Journal of Advanced Engineering Research
ISSN: 2393-8447
Volume 1, Issue 1, 2014, pp.36-40

Adsorption of methylene blue dye from surface water onto aquifer material during batch experiments

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ABSTRACT

The removal of Methylene Blue (MB) dye from the surface water during river bank filtration (RBF) was studied at 298 K in terms of its adsorption behavior. Aquifer material from the Srinagar RBF site, India was used as a representative of river bank media for the experiments. The textural properties of the aquifer material including surface area, mean pore area and total pore volume were examined from the low-temperature adsorption of nitrogen at 77 K. The conditions for maximum adsorption of the methylene blue dye on aquifer material were optimized. The removal efficiency of dye was obtained above 90% at initial concentration of 2 mg/L. From the kinetic study, the adsorption data followed the second-order kinetic model (R^2=0.999). Equilibrium data were fitted to Langmuir, Freundlich, isotherms and the equilibrium data were best described by the Langmuir isotherm model (R^2=0.99). Thus from lab-scale results, RBF shows a significant barrier for dye transport.

Keywords - Adsorption, Kinetics, Isotherm, Methylene blue dye, River bank filtration.

1. INTRODUCTION

Removal of hazardous compounds from industrial effluents is one of the growing needs of the present time. Many industries, mostly textile industry, propagate colored effluents containing dyes and pigments. It has been estimated that 10–15% of the dye is lost in the dye effluent [1]. The discharge of dyes in the environment is a matter of concern for both toxicological and esthetical reasons, causing serious water pollution problems to aquatic life due to the reduced light penetration. The presence of even very small amounts of dyes in water less than 1ppm for some dyes is highly visible and undesirable [2].

River bank filtration (RBF) is a natural process to purify the polluted river/lake water. The quality of surface water improves when it flows through bank of the river/lake and adjacent aquifer material. The processes responsible for changes in quality are sorption, filtration, acid-base reaction, oxidation, reduction, hydrolysis, bio-chemical reactions, mixing with background groundwater etc. Reference [3] reported three anthraquinone blue disperse dyes associated with textile discharges in the Savannah River (USA). Reference [4] reported 15 dye compounds in the river Yamaska water, in suspended solids, and in sediments downstream of textile mills in Quebec, Canada. The identified dyes included C.I. Disperse Red 60, C.I. Disperse Blue 26, and C.I. Disperse Blue 79.

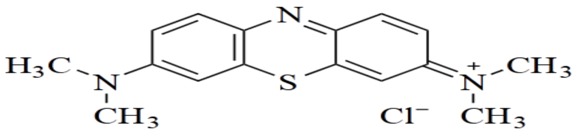
Methylene blue (MB), which is classified as a basic dye has wider application including coloring paper, dyeing cottons, wools, temporary hair colorant coating for paper stock [5]. Though methylene blue is not strongly hazardous but on inhalation, it can show various harmful effects. It may cause nausea, and gastric, vomiting. Although several studies have focused on the removal/attenuation of turbidity, inorganic and organic compounds and pathogens during RBF, [6-8]. However, no study has been done on the removal/attenuation of dyes during RBF.

The objective of this study was to determine the effectiveness of the river bank filtration to remove the methylene blue dye. Since biodegradability of MB is less so mainly adsorption was studied. Batch studies were conducted to determine the adsorption kinetics and adsorption isotherm. Aquifer from the Srinagar river bank filtration site, India was used as a representative river bank media for the experiments.

2. MATERIALS AND METHODOLOGY

2.1 Adsorbate

The MB was used in this study purchased from SD Fine-Chem Limited. The molecular weight of MB is 319.8 with three groups of water. The molecular formula is C16H18ClN3S. The structure of Methylene Blue is shown as below:



The dye solution shows an intense absorption peak in at 664 nm. Octanol/Water Partition Coefficient of the dye (log K_{ow}) is 5.85. Solubility of the dye in water is 43,600 mg/L at 25ºC. The compound consisting of dark green crystals or crystalline powder, having a bronze-like luster.

2.2 Characterization of Aquifer material

Aquifer material was collected from Alakananda river bank, Srinagar India (30.22°N 78.78°E). It was transported to geotechnical laboratory, IIT Roorkee for grain size analysis. The grain size analysis of oven dried aquifer material was carried out as per the Indian Soil Classification 1498 (1970).

2.3 Point of Zero Charge

Determination of pHzpc was done to investigate how the surface charge of adsorbent material depended on pH. For the determination of pHzpc of aquifer material, 0.01 M NaCl was prepared, and its initial pH was adjusted between 2.0 to 12.0 by using NaOH/HCl in each batch system. Then 50 mL of 0.01 M NaCl was taken in 250 mL. Erylenmeyer flasks and 0.20 g of adsorbent was added to each solution. These flasks were kept for 48 h in incubator, and the final pH of the solutions was measured by using a pH meter. A graph was plotted between "pH final vs. pH initial". The point of intersection on the curves of pH final vs. pH initial was recorded as pHzpc of the aquifer material.

2.4 Synthetic solution preparation

A stock solution of 100 mg/L was prepared by dissolving 10 mg of dye in 100 ml distilled water. Each solution of dye concentration 0.5 ppm, 1 ppm, 1.5 ppm, 2 ppm, 2.5 ppm, 3 ppm, 5 ppm was scanned in the range of 200–700 nm Maximum adsorption was found at wavelength 664nm.

2.5 Batch adsorption test

The adsorption studies were conducted with 1.5 g of adsorbent and 100 of MB solution at desired concentration, pH on an orbital shaking incubator with a constant speed of 200 rpm and constant temperature of 25^0C. The solution was centrifuged at 3000 rpm for 10 min and the concentration of MB in the supernatants was examined with a HACH UV/VIS spectrophotometer at the wavelength of 664 nm at which the maximum absorbency occurred. Then the amounts of MB adsorbed per unit mass of adsorbent were calculated from the differences between the initial and final MB concentrations in solution by (1):

$$q_{eq} = \frac{(C_0 - C_{eq})V}{W} \tag{1}$$

where q_{eq} (mg/g) is the amount of MB adsorbed in adsorbent, C_0 and C_t (mg/L), initial and final concentration of MB solution, V (L), the volume of MB solution used, W (g), the weight of the adsorbent.

3. RESULTS AND DISCUSSION

3.1 Grain size analysis of aquifer material

Average grain size (d_{50}) of the aquifer was 0.13 mm with 82.5 percent sand and 17.5 percent fines. The uniformity coefficient was 3.75. The grain size finer than 1mm were used for the batch experiments. The BET surface area of this aquifer material was found to be 2.1724 m^2/g by using the nitrogen adsorption method whereas the average cross sectional area was determined to be 0.162 nm^2 and the total pore volume was estimated to be 0.0011 m^2/g. Adsorption of cations is favored at pH>pHzpc, while the adsorption of anions is favored at pH<pHzpc [9]. pHzpc value for the aquifer material is 8.8 (Fig. 1). So adsorption is favored.

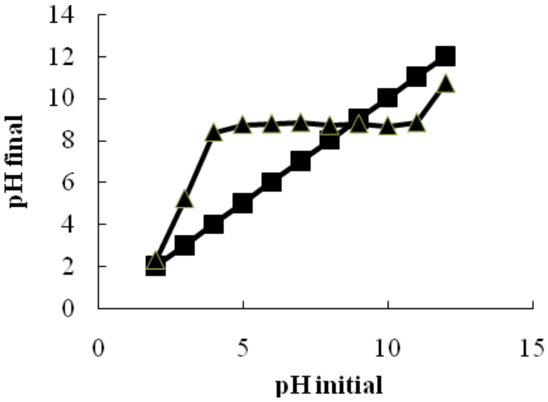


Fig. 1 pHzpc curve

3.2. Kinetics of batch sorption process

The objective of adsorption kinetic study is to investigate the possible mechanisms for the sorption process and to determine the time required to attain equilibrium. Fig. 2 shows the effect of the adsorption time on the adsorption capacities of MB by the aquifer material. It is clear that the adsorption capacities of aquifer material increased rapidly with the increase of the adsorption time from 0 to 40 min and more than 90% of the equilibrium adsorption capacities of aquifer material occurred within 40 min and gradually increased from 40 to 120 min until equilibrium. Therefore, under our experimental conditions, the equilibrium times for the adsorption of MB on aquifer material all 120 min.

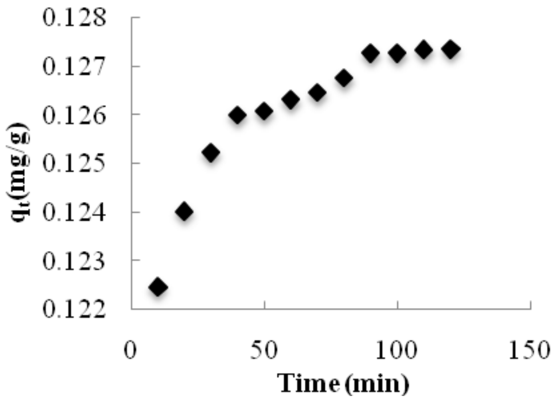


Fig. 2 Kinetics of MB uptake by the aquifer

To investigate the potential rate-controlling steps involved in the adsorption of MB onto aquifer material, both pseudo first- order and pseudo-second-order kinetic models were used to fit the experimental data.

The pseudo-first-order rate expression of Lagergren model is generally expressed as (2):

$$\frac{dq_e}{dx} = k_1(q_e - q_t) \tag{2}$$

The pseudo-second-order rate equation is given as (3):

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{3}$$

Where q_e and q_t are the amounts of adsorption dye (mg/g) at equilibrium and at time t (min), k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the adsorption rate constant of pseudo-first-order and pseudo second-order adsorption rates, respectively [10]. The linear plots of log (q_e–q_t) versus t and (t/q_t) versus t are drawn for the pseudo-first order (Fig. 3) and the pseudo-second-order models, (Fig. 4) respectively (Table 1).

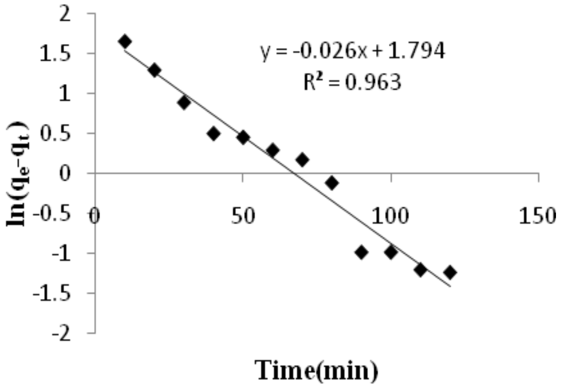


Fig. 3 Pseudo first order Kinetics 2 mg/L, pH: 8.91

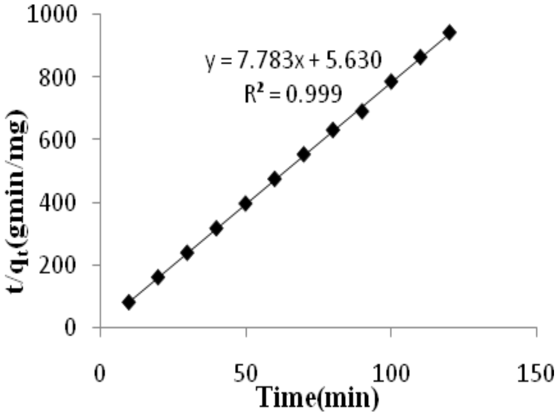


Fig. 4 Pseudo second order Kinetics

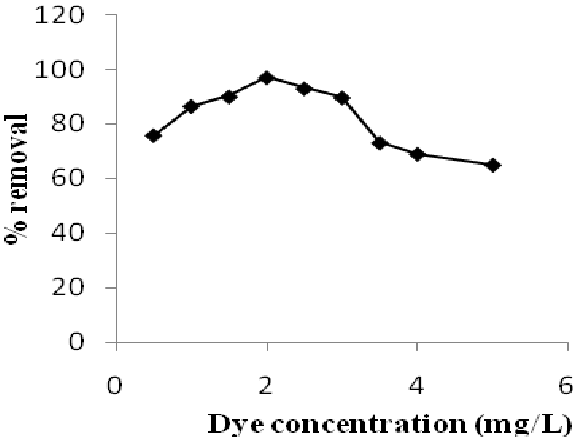


Fig. 5 % removal of due to change in initial concentration of the dye

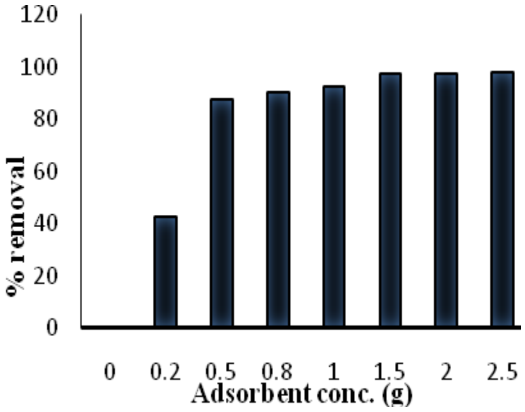


Fig. 6 Percentage removal of due to change in adsorbent dosage

3.3.1 Effect of MB concentration

The effect of MB concentration on its uptake by aquifer material was studied at constant temperature 25^0C using 1.5g of the sorbent. The results obtained showed that the increase in MB dye concentration resulted in an increase in the MB dye uptake. (Fig. 5)

3.3.2. Effect of sorbent concentration

Examination of the effect of aquifer material on the removal of MB dye from aqueous solution showed that the concentration of MB dye were further decreased with the additional amounts of aquifer material in the suspension from 0.2 to 2.5 g in 100 ml. The reason for such behavior is attributed to the larger number of binding sites on the adsorbent available to the dye. According to the data of this work, at initial MB concentration of 2 mg/L, the maximum amount of MB removal is more than 90% is achieved when using 1.5 g of aquifer material (Fig. 6).

3.4. Adsorption isotherms

The equilibrium adsorption data were generally interpreted using Langmuir and Freundlich models which are represented by the following (4), (5) respectively:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad (4)$$

$$q_e = k_f C_e^{\frac{1}{n}} \qquad (5)$$

Where q_m (mg/g) and b (L/mg) are Langmuir isotherm coefficients (Fig. 7). The value of q_m represents the maximum adsorption capacity. K_f (mg/g) and n are Freundlich constants (Fig.8). Two adsorption isotherms were constructed by plotting the Ce/q versus C_e, log q versus log C_e, respectively.

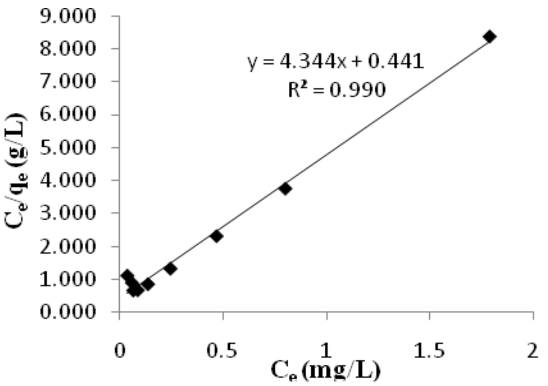


Fig. 7 Langmuir Isotherm for methylene blue

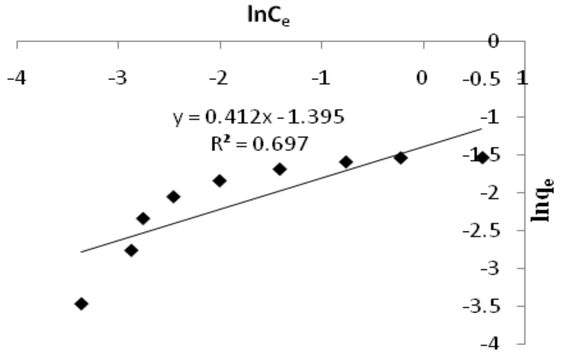


Fig. 8 Frendulich isotherm for methylene blue

Table 1 Parameters of kinetic models for the adsorption of methylene blue onto aquifer material

$q_e$exp(mg/g)	0.127
Lagergren-first-order	
q_e cal (mg/g)	5.65
k_1 (1/min)	0.026
R^2	0.963
Pseudo-second-order	
q_e cal (mg/g)	0.128
k_2 (g/mg min)	10.84
R^2	0.999

The adsorption equilibrium data were analyzed by the isotherm equations mentioned above, and corresponding parameters calculated were tabulated in Table 2. The values of R^2 obtained from Langmuir isotherm equation were higher than those from Freundlich isotherm equations. Furthermore, the values of experimental adsorption capacity (q_e) were close to those of theoretical adsorption capacity (q_m) calculated from Langmuir isotherm equation. This information suggested Langmuir isotherm model could well describe the adsorption equilibrium process, indicating monolayer coverage of MB on the composite adsorbents.

Table 2 Isotherm constants for methylene blue adsorption onto aquifer material

Isotherm models					
Langmuir isotherm			**Freundlich isotherm**		
q	**K_L**	**R^2**	**K_F**	**l/n**	**R^2**
0.232	9.85	0.99	0.247	0.412	0.697

4. CONCLUSIONS

From lab-scale results, RBF shows promise as a significant barrier for Dye transport. The removal of methylene blue dye from aquifer material was studied in batch-experiments. The batch-suspension tests showed that the MB uptake increases with increasing adsorbent concentration and that equilibrium was attained within 2 hours. The kinetics data followed the second order kinetics model indicating the chemisorptions nature of the process. Equilibrium data were fitted to Langmuir and Freundlich isotherms and the equilibrium data were best described by the Langmuir isotherm model. The maximum % removal of MB obtained was 97.2% at dye concentration of 2 mg/L using adsorbent dose with 1.5 g at pH 8.91 and temperature 25^0C.

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