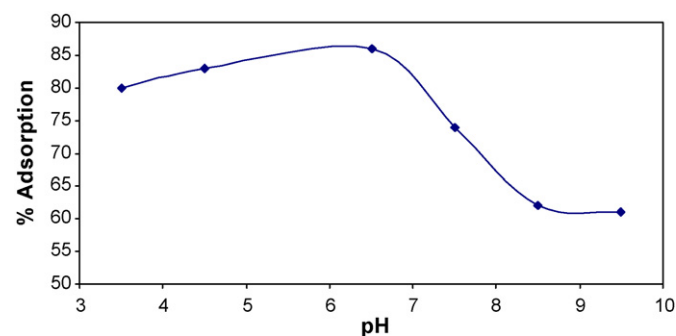


Fig. 3. Effect of pH on TB adsorption on gypsum (dye = 1×10^{-4} M, gypsum = 0.1 g, temperature = 25 $^{\circ}$ C).

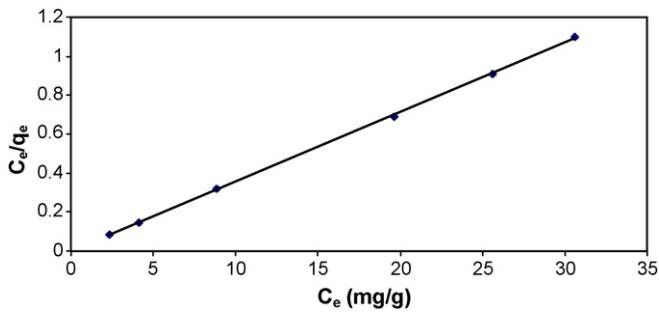


Fig. 4. Langmuir isotherm of the adsorption of Toluidine Blue on gypsum (gypsum = 0.1 g, contact time = 60 min, pH 6.5, temperature = 25 °C).

adsorption of dyes from aqueous phase onto a solid surface can be well described as a reversible reaction under an equilibrium condition established between the two phases [23,24].

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 Langmuir, Freundlich and the Temkin isotherms were used to analyze the adsorption data. The main difference between these three isotherm models is in the variation of heat of adsorption with the surface coverage. Langmuir model assumes uniformity, Freundlich model assumes logarithmic decrease and Temkin model assumes linear decrease in heat of adsorption with surface coverage [20].

The first isotherm namely the Langmuir isotherm in its linear form is given by the following equation [25,26]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{b}(q_{\max}) \quad (2)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium, C_e is the final concentration at equilibrium, q_{\max} is the maximum adsorption at monolayer coverage and b is the constant related to the extent of adsorption.

A plot of specific adsorption (C_e/q_e) versus equilibrium concentration (C_e) is shown in Fig. 4 ($R^2 = 0.9968$). The values of q_{\max} and b from this graph were found to be 28 mg/g and 0.008 L/mg. The results also demonstrated the formation of monolayer coverage of dye molecules at the outer surface of gypsum. Table 3 gives the comparison of q_{\max} values of TB adsorption on various adsorbents. One can see from this table that the adsorption capacities of TB on various surfaces are quite different. This may be attributed due to the varying nature of surface properties of different adsorbents.

Experimental data for the dye adsorption on gypsum was also subjected to Freundlich equation, which has the following form [30,14]:

$$\log A_{\text{ads}} = \log A + \left(\frac{1}{n}\right) \log A_i \quad (3)$$

where A_{ads} is the concentration of dye adsorbed on gypsum and A_i is the bulk concentration of dye; A and n are characteristic constants for a sorption system.

Graphical conformity to this equation for Toluidine Blue is shown in Fig. 5 ($R^2 = 0.9850$). The value of n was found to be 1.2 and indicates favorable adsorption, whereas the value of A was found to be 6. The slope $1/n$ ranging between 0 and 1, is a measure of

Table 3
Comparison of adsorption capacities of various adsorbents for TB at 25 °C.

Adsorbent	q_{\max} (mg/g)	Reference
Gypsum	28	This work
Turkish zeolite	64	[27]
Pulp fiber	25	[28]
Flyash	6	[29]

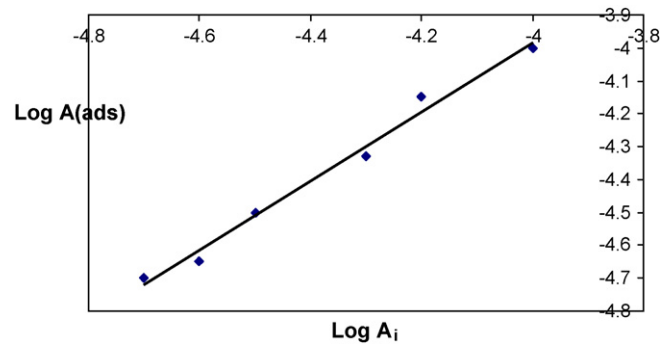


Fig. 5. Freundlich isotherm of the adsorption of Toluidine Blue on gypsum (gypsum = 0.1 g, contact time = 60 min, pH 6.5, temperature = 25 °C).

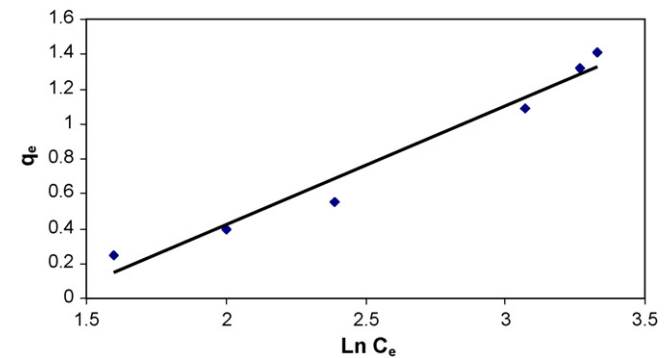


Fig. 6. Temkin isotherm of Toluidine Blue adsorption on gypsum (gypsum = 0.1 g, contact time = 60 min, pH 6.5, temperature = 25 °C).

adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for $1/n$ below 1 indicates a normal Langmuir isotherm while $1/n$ above 1 is indicative of cooperative adsorption [20].

The adsorption data was also analyzed by using the Temkin equation, which is mathematically given by [31]:

$$q_e = RT \ln A \left(\frac{C_e}{b}\right) \quad (4)$$

In its linear form the above equation can be written as:

$$q_e = k \ln A + k \ln C_e \quad (5)$$

where k is Temkin isotherm energy constant (RT/b) and A is the Temkin isotherm constant. A plot of q_e versus $\ln C_e$ as in Fig. 6 shows the conformity of the data to the Temkin model ($R^2 = 0.9595$) with a k value of 0.6706. Table 4 summarizes the various parameters for the model equations used in this work. A

Table 4

Langmuir, Freundlich and Temkin isotherm model constants and correlation coefficients for adsorption of Toluidine Blue onto gypsum.

Isotherm parameters	Parameters
Langmuir	
Q_0 (mg/g)	28.0
b (L/mg)	0.008
R^2	0.9968
Freundlich	
A	6
n	1.2
R^2	0.9850
Temkin	
k	0.6706
R^2	0.9595

comparison of R^2 values for the above three models indicate that the Langmuir model represents best the equilibrium isotherms tested in this work. The fact that the Langmuir isotherm fits the experimental data very well may be due to the homogenous distribution of active sites on the gypsum surface, since the Langmuir equation assumes that the surface is homogenous.

3.5. Kinetic studies

The adsorption kinetics of the dye adsorption on gypsum was also analyzed by using two different kinetic models namely the pseudo first order and the pseudo second order equations. These models are commonly used to describe the adsorption behavior of pollutants on solid surfaces.

In the first case, the pseudo first order reaction model was used which in general is given by [32]:

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (6)$$

In the linear form this equation can be written as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

where q_e and q_t are amounts of dye adsorbed at equilibrium and at any time t , k_1 is the pseudo first order rate constant and t is the time.

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 [32]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where q_e and q_t are amounts of dye adsorbed at equilibrium and at any time t , and k_2 is the pseudo second order rate constant.

The adsorption data did not fit linearly to pseudo first order kinetics over the entire region. However, the data fitted very well ($R^2 = 0.9992$) to pseudo second order kinetic equation as seen from Fig. 7. The value of k_2 was found to be 0.326 g/(mg min).

Most of the adsorption processes may be described by either the external mass transfer (boundary layer diffusion) or intraparticle diffusion model. The later is given by the Weber–Morris equation [33,34]:

$$q_t = k_i t^{1/2} \quad (9)$$

where the parameter k_i is the diffusion coefficient value (in mg/(g min^{1/2})), t is the time (in min) and q_t is the amount of dye adsorbed (in mg/g). Fig. 8 shows the data fitting to the above equation for TB dye adsorption on gypsum ($R^2 = 0.9803$). The diffusion coefficient rate value k_i obtained from this equation was found to be 0.1238 mg/(g min^{1/2}) in the present study. Since the plot does not pass through the origin, it indicates some degree of boundary layer control and also that intraparticle diffusion is not the only rate-limiting step.

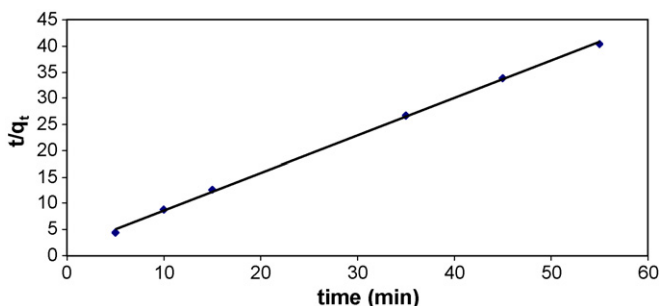


Fig. 7. Pseudo second order kinetics of Toluidine Blue adsorption on gypsum (dye concentration = 1×10^{-4} M, gypsum = 0.1 g, pH 6.5, temperature = 25 °C).

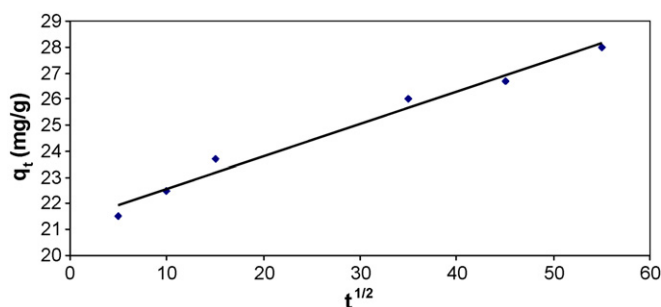


Fig. 8. Plot for evaluating the intraparticle diffusion rate constant for the adsorption of Toluidine Blue on gypsum (dye concentration = 1×10^{-4} M, gypsum = 0.1 g, pH 6.5, temperature = 25 °C).

4. Conclusion

The choice of gypsum was made for this work as it is much cheaper as compared to other commercially available adsorbents such as activated coal or inorganic substances used for adsorption studies. This study is also novel in a way as no literature citations are available where gypsum has been used for removing dyes from aqueous solution. Toluidine Blue was removed from aqueous solution onto gypsum surface at room temperature. The maximum adsorption capacity of the dye was found to be 28 mg of the dye per gram of the gypsum surface. The equilibrium data were analyzed using the Langmuir, Freundlich, and Tempkin isotherm models. The adsorption data for the dye investigated in this work fitted well to Langmuir equation. Sorption kinetic data revealed that the adsorption kinetics followed the pseudo second order equation.

Acknowledgement

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.

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