World Journal of Pharmaceutical Sciences
ISSN (Print): 2321-3310; ISSN (Online): 2321-3086
Published by Atom and Cell Publishers
Available online at: http://www.wjpsonline.org/
Original Article

Adsorption behavior of methylene blue onto gellan gum-bentonite composite beads for bioremediation application

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Received: 02-12-2015 / Revised: 24-12-2015 / Accepted: 27-12-2015 / Published: 01-01-2016

ABSTRACT

Biopolymer Gellan Gum (GG) was made into insoluble composite bead using Bentonite (BT), a clay material. This insoluble composite formation was carried out using ionotropic gelation method where calcium chloride was a cross-linker to hold the organic polymer GG and inorganic material BT together. The composite (GG-BT) beads thus formed were used 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 mg/L showed maximum adsorption after 30 minutes contact time at adsorbent dosage of 25 mg. Maximum adsorption capacity was found to be 1140 mg/gm at room temperature. The experimental data's were analyzed by Langmuir, Freundlich and BET models of adsorption isotherms. The adsorption data for MB, best fits to Langmuir isotherm at room temperature with coefficient of correlation (R^2) value of 0.961. The results suggest that GG-BT beads provide a homogeneous surface for chemisorption of MB and irreversible in nature. Hence conclusion may be made that GG-BT composite can be utilized as adsorbent for MB and could be used in dye removal bioremediation application.

Key Words: Adsorption; Methylene blue; Gellan gum, Bentonite, Composite beads, Isotherms

INTRODUCTON

Dyes are very popularly used in textile, paper, printing, leather, food and cosmetic industries to color their product. That is why these industries generate huge quanta of colored waste effluents. These effluents are very difficult to treat as the dyes are recalcitrant organic molecules, resistant to aerobic digestion and stable to light [1]. The presence of dyes even in lower concentration is highly visible and causes enormous harm to the environment and toxic to marine life [2, 3]. Methylene blue is a hazardous chemical and used in dying cotton, wood and silk. It may cause eye burn leading to permanent eye injury. Its inhalation gives rise to short period of rapid or difficult breathing, nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [4]. Various techniques like ion exchange, activated carbon adsorption, membrane technology and coagulation, etc. [5] have been studied to treat these colored effluents. Though activated carbon has been found to be efficient as adsorbent for dye removal, its use is limited due to higher operation cost. Moreover, this adsorbent is difficult to regenerate and separate from wastewater after its use [6]. Composite biomaterials are known for their stronger yet light architectures imparting multifaceted functionalities. This has ignited our work to develop easily fabricable composite biomaterial as adsorbent for such bioremediation application. In this study attempt has been made to prepare calcium chloride cross-linked GG-BT composite beads and to study the adsorption behavior of methylene blue (MB) onto it.

MATERIALS AND METHODS

Materials: Gellan gum was procured from Sigma, USA. Methylene blue supplied by Qualigens, Mumbai, India. Bentonite was procured from Merck, India and used without further purification. 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.

Methods

Preparation of GG-BT Composite Adsorbent Beads: GG and BT were dispersed in 1:1 ratio in

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double distilled water with continuous stirring. The stirring was continued for 30 minutes using a magnetic stirrer. Then 10 ml of this 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-BT insoluble composite beads were produced. The beads were hardened for 15 minutes in calcium chloride solution. The beads are then washed with distilled water to remove the excess 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 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: To study the adsorption behavior, different initial concentrations (100-500 mg/L) of MB onto GG-BT beads were undertaken and represented in **figure 1**. The study was conducted at room temperature for 15 minutes without changing the pH of the dye solution. The amount of dye adsorbed was found to be depended on initial MB dye concentration. This indicates that MB concentration is the driving force to overcome mass transfer resistance for dye between solution and surface of GG-BT adsorbent beads [7]. MB being a positively charged dye, strongly attracted to GG-BT composite beads due to the dissociation of carboxyl groups of gellan gum and negatively charged bentonite and show strong electrostatic interactions to positively charged MB dye molecules [8].

Effect of Adsorbent Dosage: This study was conducted to evaluate the adsorption capacity of GG-BT beads. Different amount of beads i.e. 0.025, 0.05, 0.075 & 0.1 gm were under the investigation purview. It is interesting to note that lower the quantity of adsorbents more the dye adsorption. The study reveals 0.025 gm of GG-BT beads to adsorb 1140 mg/gm of MB from dye solution (400 mg/L) in 15 minutes (**figure 2**). This huge quantum of adsorption may be attributed to the strong electrostatic attraction between negatively charged composite beads and the oppositely charged MB dye [8] and also due to lesser availability of surfaces for adsorption.

Effect of Contact Time: The effect of contact time on MB sorption 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 adsorption of 432 mg/gm was reached in 15 minutes and then raised to 444 mg/gm in 30 minutes to give homogeneous adsorption at fixed number of definite localized sites. Therefore, 30 minutes experiments were deemed fit to establish subsequent measurements.

ADSORPTION ISOTHERMS

Adsorption isotherms are important tool to understand the adsorption process. Though several isotherms are available to explain the adsorption, but we have considered three important isotherms namely Langmuir, Freundlich and BET.

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

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

where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/gm), C_e is the equilibrium concentration (mg/L), and q_{max} (mg/gm) and KL are the Langmuir isotherm constants related to free energy. The above equation can be linearized to get the maximum capacity, q_{max} by plotting a graph of C_e/q_e vs. C_e.

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)**:

$\log q_e = \log K_F + 1/n \log C_e$

where K_F and 1/n are Freundlich isotherm constant (mg/gm) $(dm^3/gm)^n$ related to adsorption capacity. A plot of log q_e vs log C_e yields a straight line, with a slope of 1/n and intercept of ln K_F.

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:

C_e/C_s vs $C_e/q_e (C_s-C_o)$

Where, C_e is the equilibrium concentration (mg/L), C_s is the saturation concentration (mg/L), q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/gm), C_o is the initial concentration (mg/L).

The Langmuir, Freundlich and BET isotherms regression coefficients (R^2) values for MB adsorption are 0.961, 0.801 and 0.303 respectively. This data seems to be fit better into Langmuir isotherm. This indicates that the adsorption of MB on GG-BT beads is chemisorptions and irreversible homogeneous in nature.

CONCLUSION

The present study concludes that GG-BT composite beads effectively adsorb MB from aqueous solutions. The highest adsorption value of 1140 mg/gm reached in 30 minutes. The data's obtained from batch adsorption study showed MB adsorption to corroborate well with Langmuir model. Hence conclusion may be made that this low-cost, easily fabricable GG-BT composite could be a promising adsorbent for the removal of such toxic dye from industrial effluent and could be used successfully in bioremediation application.

ACKNOWLEDGEMENT

The author's are gratefully acknowledging the support extended by Regional Institute of Pharmaceutical Science & Technology (RIPSAT), Agartala, Tripura, India to carry out this piece of work.

Fig: 1 Effect of initial MB Concentration on Adsorption

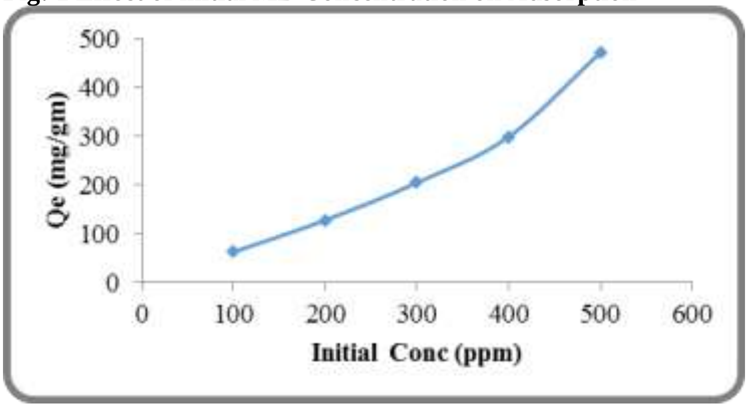


Fig: 2 Effect of Adsorbent Dosage on Adsorption

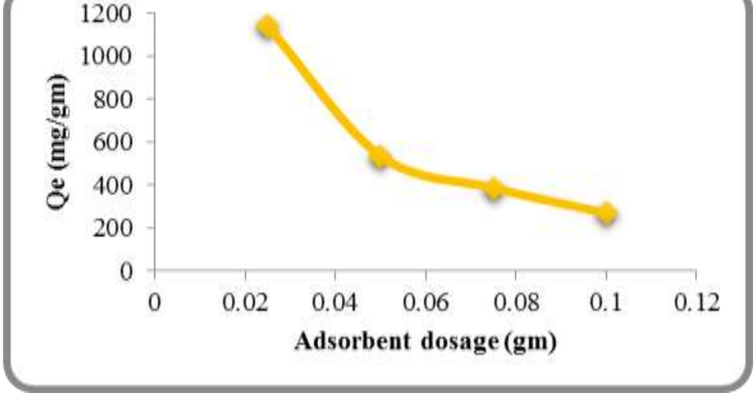


Fig: 3 Effect of Time (min) on Adsorption

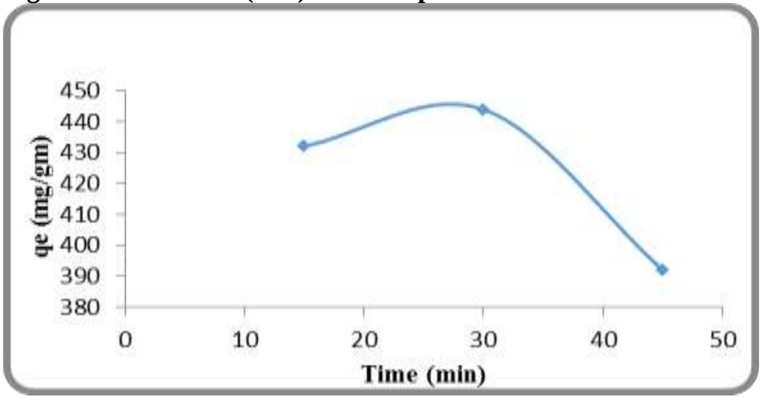


Fig: 4 Langmuir plot

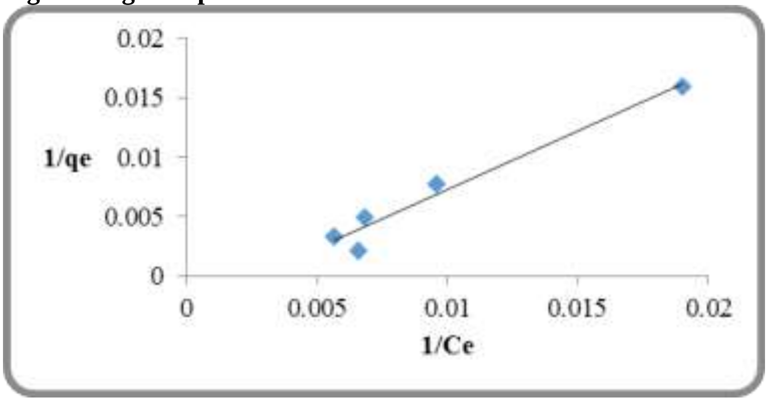


Fig: 5 Freundlich plot

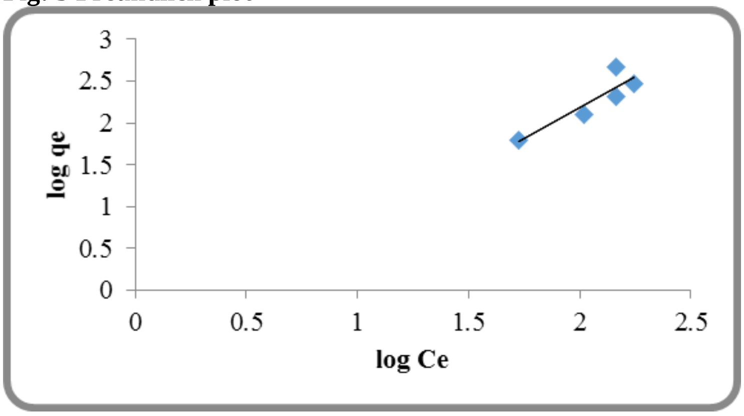
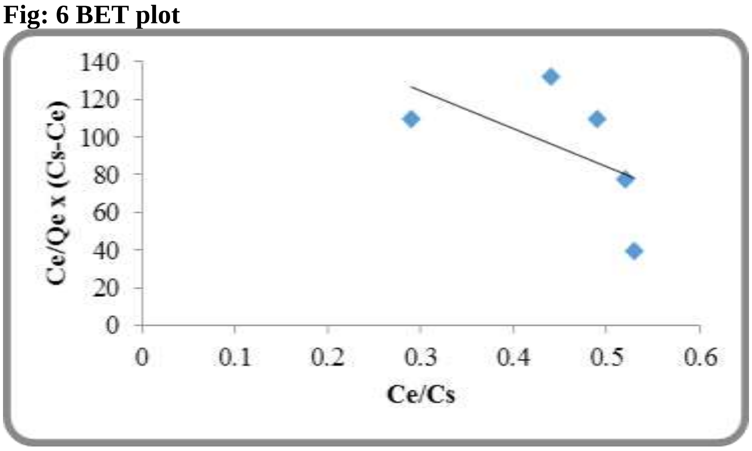


Fig: 6 BET plot



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