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Removal of Methylene Blue from aqueous solution by adsorption on sand

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Abstract

The removal of Methylene Blue (MB) dye from aqueous solution present as a pollutant material in textile waste water was studied at 298 K in terms of its adsorption behaviour. Local sand sample was used as an adsorbent in this work. The textural properties of the sand including surface area, mean pore radius and total pore volume were examined from the low-temperature adsorption of nitrogen at 77 K. The conditions for maximum adsorption of the dye on sand were optimized. It was seen that under optimized conditions, up to 92% dye could be removed from solution onto the sand surface. The adsorption data were fitted to Freundlich and Dubinin–Raduushkevich equations for the calculation of various adsorption parameters. The Freundlich constants n and A were determined as 0.9682 and 0.639 mol/g, respectively. The sorption energy calculated by the Dubinin–Raduushkevich equation was found to be 1.22 kJ/mol. The adsorption behaviour of the dye was also investigated in terms of added cations and anions. It was found that the dye adsorption decreased considerably in the presence of thiosulphate, potassium, nickel and zinc ions.

Keywords: Methylene Blue; Adsorption; Sand; Freundlich isotherm; Dubinin–Raduushkevich equation

1. Introduction

Many industrial processes use different synthetic chemical dyes for various purposes. Some frequent users of these chemicals include paper and pulp manufacturing, dyeing of cloth, leather treatment, printing, etc. Most of the used solutions containing such dyes are discarded as effluents. Since some of these dyes are toxic in nature, their removal from the industrial effluents is a major environmental problem [1–4]. Quite apart from the aesthetic desirability of colored streams resulting from dye waste, some dyes in particular can undergo anaerobic degradation to potentially carcinogenic amines [5]. Literature review on this subject matter has revealed the importance of various approaches to handle such wastes. These include biodegradation, photocatalytic, photolytic and advanced oxidative degradation of various dye solutions [6–10]. A considerable amount of work has also been reported in the literature regarding the adsorption of some dyes on various adsorbent surfaces such as clays, fly ash, polymers and activated carbon; however, no such study is available on sand surfaces [11–15]. The purpose of this study is to focus attention on the adsorption of Methylene Blue (MB) on local sand, which is a cheap commodity and available around in abundance in the developing countries. The study was carried out in the absence and presence of various ions. Optimized parameters of maximum adsorption were evaluated. The adsorption data were fitted to various equations to obtain certain constants related to the adsorption phenomena.

2. Experimental

The dye, namely Methylene Blue (MB) with a labeled purity of more than 98% was obtained from Fluka and used as such. Deionized water was used to make the dye solutions of desired concentration. The dye solution shows an intense

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absorption peak in the visible region at 665 nm. In an adsorption process, a change in the intensity of this peak can be used to characterize the removal of dye from the solution.

In this study, sand was used as an adsorbent because of its enormous availability in the local environment. The sand sample was procured from the local dunes in the vicinity of Al-Ain city located in the south-eastern region of UAE. The sand sample used in this study was not treated in any other way except sieving it to obtain different portions of it.

Sieve analysis carried out on the sand sample gave the following composition: coarse sand, 0.02%; 350 μm, 0.41%; 250 μm, 65.75%; 180 μm, 21%; 125 μm, 7.5%; 88 μm, 3.6% and the remaining fraction below 88 μm. For the present work, 250 μm fraction was used. The BET surface area of this sand fraction was found to be 5.2176 m^2/g by using the nitrogen adsorption method, whereas the average pore diameter was determined to be 37.2498 Å. The pore volume was estimated to be 1.198 cm^3/g. The adsorption of dye on sand surface was calculated by monitoring the changes in absorption value of the solution on a CARRY 50 UV/vis spectrophotometer, using a 1 cm quartz cell. In general, Methylene Blue (MB) 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 given amount of sand sample (usually 0.1–0.5 g) was added to 5 mL of this diluted solution. The contents of the dye solution were then shaken for a given amount of time using a magnetic stirrer operated at a constant speed. The contents were then centrifuged and the supernatant solution was pipetted out and monitored instantaneously on a spectrophotometer for absorption values. The absorbance value obtained in each case was then used to calculate the percentage adsorption of the dye on sand.

$$\% \text{ Adsorption} = \left[\left(A_i - A_f\right)/A_i\right] \times 100 \tag{1}$$

where A_i and A_f are the initial and the final absorbance values, respectively.

3. Results and discussion

Initially, the optimum conditions for maximum adsorption of the dye on sand sample were investigated. For this purpose, the amount of sand, the concentration of the dye solution and the shaking time were varied over a wide range. From these studies it was found that maximum adsorption took place when the dye concentration was 1.8×10^{-5} M, the sand sample was 0.1 g and the shaking time was 5 min. These conditions were fixed for subsequent studies. Table 1 shows the variation of percentage adsorption values for this study when the dye concentration was changed keeping the other conditions constant.

Table 1
Variation of percentage adsorption values of Methylene Blue on sand (sand = 0.1 g, shaking time = 5 min)

Dye concentration (10^{-5} M)	Percent adsorption
3.0	85
2.7	87
2.4	89
1.8	92
1.5	91
0.9	91

Table 2
Effect of various ions on the percent adsorption of Methylene Blue on sand (sand = 0.1 g, [Dye] = 1.8×10^{-5} M, shaking time = 5 min)

Anions	% Adsorption	Cations	% Adsorption
Oxalate	85.6	Silver	88.4
Acetate	83.0	Nickel	75.0
Sulphate	90.6	Potassium	81.2
Thiosulphate	78.2	Zinc	65.6

Anions were added as sodium salts, whereas cations were added as nitrates (concentration of each ion in solution = 1×10^{-3} M).

Since the industrial effluents are always contaminated with various ions, it is therefore important to study the effect of these ions on the adsorption property of dye solution. The adsorption of dye in the presence of anions (added as sodium salts) and cations (added in the nitrate form) were therefore carried out. The concentrations of all these ions in solution were kept at 1×10^{-3} M in each case. The results are tabulated in Table 2. It can be seen that adsorption of the dye decreased substantially in the presence of thiosulphate, nickel and zinc ions. Thus these ions should be removed from the dye solution prior to its adsorption on sand.

The data for MB adsorption on sand were subjected to various equations. In this regard the data were first fitted to Freundlich equation which has the following form

$$\log A_{\text{ads}} = \log A + n \log A_i \tag{2}$$

where A_i and A_{ads} are the concentrations of the dye in solution, and on the sand surface at equilibrium, respectively, and A and n are constants for a particular system. A plot of log A_{ads} versus log A_i gave a straight line ($R^2 = 0.9984$) as shown in Fig. 1. From the slope and the intercept of this graph, the values of n and A were found to be 0.9682 and 0.639 mol/g, respectively. The slope value of nearly one indicates the monolayer sorption of dye solution on sand.

The adsorption data were also analyzed by using the Dubinin–Raduushkevich equation which is a more general

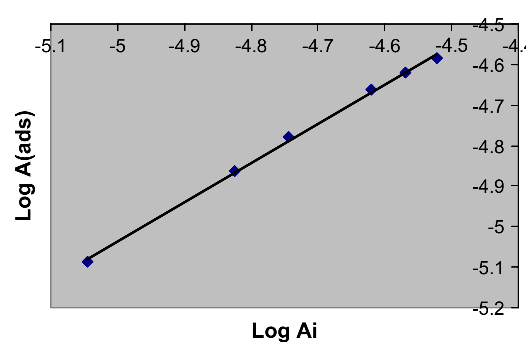

Fig. 1. Application of Fredulich equation to the adsorption of Methylene Blue on sand.

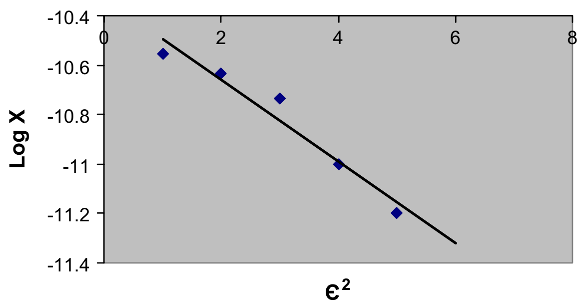

Fig. 2. Application of Dubinin–Raduushkevich equation to the adsorption of Methylene Blue on sand.

expression [16]. It assumes a very small subregion of the adsorption surface which is uniform and energetically homogeneous (Fig. 2). This equation is given by

$$\ln X = \ln X_m - B\epsilon^2 \quad (3)$$

where X and X_m are the amount of adsorbed dye and the maximum amount of the dye adsorbed, respectively, B is a constant and ϵ is the Polanyi potential which in turn is given by

$$\epsilon = RT \ln(1 + 1/C) \quad (4)$$

where C is the concentration of the dye in solution at equilibrium. A plot of ln X versus ϵ^2 gives a straight line. In this case a graph with $R^2 = 0.951$ was found to have a slope of 0.16534 which corresponds to B, whereas the intercept value of 4.7×10^{-11} corresponds to X_m value. The B value was then used to calculate the sorption energy (E_s) by using the Hobson's equation [16].

$$E_s = 1/(1 - 2B)^{1/2}. \quad (5)$$

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In this case the E_s value was found to be 1.22 kJ/mol. For an ion exchange process, this value should lie between 8 and 16 kJ/mol. Thus the adsorption of Methylene Blue does not obey the ion exchange mechanism.

4. Conclusion

Removal of Methylene Blue (MB) dye from aqueous solution onto sand surface was carried out at room temperature. The conditions of maximum adsorption of the dye were optimized. It was seen that under optimized conditions, up to 92% dye can be removed from solution onto the sand surface. The adsorption data were fitted to Freundlich isotherm which showed that adsorption was monolayer in nature. Furthermore, the Dubinin–Raduushkevich equation revealed that the adsorption process was physical in nature. The adsorption of the dye decreased in the presence of thiosulphate, potassium, nickel and zinc ions.

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