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ADSORPTION BEHAVIOR OF METHYLENE BLUE ONTO GELLAN GUM BEADS FOR BIOREMEDIATION APPLICATION

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Abstract

Biopolymer Gellan Gum (GG) was modified into insoluble beads using ionotropic gelation method to study the adsorption behavior of cationic dye Methylene Blue (MB) from aqueous solution. The investigation incorporates initial dye concentrations (100-500 mg/L), contact time (15-45 minutes) and adsorbent dosage (25-100 mg) effects on adsorption process. It was observed that initial MB concentration of 500 ppm showed maximum adsorption after 15 minutes contact time at adsorbent dosage of 25 mg. Maximum adsorption capacity was found to be 576 mg/gm at room temperature. The experimental data's were analyzed by Langmuir, Freundlich and BET models of adsorption. The adsorption isotherm data for MB were fitted to Langmuir and Freundlich isotherm at room temperature with regression coefficient (R^2) value of 0.877 & 0.873 respectively. The results suggest that GG beads can be utilized as adsorbent for MB and could be used in dye removal bioremediation application.

Key words

Adsorption, methylene blue, gellan gum, beads, isotherms

INTRODUCTION

Dyes are widely used in industries like textile, paper, printing, leather, food and cosmetic. As a result, huge quantities of colored waste effluents are generated. These effluents are very difficult to treat as the dyes are recalcitrant organic molecules, resistant to aerobic digestion and stable to light **[1]**. Presence of very low concentration dyes is highly visible and causes enormous harm to the environment and marine life **[2, 3]**. Methylene blue is a hazardous chemical and may cause eye burn leading to permanent eye injury. Its inhalation gives short period of rapid or difficult breathing and also causes nausea, vomiting, profuse sweating, mental confusion and methemo globinemia **[4]**. Various techniques like ion exchange, activated carbon adsorption, membrane technology and coagulation, etc. **[5]** have been studied extensively to treat these effluents. Activated carbon has been found to be efficient adsorbent for dye removal, but its use is limited due to higher operation cost. Moreover, this adsorbent is difficult to regenerate and separate from wastewater after its use **[6]**. Hence, the authors made an attempt to prepare calcium chloride cross-linked GG beads and to study the adsorption behavior of methylene blue (MB) onto it.

Nilimanka et.al / UJPSR / 2 (1), 2016, 9-12
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MATERIALS AND METHODS

Materials

Gellan gum was procured from Sigma, USA. Methylene blue supplied by Qualigens, Mumbai, India. Calcium chloride dihydrate was procured from Merck, India. Double distilled water is prepared in our laboratory and used for the study. All other chemicals and reagents used are of analytical grade.

Preparation of GG Adsorbent Beads

1% w/v GG was dispersed in double distilled water with continuous stirring. The stirring was continued for 30 minutes using a magnetic stirrer. Then 10 ml of the dispersion was added drop wise in 20 ml of 0.5M calcium chloride dihydrate solution with constant stirring at 100 rpm using magnetic stirrer. Immediately GG insoluble beads were produced. The beads were hardened for 15 minutes in calcium chloride solution. Then the beads were washed with distilled water to remove the unreacted calcium chloride present on the surface of the beads. These beads were used as adsorbent.

Preparation of Adsorbate Solution

Stock solution was prepared by dissolving 500 mg of MB in 100 ml distilled water. This stock solution was used for further investigation. The maximum wavelength for MB is 480 nm using colorimeter.

BATCH ADSORPTION STUDIES

Batch adsorption studies were carried out by adding 0.05 g of adsorbent into five 250 ml conical flask containing 100 ml aqueous solution of different initial MB concentration (100-500 mg/L) without changing pH and temperature. The flask content was agitated at 100 rpm for 45 min for the batch adsorption study. The samples were analyzed first after 15 minutes, followed by 30 min and 45 min for estimation of final dye concentration in the solution using colorimeter at 480 nm. The quantity of dye adsorbed can be calculated using the following equation:

Amount of dye adsorbed at equilibrium, $q_e = (C_0 - C_e)V/W$

Where, C_0 and C_e (mg/L) are initial and equilibrium dye concentration in liquid phase respectively. V (L) is the volume of the solution and W (gm) is the mass of beads used.

RESULTS AND DISCUSSION

Effect of Initial Dye Concentration

Different initial concentrations (100-500 mg/L) of MB were considered to study its adsorption behavior onto GG beads and represented in figure 1. The study was conducted at room temperature for 15 minutes without changing the pH of dye solution. The amount of dye adsorbed was found to be depended on initial MB dye concentration and maximum 424 mg/gm adsorbed when the dye concentration was 500 mg/L. From the figure it is evident that the adsorption efficiency of GG beads increases by increasing the MB concentration. This indicates that MB concentration is the driving force to overcome mass transfer resistance for dye between solution and the surface of GG adsorbent beads. It also indicates that saturation of adsorption sites took place at higher dye concentration accompanied by possible monolayer formation **[7]**.

Effect of Adsorbent Dosage

To evaluate the adsorption capacity of GG beads, different amount of beads i.e. 0.025, 0.05, 0.075 & 0.1 gm were under the investigation purview. An adsorption of 576 mg/gm was observed when 0.025 gm of GG beads was studied in dye solution of 400 mg/L for 15 minutes (Figure 2).

Effect of Contact Time

The effect of contact time on the sorption of MB was investigated over time intervals of 15 to 45 minutes. Figure 3 shows the adsorption yield as a function of contact time. It is evident from the figure that maximum adsorption of 200 mg/gm was reached in 15 minutes and dropped to 192 mg/gm after 30 minutes and again 96 mg/gm after 45 minutes. Therefore, 15 minutes experiments were deemed fit to establish subsequent measurements.

ADSORPTION ISOTHERMS

Adsorption isotherms are important tool to understand the type of adsorption systems. Though several isotherms are available, but three important isotherms namely Langmuir, Freundlich and BET were studied.

The Langmuir isotherm

Langmuir isotherm refers to homogeneous adsorption, which adsorption can only occur at a fixed number of definite localized sites, with no transmigration of the adsorbate in the plane of the surface. The Langmuir model can be given as:

$$C_e/q_e = 1/q_{max} K_L + 1/q_{max} C_e$$

Nilimanka et.al / UJPSR / 2 (1), 2016, 9-12
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where qe is the amount of adsorbate in the adsorbent at equilibrium (mg/gm), Ce is the equilibrium concentration (mg/L), and qmax (mg/gm) and KL are the Langmuir isotherm constants related to free energy. The above equation can be linearized to get the maximum capacity, qmax by plotting a graph of Ce/qe vs. Ce.

This isotherm is used for the description of monomolecular adsorption with interaction between adsorbed molecules. The model applies to adsorption onto homogeneous surfaces with a uniform energy distribution and irreversible adsorption (Figure 4).

The Freundlich isotherm

The Freundlich equilibrium isotherm is used to describe the multilayer adsorption with interaction between adsorbed molecules. The model applies to adsorption onto heterogeneous surfaces with a uniform energy distribution and reversible adsorption. The linear form of the Freundlich isotherm is given below (Figure 5):

$$\log qe = \log KF + 1/n \log Ce$$

where KF and 1/n are Freundlich isotherm constant (mg/gm) (dm3/gm)n related to adsorption capacity. A plot of log qe vs log Ce yields a straight line, with a slope of 1/n and intercept of ln KF.

The BET isotherm

The Brunauer, Emmett and Teller (BET) isotherm is used to describe the multilayer adsorption where some are adsorbed on already adsorbed molecules and the Langmuir isotherm is not valid (figure 6). BET isotherm lights on the morphology of the adsorbent like smooth or rough surface and porosity of the adsorbent material. The BET plot can be obtained as follows:

Ce/Cs vs Ce/qe (Cs-Co)

Where, Ce is the equilibrium concentration (mg/L), Cs is the saturation concentration (mg/L), qe is the amount of adsorbate in the adsorbent at equilibrium (mg/gm), Co is the initial concentration (mg/L).

The Langmuir, Freundlich and BET isotherms regression coefficients (R^2) for MB adsorption are 0.877, 0.873 and 0.650 respectively. This data seems to be fit better into Langmuir isotherm than the two other. This indicates that the adsorption of MB on GG beads is chemisorptions and irreversible homogeneous in nature.

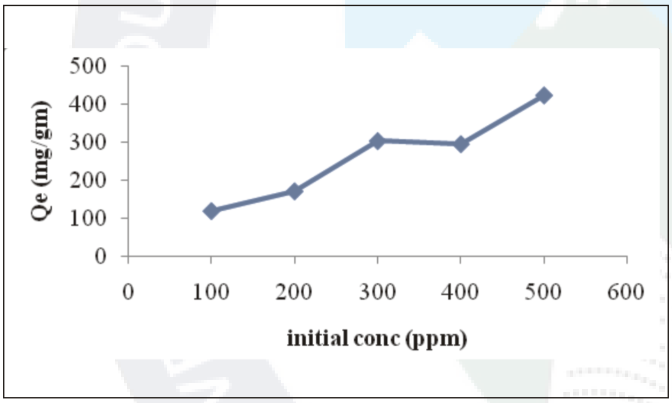

Fig.1: Effect of initial MB Concentration on Adsorption

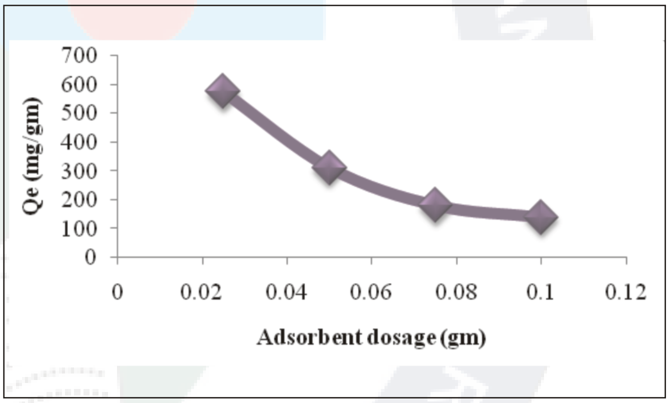

Fig.2: Effect of Adsorbent Dosage on Adsorption

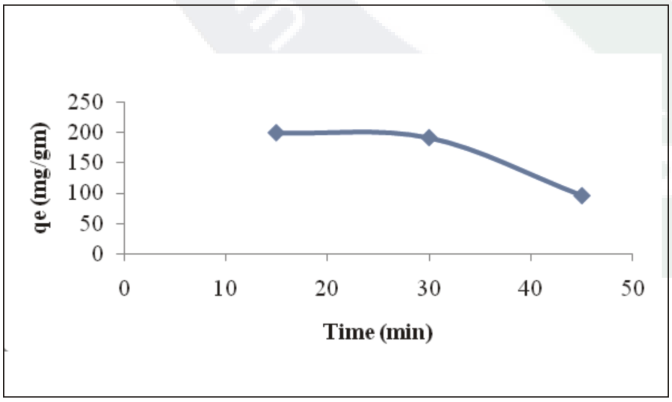

Fig.3: Effect of Time (min) on Adsorption

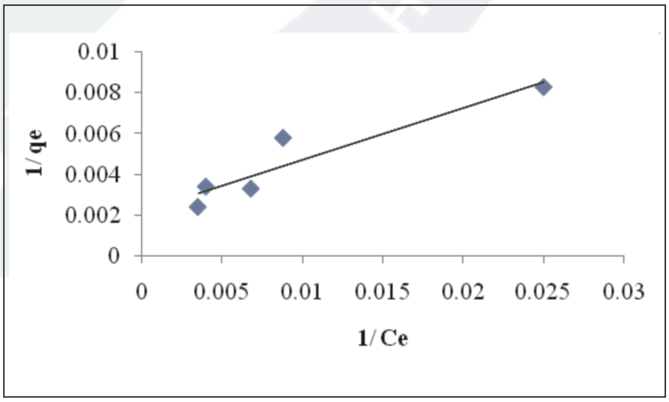

Fig.4: Langmuir plot

Nilimanka et.al / UJPSR / 2 (1), 2016, 9-12
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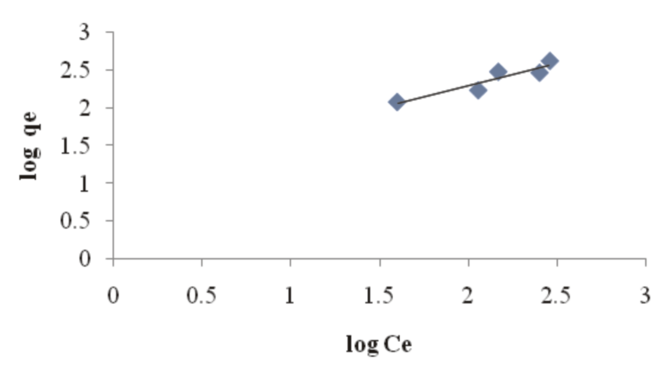

Fig.5: Freundlich plot

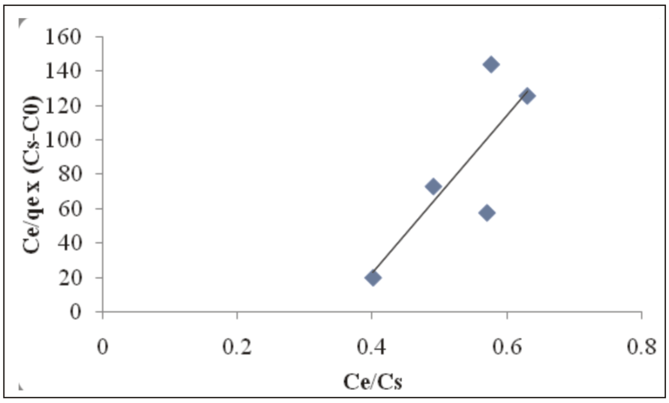

Fig.6: BET plot

CONCLUSION

The present study indicates that GG beads are effective adsorbent for the removal of MB from aqueous solutions. The maximum adsorption of MB was found to be 576 mg/gm when the adsorbent dosage was 25 mg. The Adsorbate quickly formed a monolayer on GG smooth beads in 15 minutes. Though both correlation coefficients (R2) of Langmuir and Freundlich posses sufficiently high value, but yet the batch adsorption data fits better in Langmuir model. Low-cost, easily fabricable beads and high dye uptake makes the GG beads very promising adsorbent for the removal of toxic dye like MB from industrial effluent and could be used successfully in bioremediation application.

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