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Batch and Continuous (fixed bed column) Adsorption of Methylene Blue by Rubber Leaf Powder

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Abstract

Batch and fixed bed column experiments were conducted to investigate the potentiality of rubber leaf powder (RLP) as a low cost adsorbent for the removal of methylene blue (MB) from aqueous solution. Batch mode experiments were carried out by varying operational parameters such as adsorbent dosage, pH and temperature of solution. The adsorbent was characterized by Fourier Transform-Infrared Spectroscopy (FTIR). The extent of MB removal was found to increase with increasing pH and decreasing temperature. The equilibrium data were well fitted by Langmuir isothermal model with monolayer adsorption capacity of 111mg/g and the sorption kinetics was found to follow a pseudo-second-order kinetic model. From thermodynamic study the adsorption process was found to be spontaneous and exothermic in nature. In order to investigate the industrial applicability of RLP, fixed bed column studies were also carried out. The total adsorbed quantities, equilibrium uptakes, breakpoint time, and saturation time were determined at different bed height for RLP. The experimental results showed good agreement with the Thomas model. RLP appears as a promising low cost adsorbent for the removal of methylene blue from aqueous solution.

Keywords: Adsorption, rubber leaf powder (RLP), pH, Thermodynamics, Isotherms, column study.

1. Introduction

Dyes are widely used by textile industries to color their products. One of the major problems concerning textile wastewaters is colored effluent. Color is one of the characteristics of an effluent which is easily detected. Most of the dyes are stable to biological degradation. Color affects the nature of the water and inhibits sunlight penetration into the stream and reduces photosynthetic action. Some of dyes are carcinogenic and mutagenic [1].

Various physicochemical processes/methods are used for removal of dyes from aqueous wastes and among them the adsorption is one of the most effective one[2]. Activated carbon has been widely used as an adsorbent for the removal of various pollutants due to its high adsorption capacity [3]. However, it exhibits relatively high operation costs, regeneration trouble, and it is difficult to separate the treated activated carbon from the bulk solutions after use [4].This has prompted the use of various materials as adsorbents in order to develop cheaper alternatives by utilizing agricultural and other wastes.Over the last decade, numerous approach have been done to develop cheaper and effective adsorbents to remove dyes from a variety of starting materials such as modified sawdust [5], raw and modified pine cone [6], coffee residues [7], Pineapple leaf powder [8], Hazelnut Husks [9], Red Mud [10], Pine Cone [11], and Peanut Hull [12].

In the present work, rubber (Heveabrasiliensis) leaf powder has been used as an adsorbent to remove MB from aqueous solution. MB has been selected as a model dye. Rubber leaves are solid wastes largely generated from rubber plantations and left unutilized on the ?elds, causing a signi?cant disposal problem. Rubber leaf powder (RLP) has already been used for the removal of Cu (II) [13]andPb(II) [14]. To the best of our knowledge, no reference to work involving the use of RLP as an adsorbent for the removal of dye from aqueous solutions has been found in the literature.There is no evidence of column study with RLP which is very important to ascertain the practical applicability in industrial scale.

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The main objective of this study is to evaluate the potentiality of RLP for removal of MB in batch and dynamic flow states. Factors affecting adsorption process such as pH, initial MB concentration, temperature were studied in batch operation. Langmuir, Freundlich isotherm models and pseudo-first-order, Pseudo-second-order kinetic models were used to determine equilibrium and kinetic parameters describing MB adsorption on RLP. Thermodynamics of the MB adsorption on RLP was also studied. Fixed bed column studies were also performed to evaluate the practical applicability of the adsorbent.

2. Materials and Methods

2.1 Preparation of Adsorbent

Rubber leaves were collected from local area in Sylhet. The leaves were washed with tap water to remove dust and soluble impurities. Rubber leaves werethen dried in an oven at 105°C for about 16 h and subsequently ground and boiled the ground powder to remove coloring components. After boiling the powder was dried at 105°C for about 20 h, sieved and stored in glass bottle.

2.2 Characterization of adsorbent

Infrared spectrums of adsorbents were obtained with Fourier transform infrared (FTIR) spectroscopy (Model: FTIR 2000, Shimadzu, Kyoto, Japan) to investigate the surface functional groups of the adsorbent. The point of zero charge (pH_{PZC}) of the adsorbent in aqueous phase was analyzed by titration method. The titration was carried out with 0.1 M NaOH and 0.1 M HCl, respectively.

2.3 Adsorption studies

The batch adsorption experiments were conducted in 250 ml Erlenmeyer flask containing MB solution of varying concentration, pH and adsorbent dosages. Equilibrium isotherms were evaluated by shaking 0.2g of RLP in 200ml of MB solution with varying initial concentration (50, 75, 100, 150 and 200 mg/L) at three different temperatures (293K, 303K and 323 K) and at pH = 6.4. The influences of pH (3.55 to 10), adsorbent dosages (0.1g to .4g) were investigated at room temperature (30±2^{0}C) by shaking a fixed amount of RLP with 200ml of 100 mg/L MB solution for 5 hours. At the end of each adsorption test, sample was centrifuged and the concentration of residual MB in the supernatant solution was analyzed using a UV/VIS spectrophotometer (Shimadzu Model UV-1601) by monitoring the absorbance at a maximum wavelength (λ_{max}) of 664 nm.

Fixed bed adsorption experiments were conducted in a plastic cylindrical column with internal diameter of 3.2 cm and length of 50 cm. At the bottom of the column, a stainless sieve was attached followed by cotton wool. A 1 cm thick layer of cotton was placed at the column base and another one above the adsorbent as a support to hold the adsorbent in the column. A regulating valve at the bottom of the reservoir and another valve at the outlet of the diaphragm pump ware used to control the flow rate of the effluent. Samples were collected from the exit of the column at different time intervals and were analyzed as before.

The amount of adsorption at equilibrium, q_e (mg/g), was calculated by using the following equation

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where C_o and C_e (mg/L) are the liquid-phase concentrations of dye at initial and at equilibrium respectively. V is the volume of the solution (L) and *W* is the mass of dry adsorbent used (g).

The MB adsorbed at any time, q_t (mg/g), was calculated by the following expression,

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

Where C_t (mg/L) is the liquid-phase concentrations of dye at time *t*.

The percentage e removal of MB was given by the following equation,

$$\text{Removal (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (3)$$

3. Result and Discussion

3.1 Characterization of adsorbent

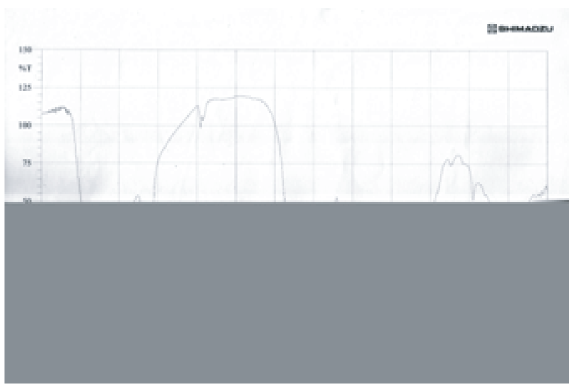

Fig.1: FTIR spectra of RLP (before adsorption)

The FTIR spectra of RLP adsorbent is shown in Fig 1. As shown Fig., the spectra displays a number of adsorption peaks, indicating the complex nature of the material examined. The broad and strong band ranging from 3200 to 3600 cm^{-1} correspond to the O-H stretching vibrations. The band observed at 1732 cm^{-1} and 1516 cm^{-1} were assigned to a carbonyl band (C=O) of unionized carboxylate stretching of carboxylic acid and $-NH_2$ group, respectively. Thus, the FTIR analysis indicated that the OH, COOH, NH_2 could be potential adsorption sites for interaction with the cationic methylene blue dye.

The point of zero charge (pH_{zpc}) of the adsorbent determined by titration method was found to be 6.00 ± 0.2.

3.2 Adsorption studies

3.2.1 Batch studies

Theeffects of initial concentration and contact time on the adsorption of MB onto RLP are shown in Fig.2. From Fig.2 it can be seen that the actual amount of methylene blue adsorbed per unit mass RLP increased with increase in methylene blue concentration.The Fig. 2 also showed that 80±5% of the total amount of dye uptake was found to occur in the first rapid phase (30 min) and thereafter the sorption rate was found to decrease. The higher sorption rate at the initial period (first 30 min) may be due to an increased number of vacant sites on the adsorbent available at the initial stage, which resulted in increased concentration gradients between adsorbate in solution and adsorbate on adsorbent surface.

The effect of pH on the adsorption of MB onto RLP is shown in Fig.3.From Fig.3 it can be seen that the amount of MB adsorbed increased with increasing pH.The adsorption of dye increased suddenly after pH of 4.5. The increased adsorption at higher pH can be explained with the help of pHpzc. The point of zero charge,pHpzcof rubber leaf is 6.0±0.2. At $pH<pH_{pzc}$, rubber leaf surface may get positively charged due to the adsorption of H+. Thus a force of repulsion occurs between the dye cations and the adsorbent surface resulting in low adsorption. The reverse situation occurs at $pH>pH_{Pzc}$. At pH $>pH_{Pzc}$, the rubber leaf surface may get negatively charged due to adsorption of OH^-, which increases the removal of positively charged dye cations through electrostatic forces of attraction. At higher pH, the functional groups such OH and COOH also deprotonated to yield negatively charged $-O^-$ and $-COO^-$ resulting higher adsorption capacity.

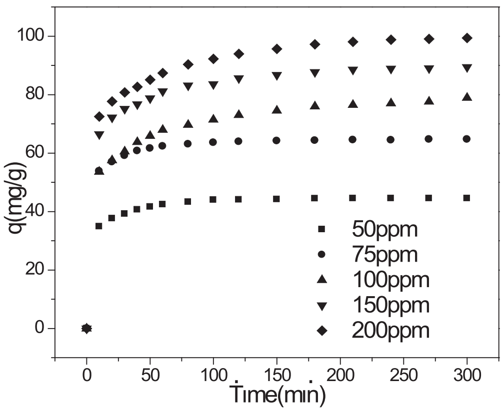

Fig.2: Effect of Contact time and initial concentration

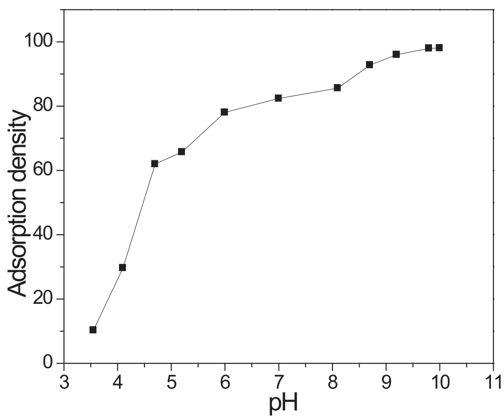

Fig.3: Effect of pH on the Adsorption density

The equilibrium adsorption isotherm is of importance in the design of adsorption systems [17]. In general, the adsorption isotherm describes how adsorbates interact with adsorbents. In this work, Langmuir and Freundlich models were used to describe the relationship between the amount of methylene blue adsorbed and its equilibrium concentration in solutions. Linear form of Langmuir equation, which is valid for monolayer sorption onto a surface, is given by equation (4) [18]

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_0 K_L} \cdot \frac{1}{C_e} \tag{4}$$

Where q_0 and K_1 are Langmuir parameters. Freundlich model is an empirical equation based on sorption on heterogeneous surface. The linearized form of the Freundlich equation can be expressed by the following equation:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{5}$$

Where K_f and n are the Freundlich constants.

The adsorption of MB onto RLP followed Langmuir isotherm model. The linear plot of $1/q_e$ against $1/C_e$ for MB adsorption onto MLP is shown in Fig. 4. From Fig. 4, it is obvious that experimental data fitted well in Langmuir isotherm model indicating monolayer adsorption on RLP with adsorption capacity of 111 mg/g.

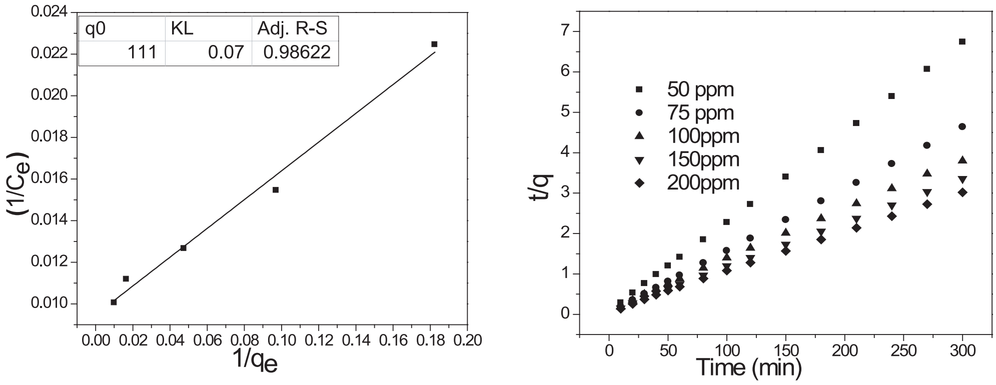

Fig. 4: Langmuir isotherm for methylene blue adsorption on to RLP.

3.2.3 Adsorption kinetics

The prediction of batch sorption kinetics is necessary for the design of industrial sorption columns. The nature of the sorption process will depend on physical or chemical characteristics of the adsorbent system and also on the system conditions. In the present study, the applicability of the pseudo-first-order and pseudo-second-order model has been tested for the sorption of methylene blue onto rubber leaf particles.

The linear form of pseudo-first-order equation is generally expressed as follows [15]:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (6)$$

The pseudo-second-order equation is expressed as follows [16]:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where q_e and q are the amounts of methylene blue adsorbed (mg/g) at equilibrium and at time t (min), respectively. k_1 and k_2 are the rate constant of pseudo-first-order and pseudo-second-order sorption (min^{-1}), respectively. In the present study, the adsorption of MB onto RLP followed pseudo-second-order kinetic model. Fig.5 shows the linearized form of the pseudo-second-order kinetic model. FromFig.5, it can be said that the pseudo-second-order kinetic model provided a good correlation for the adsorption of methylene blue onto rubber because of high correlation coefficientthan that of pseudo-first-order. Calculated value of adsorption density with pseudo-second-order kinetic model onto RLP also showed good agreement with experimental value.

3.2.4 Thermodynamic study

In engineering practice, thermodynamic study of an adsorption process is necessary to determine whether the process is spontaneous or not. For a spontaneous process the value of Gibb's free energy, ΔG must be negative. In this experiment the removal of methylene blue onto rubber leaf powder was studied at 293, 303, and 323K to determine the thermodynamic parameters such as ΔG, enthalpy change, ΔH and entropy change, ΔS for the characterization of temperature effect.The ΔH and ΔS were found to be -11.69KJ/mole and -26.49J/mole, respectively. The negative value of ΔH confirmed that the adsorption process was exothermic. The negative Values of ΔG, -4.0, -3.6, -3.2 KJ/mole at 293K, 303K and 323K, respectively, indicated that the adsorption of MB on RLP was spontaneous.

3.2.5 Column study

Effects of bed height on column performance were investigated in column study. Thomas model was used to predict column performance. Linear form of Thomas model are expressed by following equation

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{TH} q_e X}{Q} - \frac{k C_0 V_{eff}}{Q} \quad (8)$$

Where k_{TH} is the Thomas rate constant (ml/min mg), X the mass of adsorbent (g), and Q is the flow rate (ml/min). Fig.6 shows the breakthrough curve for three different bed heights. The breakthrough time, equilibrium adsorption capacity, Thomas model constants obtained from linearized from of Thomas model are shown in Table 1. From Table 1, it can be seen that breakthrough time and equilibrium uptake increased with increasing bed height. This is because as the bed height increases solute particles have more time to contact with adsorbent resulting in higher dye removal efficiency.Table 1.also indicated that Thomas model can be successfully used to predict the column performance.

Table-1.The measured and Thomas model parameters at different bed height.

Bed Height(cm)	Breakthrough time (min)	$q_{e,exp}$(mg/L)	$q_{e,cal}$(mg/L)	Thomas rate constant, K_{TH}	R^2
5	67	85	114.77	0.163	0.953
7.5	120	92.62	94.50	0.130	0.940
10	167	96	99.17	0.110	0.967

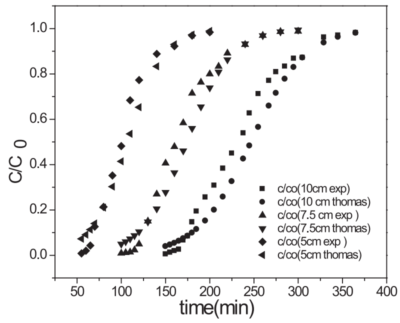

Fig.6: The measured and modeled breakthrough curves for MB biosorption onto rubber leaf at different bed height

4. Conclusion

The present study illustrated that RLP could be used as aprospective adsorbent for the removal of methylene blue from its aqueous solutions. Batch experiments described the dependency of adsorption process on pH and temperature. The adsorption process demonstrated good agreement with Langmuir isotherm indicating monolayer adsorption and from kinetic study it was revealed that the adsorption process followed pseudo-second-order kinetic model. Thermodynamic study showed that the adsorption process was exothermic and spontaneous. Fixed-bed adsorption depicted that column performance with RLP could be predicted by using Thomas model with high correlation coefficient. Attempts such as treating RLP with others chemicals can be done to make it more efficient.

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