

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 Instrumentation

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]:

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

