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Continuous biosorption of Malachite Green by *Ananus comosus* (pineapple) leaf powder in a fixed bed reactor: experimental, breakthrough time and mathematical modeling

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ABSTRACT

A continuous biosorption study was carried out using pineapple leaf powder as biosorbent in a fixed packed bed column for the removal of malachite green (MG) from aqueous solution. The experimental data were fitted to three well-established adsorption models, namely, Adams-Bohart, Bed Depth Service Time and Thomas models. It was observed that the breakthrough time decreased with increasing flow rate and inlet dye concentration while it increased with increase in bed height. The Thomas model described the column biosorption behavior more efficiently than other adsorption model. The present findings suggest that biosorbent has potential capacity as an environment friendly and economical biosorbent for removal of MG.

Keywords: Biosorption; Pineapple leaf powder; Low cost adsorbent, malachite green, fixed-bed column, breakthrough time

1. Introduction

Contamination of water bodies by synthetic dye stuffs may be responsible for several damages to the environment and can have adverse effects on many forms of life [1,2]. Biosorption, using low-cost sorbent materials, has been widely suggested as an efficient and economically sustainable technology for the removal of synthetic dyes from industrial effluents [3]. Till date, hundreds of investigation on dye removal using natural materials or the waste/by-products of industries (which cost less) with varying levels of success has been reported [4–6]. However, most of the above-mentioned sorption studies are limited to batch processes using simple agitated closed vessel tests. Although the sorbent behavior obtained from the kinetic and equilibrium studies in batch conditions is useful for the design of a specific sorbate/sorbent system, this data may not be applicable to other, more realistic treatment configurations (e.g. fixed-bed columns) [7]. Therefore, studies on fixed-bed column are necessary for the design of continuous-flow biosorption processes, which allow a more efficient utilization of the sorbent and provide a better quality effluent.

In our previous study, we have demonstrated that pineapple leaf powder (PLP) can be used as an effective biosorbent for the removal of malachite green (MG) from aqueous solutions [8]. Due to its availability in abundance, PLP can be disposed off after use

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without need for expensive regeneration. The MG-loaded adsorbent can be dried and used as a fuel in boilers/incinerators, or can be used for the production of fire briquettes. The ash may be further used to make fire bricks, thus disposing of MG through chemical fixation. In order to ascertain the practical applicability of the biosorbent, for the treatment of real industrial wastewaters, the current study extends our previous study by considering the biosorption of MG by PLP in a fixed-bed column system. The effect of important design parameters, such as feed flow rate, inlet concentration of dye solution and column bed height, were investigated using a laboratory-scale fixed-bed column. Different kinetic models, namely Adams–Bohart model, BDST model, and Thomas model were used to analyze the column biosorption data.

2. Materials and methods

2.1. Biosorbent

Mature pineapple leaves were collected from the local countryside of Durgapur, West Bengal, India. The leaves were first thoroughly washed with tap water to remove dust, dirt and any unwanted particles. The leaves were then sun-dried and subsequently oven-dried at 363 ± 1 K for 24 h. The dried leaves were ground to fine powder using a grinder and sieved to a constant size (100–125 μm) and used as biosorbent without any pretreatment for MG biosorption. The characterization of the biosorbent has been reported previously [8].

2.2. Dye

MG used in this study was of commercial quality (CI 42,000, FW: 365, MF: $C_{23}H_{25}N_2Cl$, λ_{max}: 618 nm) and was used without further purification. Stock solution (1,000 mg L^{-1}) was prepared by dissolving accurately weighed quantity of the dye in double-distilled water. Experimental dye solution of different concentrations was prepared by diluting the stock solution with suitable volume of double-distilled water. The initial solution pH was adjusted using 0.1 (M) HCl and 0.1 (M) NaOH solutions.

2.3. Continuous fixed-bed biosorption studies

Continuous flow biosorption experiments were conducted in a fabricated glass column (3 cm internal diameter and 50 cm height). PLP was packed into the glass column to yield the bed height. A porous sheet was attached at the bottom of the column in order to support the adsorbent bed and to ensure uniform inlet flow and a good liquid distribution into the column. The top of the bed was covered by a layer glass beads (1 mm in diameter) in order to avoid the loss of adsorbent and also to ensure a closely packed arrangement. Dye solution of known concentration at pH 9.0 was pumped downward through the column by a peristaltic pump (Rivotek, India). A series of experiments were conducted with various feed flow rates (F = 10, 20, 30 mL min^{-1}), bed heights (Z = 5, 10, 15, and 20 cm) and influent dye concentrations (C_0 = 50, 100, 150, 200 mg L^{-1}). All the experiments were carried out at 303 ± 1 K. Samples were collected at regular intervals and the concentration of MG in the effluent was analyzed using UV/VIS spectrophotometer (Perkin Elmer, USA) by monitoring the absorbance changes at a wavelength of maximum absorbance at 618 nm. Operation of the column was stopped when the effluent MG concentration exceeded a value of 99.5% of its initial concentration.

The time for breakthrough appearance and shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of a sorption column. Therefore, breakthrough curves, i.e. C_t/C_0 vs. time were plotted, where C_t is the solute concentration in the liquid phase (mg L^{-1}) and C_0 is the inlet dye concentration in the solution (mg L^{-1}). The breakthrough time (t_b, the time at which dye concentration in the effluent/influent reached 0.1) was used to evaluate the breakthrough curves.

Data presented in this paper are the average values from two replicates, and the standard deviation was within 2%. Microsoft Excel and Origin 6.0 software was employed for data processing for linear regression analysis and nonlinear regression analysis.

2.4. Modeling of column data

In recent years, various mathematical models are used to describe fixed-bed column biosorption data. In the present study, the Adams–Bohart model [9], Bed Depth Service Time (BDST) model [10] and the Thomas model [11] were used to describe the fixed-bed biosorption dynamics of MG.

$$\text{Adams–Bohart}: \left(\frac{C_t}{C_0}\right) = \exp\left[(k_{AB}C_0\, t - k_{AB}N_0\left(\frac{Z}{v}\right)\right] \tag{1}$$

$$\text{BDST}: t = \left(\frac{N\,Z}{C_0\,F}\right) - \left(\frac{1}{C_0 k}\right)\ln\left[\frac{C_0}{C_t} - 1\right] \quad (2)$$

$$\text{Thomas}: \left[\left(\frac{C_0}{C_t}\right)\right] = 1 + \exp\left[\left(\frac{k_{\text{Th}} q_0 m}{F}\right) - \left(\frac{k_{\text{Th}} C_0 V_{\text{eff}}}{F}\right)\right] \quad (3)$$

where k_{AB} is the kinetic constant (L mg^{-1} min^{-1}), N_0 is the saturation concentration (mg L^{-1}), F is the flow rate (ml min^{-1}), v is the linear flow rate (cm min^{-1}) calculated by flow rate/column section area, Z is the bed height in the column (cm), k is the sorption rate constant (L mg^{-1} min^{-1}), k_{Th} is the Thomas rate constant (mL mg^{-1} min^{-1}), q_0 is the equilibrium adsorbate uptake (mg g^{-1}), N is the adsorption capacity per unit bed volume and m is the mass of the adsorbent in the column (g).

3. Results and discussion

3.1. Effect of flow rate

For evaluation of performance of a continuous column, flow rate is an important parameter mainly for treatment of wastewater of industrial scale [12]. Effect of flow rate on biosorption of MG by PLP was investigated by varying the flow rate from 10 to 30 mL min^{-1} at constant initial dye concentration (50 mg L^{-1}) and bed height (5 cm) constant. The effect of flow rate on breakthrough performance at the above operating conditions is shown in Fig. 1. It was observed that the biosorption efficiency was higher at lower flow rate while it decreased with increasing flow rate. The reason may be that as the flow rate was very low, the residence time of the dye solution on the biosorbent was higher, and hence, the dye molecule may get higher time to adsorb or to diffuse on the available binding sites around or inside the biosorbent [13]. As the flow rate increased, contact time of the dye with the biosorbent was very short, and as a result, the dye molecule may not able enough time to capture the binding sites on the biosorbent surface or diffuse into the pores of the biosorbent, the solution leaving the column before equilibrium occured [14]. A similar trend was also reported by Uddin et al. for biosorption of Methylene Blue, a cationic dye, by jackfruit leaf powder in a fixed-bed column system [7].

3.2. Effect of bed height

The biosorption of dye in a fixed packed bed column may influenced by the amount of biosorbent used. In this study, in order to the study of bed height, dye solution of initial MG concentration of 50 mg L^{-1} at pH 9 was passed through the biosorption column at a fixed flow rate of 10 mL min^{-1} at different bed height. Fig. 2 presents the performance of breakthrough curves at bed heights of 5, 10, 15, and 20 cm. As depicted by Fig. 2, the breakthrough time increased from 100 to 600 min with increased in bed height from 5 to 20 cm. At low bed heights, the axial dispersion phenomena predominate and reduced the diffusion of dye ions. The dye ions may not have enough time to diffuse into the whole of the biosorbent mass, resulting in earlier breakthrough [15]. With increase in bed height, the residence time of the dye solution in the column increased, allowing the dye ions to diffuse deeper inside the biosorbent. The increased in breakthrough time with increased in bed height also

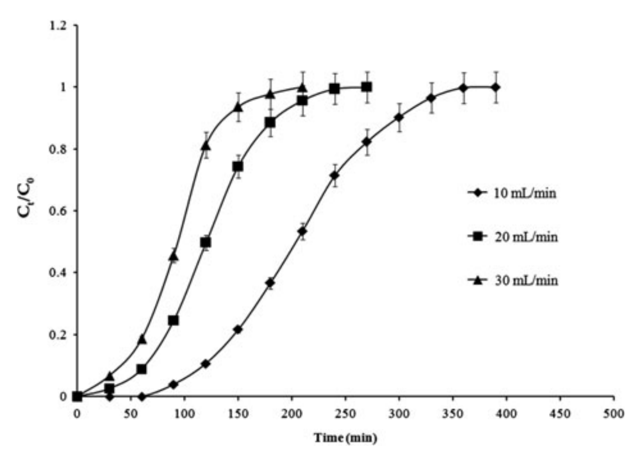

Fig. 1. Breakthrough curves for biosorption of MG by PLP at different feed flow rate (m = 8 g; Z = 5 cm; C_0 = 50 mg L^{-1}; pH 9.0; Temp. = 303 K).

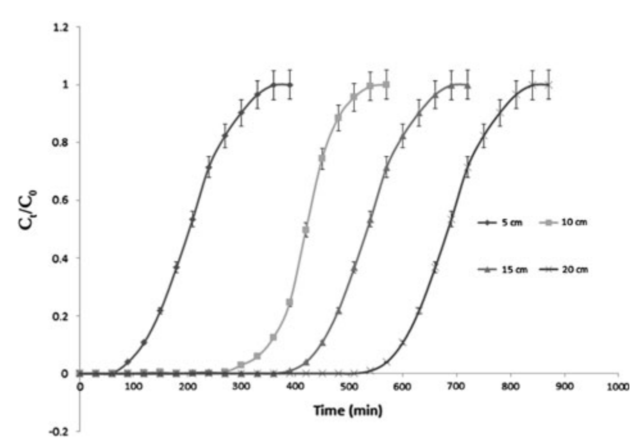

Fig. 2. Breakthrough curves for biosorption of MG by PLP at different bed heights (F = 10 mL min^{-1}; C_0 = 50 mg L^{-1}; pH 9.0; Temp. = 303 K).

been reported during column biosorption studies by many researchers [10,12–14]. The dye removal efficiency also increased with increasing bed height which may be due to increased availability of binding sites for the biosorption process.

3.3. Effect of influent dye concentration

Experiments were carried out by varying the inlet dye concentration between 50 to 200 mg L^{-1} while other parameters like pH, bed height, and flow rate were kept constant at 9.0, 5 cm and 10 mL min^{-1}, respectively. Fig. 3 presents the performance of the breakthrough curves at dye concentrations of 50, 100, 150 and 200 mg L^{-1}. The breakthrough time decreased with increasing influent MG concentration as the binding sites became more quickly saturated [7]. The larger the influent concentration, smaller was the breakthrough time. Breakthrough occurred after 90 min at 100 mg L^{-1} influent MG concentration while breakthrough appeared after 25 min at 200 mg L^{-1} influent MG concentration. These results demonstrated that the changing of concentration gradient affects the saturation rate and breakthrough time. Similar finding is reported by other researchers [16,17].

3.4. Application of Adams–Bohart model

The Adams–Bohart model was applied to the experimental data of column studies. The values of k_{AB} and N_0 were determined using nonlinear regression analysis of C_t/C_0 versus t at different flow rates, bed heights, and initial dye concentrations. The estimated values of k_{AB} and N_0 and along with the correlation coefficient values are presented in Table 1. From Table 1, it can be observed that as the inlet dye concentration increased, the maximum saturation concentration of dye increased by the bed as more dye molecule were available in this case. However, the mass transfer coefficient decreased as the inlet dye concentration increased, in the range of concentrations studied [10]. Furthermore, it is seen that mass transfer coefficient increased with increase in flow rate. This implies that the overall system kinetics may be dominated by external mass transfer. However, as can be seen from Table 1, the low R^2 (<0.90) values for the Adams–Bohart model indicate that this model was not appropriate for describing the column biosorption data of MG.

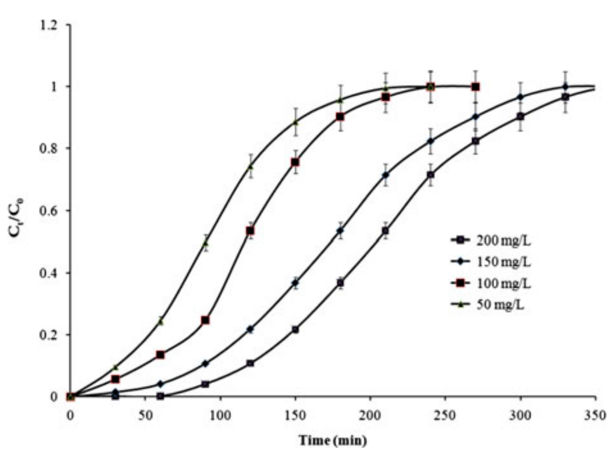

Fig. 3. Breakthrough curves for biosorption of MG by PLP at different initial dye concentration (m = 8 g; Z = 5 cm; F = 10 mL min^{-1}; pH 9.0; Temp. = 303 K).

3.5. Application of BDST model

Experimental data obtained from the column biosorption studies were further fitted to the BDST model. The values of k and N as estimated from the graph between t versus Z at values of C_t/C_0 at 0.2, 0.5, and 0.7 and from intercept and slopes, kinetic constant, and N values are calculated and listed in Table 2. Kinetic rate constant will characterize the rate of solute transfer from the liquid phase to adsorbent phase and N is the adsorption capacity per unit bed volume. From Table 2, the BDST model showed satisfactory fit to the experimental biosorption data as R^2 value are high in all the cases. Furthermore, it was observed from Table 2, that with increasing C_t/C_0, N, and k value increased. Similar observation is also found in other study [10,18].

3.6. Application of Thomas model

The experimental data were further fitted to the Thomas model to determine the rate constant (k_{Th}) and bed capacity (q_0). The constants, k_{Th} and q_0, were evaluated using the slope and intercept of the plot between C_t/C_0 versus t at different operational parameters, such as flow rate, bed height, and inlet adsorbate concentration. The calculated values of k_{Th} and q_0 along with regression coefficients are presented in Table 3. The relatively high R^2 (>0.97) values at all the operating conditions suggests that the Thomas model was the most appropriate model for describing the column biosorption data of MG on PLP. From Table 3, the bed capacity (q_0) decreased, while the Thomas rate constant (k_{Th}) increased with increase in feed flow rate. On the other hand, the bed capacity (q_0) increased and the Thomas rate constant (k_{Th}) decreased with increased in initial dye concentration.

Table 1
Adams-Bohart model parameters at different experimental conditions

F (mL min^{-1})	C_0 (mg L^{-1})	Z (cm)	k_{AB} (L mg^{-1} min^{-1})	N_0 (mg L^{-1})	R^2
10	50	5	0.3175	7,618	0.882
20	50	5	0.3893	8,139	0.891
30	50	5	0.4461	8,917	0.876
10	50	10	0.1289	6,513	0.899
10	50	15	0.0872	5,145	0.865
10	50	20	0.0278	4,620	0.872
10	100	5	0.2367	9,108	0.874
10	150	5	0.1629	10,374	0.891
10	200	5	0.0172	11,451	0.886

Table 2
BDST model parameters at different experimental conditions

F (mL min^{-1})	C_0 (mg L^{-1})	C_t/C_0	k (mL mg^{-1} min^{-1})	N (mg L^{-1})	R^2
10	50	0.2	0.855	3,060	0.965
10	50	0.5	0.322	3,120	0.986
10	50	0.9	0.296	3,180	0.998

Table 3
Thomas model parameters at different experimental conditions

F (mL min^{-1})	C_0 (mg L^{-1})	Z (cm)	k_{Th} (mL mg^{-1} min^{-1})	q_0 (mg g^{-1})	R^2
10	50	5	0.2421	74.715	0.978
20	50	5	0.3163	66.874	0.982
30	50	5	0.3917	60.498	0.984
10	50	10	0.5138	77.281	0.980
10	50	15	0.5885	80.167	0.979
10	50	20	0.6569	82.469	0.983
10	100	5	0.1524	81.368	0.980
10	150	5	0.1033	83.795	0.981
10	200	5	0.0856	85.187	0.985

However, both q_0 and k_{Th} increased with increase in bed height. Similar observation was found by the other researcher [10].

4. Conclusion

Biosorption potential of PLP for the removal of MG from aqueous solutions was investigated in a laboratory-scale fabricated fixed packed-bed column. The effect of different operational parameters, such as feed flow rate, influent MG concentration and bed height on the biosorptive removal of MG was studied. The breakthrough time decreased with increased in flow rate and initial MG concentration was observed in the reactor, and on the other hand, it was observed that the breakthrough time increased with increasing bed height. The Thomas mathematical model showed good agreement with the experimental results at all the process parameters studied. The most popular commercial sorbent of the present time for the removal of basic and reactive dyes is activated charcoal. Compared to activated charcoal, PLP is quite a cheap material. Thus, the use of PLP as a biosorbent is a thoughtful and economic attempt for its valuable, necessitous and needy utilization for the removal of MG from dye-bearing effluents.

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