

Transport of Methylene Blue Through An Organic Porous Coco Peat Medium Column

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Abstract— Industries such as textile and paper that use dyes to color their final product discharge substantial volumes of highly colored water into natural water bodies. Understanding the mechanisms of dye removal from wastewater before discharge to surface waters is important since dyes may disrupt biological processes in the water environment. In this study, the feasibility of using coco peat in removal of methylene blue is demonstrated. A mathematical model describing the chemical transport and removal of Methylene Blue (MB) onto a highly organic biosorbent coco peat was solved in MATLAB using a semi-discrete finite difference with fourth order upwind differentiation. The needed parameters on adsorption of MB onto a biosorbent coco peat were obtained using batch experiment. The batch experiment indicated coco peat is a very good adsorbent of MB with a removal efficiency of 99.61%. It was also shown that the adsorption at equilibrium obeys the Langmuir isotherm with parameters such as maximum adsorption capacity, q_m , and the Langmuir coefficient, K_L determined for all the temperatures investigated. A column experiment was carried out to obtain effluent breakthrough curves used for calibrating the mathematical model. A linear driving force coupled with solid diffusion model was applied successfully to the experimental data to determine the three major transport parameters, axial dispersion coefficient, D_L , external mass transfer coefficient, k_f , and solid diffusivity, D_s . The model was tested and fitted well on one experimental case with $D_L = 1.1304E-05 \text{ m}^2 \text{ s}^{-1}$, $k_f = 3.6399E-04 \text{ m s}^{-1}$, $D_s = 3.34871E-08 \text{ m}^2 \text{ s}^{-1}$ (RMSE = 0.0009). The results also show that the breakthrough curves are dependent on D_L and external k_f , but not on D_s .

Keywords— *Methylene Blue removal, Coco Peat absorbent, Modeling Break-through curves*

1. INTRODUCTION

Most industries such as textile, paper, and printing that use dyes to color their final product produce substantial volumes of waste water. The highly colored effluent that is discharged into a water body causes the impedence of the penetration of light resulting into the disruption of biological processes within the stream. Some dye complexes are toxic and highly persistent that subsequently leads to the acute toxicity of ecosystem [1]. For example, dye biodegradation in simulated textile wastewater leads to generation of dye metabolites which were found to be very harmful for growth by inhibiting the respiration of aerobic microorganisms [2,3].

Proper treatment of the dye-laden wastewater effluent is therefore essential before the effluent is discharged into a water body. This has led to intensive search for the best available technology, which can be utilized for the removal of dyes in wastewater. Many biological, chemical and physical processes for color removal have been applied by many industries.

Various chemical and biological methods have been widely used for decoloration of effluent dyes with some caveats [4]–[6]. And activated carbon is the most popular and widely used adsorbent. It is cited by the United States Environmental Protection Agency (US-EPA) as one of the best available control technologies [7]–[10].

The primary influencing factors in dye adsorption are interactions between dye and adsorbent, particle size, surface area, temperature, pH, and contact time. Adsorbents which also contain nitrogen tend to have significantly larger adsorption capacity in acid dyes [11]. For instance, Achmad et al. showed very high adsorption of Direct Red 23 dye onto a novel green adsorbent developed from *Uncariagambir* extract [12]. Similarly, Dutta et al. revealed the dependence of adsorption of Direct Blue 86 onto carbon-alumina composite pellet using a fixed-bed column on the dynamic adsorption characteristics such as the effects of inlet dye concentration, feed flow rate, and bed height on the adsorption breakthrough where Yoon-Nelson, Bohart-Adams, and Clark fixed bed models were used to describe the breakthrough behavior [13]. Markovska et al. performed a study on the adsorption on basic dyes from aqueous solution onto natural zeolite and granular activated carbon using a fixed-bed column. The effects of process variables have been used to predict the effect of parameter changes on the system by using the bed depth service time approach [14].

In all above-mentioned studies, accurate profiling of solute concentrations in porous media is essential to elucidate the mechanisms of fate and mode of transport in order to properly design an environmental pollution control system in chemical and industrial processes. For example, Kim et al. modeled the adsorption kinetics of anionic surfactants onto activated carbon [15]. Yaneva et al. studied the adsorption of 4-nitrophenol and 2,4-dinitrophenol from aqueous solutions onto perlite, utilizing the theoretical solid diffusion control model based on the linear driving force kinetic model. Thus, the transport behavior of solute through a porous media must be well described. This is applicable not only in chemical processing systems for pollution control but also in groundwater resource management [16].

Sorption, convection, and dispersion are considered as the main mechanisms in the transport of chemicals in processes found in many practical chemical engineering applications such as solvent utilization, filtrate recovery, pollution control, separation processes in industries, and washing of pulp and filter cakes. The movement of the contaminant in a porous medium depends on both the macroscopic and microscopic behavior of the bulk fluid and on the physical and chemical conditions on the surface of and within the adsorbing material [17]. A solution neglecting sorption into the packing material was developed using a combination of analytical and numerical methods [18]. Several analytical solutions were proposed for the system with sorption and radial diffusion thereby allowing for spherical configurations of packing particles [17,19–21]. The convection-dispersion problem was solved analytically by Brenner using Laplace transforms and numerically using orthogonal collocation by Graess and Arora et al. [18,22,23]. Almost all these models involve using Danckwerts boundary conditions [24].

Several theories have already been developed and mentioned above to provide suitable modifications to the convection-dispersion problem to include reaction, retention (including absorption) terms in order to correctly capture the solute transport where the convective dispersion equation may not be adequate. Lu et al. modeled the adsorption breakthrough behavior of Pb^{2+} in a fixed bed of ETS-10 adsorbent and found good agreement between experimental and numerical results by orthogonal collocation. Selim et al. considered the mobility and retention of heavy metals in soil as a prerequisite in a study of groundwater contamination problems [25, 26]. While the theory is already well established, researchers have tried to match the transfer coefficients and diffusivities with the experimental data, while others investigated a varied array of mechanisms to gain more understanding of the transfer mechanism. Singh et al. and Kumar et al. modeled the brown stock washing of pulp by coupling transport equation with various adsorption isotherms to describe the relationship between concentration of the solute in the liquor and on the fibers [27,28].

It remains the same, however, that the main problem is essentially predicting the behavior of the solute concentration inside a bed of porous media, considering the initially sharp concentration gradient between two miscible fluids, the interstitial fluid and the fluid within the pores. Past literature has reduced the current problem to convection- dispersion-sorption transport equations. All these analytical and numerical methods introduced above to solve the sorption-convection-dispersion in a column problem are very multifarious and time consuming to solve numerically.

Model System: Methylene Blue and Coco Peat

Methylene blue (MB) is a basic dye used in textile industries and is commonly found in wastewater. It is not regarded as acutely toxic, but continuous exposure especially to large amounts could have harmful effects to the human physiology and can cause jaundice, cyanosis, vomiting, and shock [29]. Coconut bunch waste as adsorbent for methylene blue had an adsorption capacity of 70.92 mg/g at 30°C while charcoal had 62.7 mg/g at 25°C [30]. Systematic batch mode studies of adsorption of MB on teak tree powder showed an excellent adsorption capacity to MB [31]. Coco peat was once considered as waste and its disposal was once considered an environmental problem. Coco peat has a high lignin (31%) and cellulose (27%) content. Its density is on average 143 g/L. Because of the high lignin content, coco peat takes decades to decompose. Recently, cocopeat has been utilized in many ways such as organic manure, soil conditioning, biogas production, adsorbent for treatment of wastewater. The composted coco peat is also used along with organic supplements in crop fields in horticulture. Because of its polar character cocopeat can effectively remove dyes from solutions. The use of peat to remove Basic blue 3, Basic yellow 21, and Basic red 22 dyes was investigated by Allen et al. and observed that the adsorbent tends to have high cation exchange capacity [32]. For acid and basic dyes, the removal performance was comparable with that of the activated carbon, while the performance was even better for disperse dyes. Motavalizadeh et al. investigated the elimination of lead (Pb^{+2}) present in an aqueous solution using coco peat as a bioadsorbent material [33]. The maximum removal was found to be 92.5%.

In this study, a packed column of biosorbent coco peat is used to investigate the removal of MB from the aqueous solution through a column experiment. The rigorous modeling of such packed columns is commonly recognized to be essential in achieving good design and efficient performance of a dye laden wastewater treatment system, especially at the magnitude of industrial scale [34]. In the pulp and paper industry, the convection-dispersion-sorption transport equations were solved to produce high efficiency of removal of solutes from the bed with less environmental load [23,26,27,34,35,36]. Thus, the motivation of this study is to develop a model to describe the mechanism of the dynamic adsorption of methylene blue from bulk fluid onto coco peat. Batch study was conducted to obtain the parameters needed in the model. The simulated results were calibrated and compared with the experimental breakthrough curves of the column experiments.

The objectives of this paper are (1) to evaluate the removal efficiency of MB by coco peat (2) to fit a convection-dispersion-sorption model that describes the transport and sorption of MB onto a coco peat column, and (3) to compare the influence of solid diffusion coefficient, axial dispersion coefficient and external liquid film mass transport coefficient on dye removal.

2. MODEL DEVELOPMENT

Mathematical model

In a fixed bed system, convection and dispersion in the bulk fluid together with a source or sink term describe the mechanisms of transport through the column. The source (or sink) term is due to adsorption onto the adsorbent and mass transfer of solute from the bulk fluid to the adsorbent. The adsorption can be described in three steps: a) diffusion of the component from the bulk fluid to the external surfaces of particles (external or film diffusion); b) diffusion through and within the porous network of the particles (internal diffusion); and c) the binding of the component to some sorption site on the walls of the internal pores. The accuracy of the predicted breakthrough curves is hence dependent on the correct formulation of the mathematical model. Fogelberg and Fugleberg used a non-linear Langmuir type adsorption isotherm to describe the relationship between the concentration of the solute in the liquor and concentration of the solute on adsorbent fibers [37]. Arora et al. successfully used this Langmuir adsorption isotherm using one dimensional axial dispersion model for single stage washing of sodium from adsorbent fibers [35]. Thus, in the present investigation for MB, the Langmuir adsorption isotherm is used as an adsorption model needed in the solution of the transport model.

The following assumptions were made in the development of the mathematical model:

- The particle is small in comparison with the overall distance and the porous medium is macroscopically uniform.
- The sorption equilibrium relationship, describing the partitioning of solute concentration between the bulk fluid and the solid phase, is given by the Langmuir isotherm.
- The attainment of local sorption equilibrium is very rapid. The transport within the particle happens instantaneously that the solute concentration anywhere within the particle is the same as the concentration on the surface at the solid side.
- The particles may be regarded as spherical for the description of internal diffusion.
- Bulk flow is in the axial direction only and the superficial velocity is constant.
- No chemical reaction occurs in the column.
- There is negligible concentration gradient in the radial direction.
- Initially the column contains no solute and a step change in the concentration of the adsorbate is introduced.

Based on the assumptions above, the transport of MB is modeled with a combination of the methods by and Yaneva *et. al.* and Babu, *et. al.* [16], [38], [39]. The working equation is given by:

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial z} = - \frac{(1 - \epsilon)}{\epsilon} \frac{\partial}{\partial t} (\epsilon_p \bar{C} + \rho \bar{q}) + D_L \frac{\partial^2 C}{\partial z^2} \quad (1)$$

where C is the concentration of dye in the bulk fluid as a function of bed depth, z and time, t (for the other variables, please see Section 7. Notation). The corresponding upper and lower boundary conditions governing the system as given by Danckwerts [24] are:

$$z = 0, \quad t > 0, \quad uC - D_L \frac{\partial C}{\partial z} = uC_{in} \quad (2)$$

$$z = L, \quad t > 0, \quad \frac{\partial C}{\partial z} = 0 \quad (3)$$

and the initial condition of the system is:

$$0 \leq z \leq L, \quad t = 0, \quad C = 0 \quad (4)$$

The list of variables used in the equations and their corresponding definitions are listed in Section 7.

Dimensionless variables are introduced to transform the governing differential equation to non-dimensionalized form. This is usually done especially when comparing columns of different sizes, different flow rates and applications of solutes into the system. The dimensionless variables are:

$$Z = \frac{z}{L} \quad (5)$$

$$\theta = \frac{tu}{L} \quad (6)$$

$$Pe = \frac{Lu}{D_L} \quad (7)$$

Equations 1 to 4 become

$$\frac{\partial C}{\partial \theta} + \frac{\partial C}{\partial Z} = -\frac{(1-\epsilon)}{\epsilon} \frac{\partial}{\partial \theta} (\epsilon_p \bar{C} + \rho \bar{q}) + \frac{1}{Pe} \frac{\partial^2 C}{\partial Z^2} \quad (8)$$

$$Z = 0, \quad \theta > 0, \quad C - \frac{1}{Pe} \frac{\partial C}{\partial Z} = C_{in} \quad (9)$$

$$Z = 1, \quad \theta > 0, \quad \frac{\partial C}{\partial Z} = 0 \quad (10)$$

$$0 \leq Z \leq 1, \quad \theta = 0, \quad C = 0 \quad (11)$$

The uptake rate (mass transfer rate to the solid surface of coco peat), which describes the removal of solute in the aqueous solution, is given by:

$$m = \frac{d}{dt} (\epsilon_p \bar{C} + \rho \bar{q}) \quad (12)$$

This uptake rate can also be written as diffusion rate of transfer:

$$m = \frac{3k_f}{R_p}(C - C_s) \quad (13)$$

The uptake rate expression can be also written based on the linear driving force model for solid diffusion as:

$$m = \frac{15D_s}{R_p^2} \rho(q_s - \bar{q}) \quad (14)$$

Equations 13 and 14 can be combined to:

$$\frac{3k_f}{R_p}(C - C_s) = \frac{15D_s}{R_p^2} \rho(q_s - \bar{q}) \quad (15)$$

Langmuir isotherm model is used to relate adsorbed concentration with the liquid phase concentration. The Langmuir isotherm equations are:

$$q_s = \frac{q_m K C_s}{1 + K C_s} \quad (16)$$

$$C_s = \frac{q_s}{q_m K - K q_s} \quad (17)$$

the Biot number defined as:

$$Bi = \frac{R_p k_f}{D_s} \quad (18)$$

and together with the Langmuir isotherm (Equation 16), Equation 15 can be transformed to:

$$Bi \left(C - \frac{q_s}{q_m K - K q_s} \right) = 5 \rho (q_s - \bar{q}) \quad (19)$$

With Equation 12 equal to Equation 14 and considering that accumulation of solute in the pores is very much smaller than within the solid (i.e. $\epsilon_p \bar{C} \ll \rho \bar{q}$) result into the following:

$$\frac{d\bar{q}}{dt} = \frac{15D_s}{R_p^2} (q_s - \bar{q}) \quad (20)$$

Combining equations 19 and 20 and introducing the dimensionless number T defined as

$$T = \frac{D_s L}{R_p^2 \nu} \quad (21)$$

yields:

$$\frac{d\bar{q}}{d\theta} = \frac{3BiT}{\rho} \left(C - \frac{q_s}{q_m K - K q_s} \right) \quad (22)$$

Differentiating Equation 19 with respect to θ and isolating $\frac{dq_s}{d\theta}$ gives us:

$$\frac{dq_s}{d\theta} = \frac{\frac{d\bar{q}}{d\theta} + \frac{Bi}{5\rho} \frac{dC}{d\theta}}{1 + \frac{Bi}{5\rho} \frac{q_m K}{(q_m K - K q_s)^2}} \quad (23)$$

and substituting Equation 22 into Equation 23 gives:

$$\frac{dq_s}{d\theta} = \frac{\frac{3BiT}{\rho} \left(C - \frac{q_s}{q_m K - K q_s} \right) + \frac{Bi}{5\rho} \frac{dC}{d\theta}}{1 + \frac{Bi}{5\rho} \frac{q_m K}{(q_m K - K q_s)^2}} \quad (24)$$

And substituting Equation 22 into Equation 8, still holding $\epsilon_p \bar{C} \ll \bar{q}$ true, gives

$$\frac{\partial C}{\partial \theta} + \frac{\partial C}{\partial Z} = -3BiT \frac{(1 - \epsilon)}{\epsilon} \left(C - \frac{q_s}{q_m K - K q_s} \right) + \frac{1}{Pe} \frac{\partial^2 C}{\partial Z^2} \quad (25)$$

Equations 24 and 25 together with the initial and boundary conditions given by Equations 9 to 11 describe completely the mathematical model of the system. The purpose of this study is to understand the role of the three major parameters in the model, k_f , D_L , and D_s in capturing the breakthrough curves of the column experiment. The system was solved using Finite Difference Method (FDM) to transform the equations to first order differential equations. The summary of the FDM schemes is given in the next section.

Numerical solution to the mathematical model

In this study, the mathematical model was transformed into a system of first order differential equations and solved by the Finite Difference Method (FDM) using Fourth Order Upwind (FOU) difference approximations using a computer program written in a MATLAB environment. To reduce the instability and inaccuracy of the results, derivatives were approximated by finite differences using a fourth order upwind technique and are as follows:

First Derivative

$$\frac{dC_1^j}{dz} = \frac{-25C_1^j + 48C_2^j - 36C_3^j + 16C_4^j - 3C_5^j}{12\Delta z} \quad (26)$$

$$\frac{dC_2^j}{dz} = \frac{-3C_1^j - 10C_2^j + 18C_3^j - 6C_4^j + C_5^j}{12\Delta z} \quad (27)$$

$$\frac{dC_3^j}{dz} = \frac{C_1^j - 8C_2^j + 0C_3^j + 8C_4^j - C_5^j}{12\Delta z} \quad (28)$$

$$\frac{dC_i^j}{dz} = \frac{-C_{i-3}^j + 6C_{i-2}^j - 18C_{i-1}^j + 10C_i^j + 3C_{i+1}^j}{12\Delta z} \quad (29)$$

$$\frac{dC_n^j}{dz} = \frac{3C_{n-4}^j - 16C_{n-3}^j + 36C_{n-2}^j - 48C_{n-1}^j + 25C_n^j}{12\Delta z} \quad (30)$$

Second derivative with Dirichlet at the inlet and outlet boundary conditions specified.

$$\frac{d^2C_1^j}{dz^2} = \frac{45C_1^j - 154C_2^j + 214C_3^j - 156C_4^j + 61C_5^j - 10C_6^j}{12\Delta z^2} \quad (31)$$

$$\frac{d^2C_n^j}{dz^2} = \frac{45C_n^j - 154C_{n-1}^j + 214C_{n-2}^j - 156C_{n-3}^j + 61C_{n-4}^j - 10C_{n-5}^j}{12\Delta z^2} \quad (32)$$

Second derivative with Neumann boundary conditions at inlet and at outlet

$$\frac{d^2C_1^j}{dz^2} = \frac{-\frac{415}{6}C_1^j + 96C_2^j - 36C_3^j + \frac{32}{3}C_4^j - \frac{3}{2}C_5^j - 50\frac{dC_1^j}{dz}\Delta z}{12\Delta z^2} \quad (33)$$

$$\frac{d^2C_n^j}{dz^2} = \frac{-\frac{415}{6}C_n^j + 96C_{n-1}^j - 36C_{n-2}^j + \frac{32}{3}C_{n-3}^j - \frac{3}{2}C_{n-4}^j + 50\frac{dC_n^j}{dz}\Delta z}{12\Delta z^2} \quad (34)$$

Second derivative for all interior points

$$\frac{d^2C_2^j}{dz^2} = \frac{10C_1^j - 15C_2^j - 4C_3^j + 14C_4^j - 6C_5^j + C_6^j}{12\Delta z^2} \quad (35)$$

$$\frac{d^2C_i^j}{dz^2} = \frac{-1C_{i-2}^j + 16C_{i-1}^j - 30C_i^j + 16C_{i+1}^j - 1C_{i+2}^j}{12\Delta z^2} \quad (36)$$

$$\frac{d^2 C_{n-1}^j}{dz^2} = \frac{10C_n^j - 15C_{n-1}^j - 4C_{n-2}^j + 14C_{n-3}^j - 6C_{n-4}^j + C_{n-5}^j}{12\Delta z^2} \quad (37)$$

(1) The time derivative is a simple forward difference approximation as:

$$\frac{dC_i^j}{dt} = \frac{C_i^{j+1} - C_i^j}{\Delta t} \quad (38)$$

$$C_i^{j+1} = C_i^j + \Delta t \frac{dC_i^j}{dt} \quad (39)$$

3. MATERIALS AND METHODS

Methylene blue (MB; molecular formula: $C_{16}H_{18}N_3SCl$) is a basic cationic, heterocyclic aromatic dye. It has wide applications, which include paper coloring, temporary hair colorant, dyeing cottons, and wools. MB is also known for its strong adsorption onto solids. The maximum adsorption wavelength of this dye is 668 nm. In this study, a stock solution of methylene blue at 1000 mg/L was prepared by dissolving 1 g of MB powder (analytic grade, Chemline Scientifics) in 1000 mL of distilled water in a 1-L volumetric flask. Different dye solution concentrations at 50, 75, 100, 125, 150 mg/L were obtained by dilution of the stock solution with deionized water. The diluted stock solutions were placed in separate PET bottles. Concentrations of influent and effluent MB aqueous solutions were determined using a UV-Vis spectrophotometer.

To prepare the coco peat for the batch and column experiments, the obtained coco peat was first sieved using a +16/-20 mesh size. It was then washed by passing distilled water through the coco peat in a funnel with filter paper for a couple of hours until the filtrate is visually clear and the measured concentration of the sample wash water is approximately zero. The washed coco peat was then dried at 90°C for 2 hours.

For the batch experiment, 0.25 g of coco peat is placed in eight separate 250-mL Erlenmeyer flasks. For each run, 50 mL of one specific concentration from the five diluted stock solution (50, 75, 100, 125, 150 mg/L) was added into all the Erlenmeyer flasks with 0.25 g coco peat. The temperature for each run was set at 25°C and kept constant. The eight samples were placed in a shaker with 200 rpm setting. Every five minutes, a sample is taken for measuring the concentration using a spectrophotometer. A control sample was also taken directly from the diluted stock solution to measure its concentration. All in all, fifteen runs were performed. Each run lasted for approximately 40 minutes. The Langmuir coefficients were determined from the results using nonlinear least squares method.

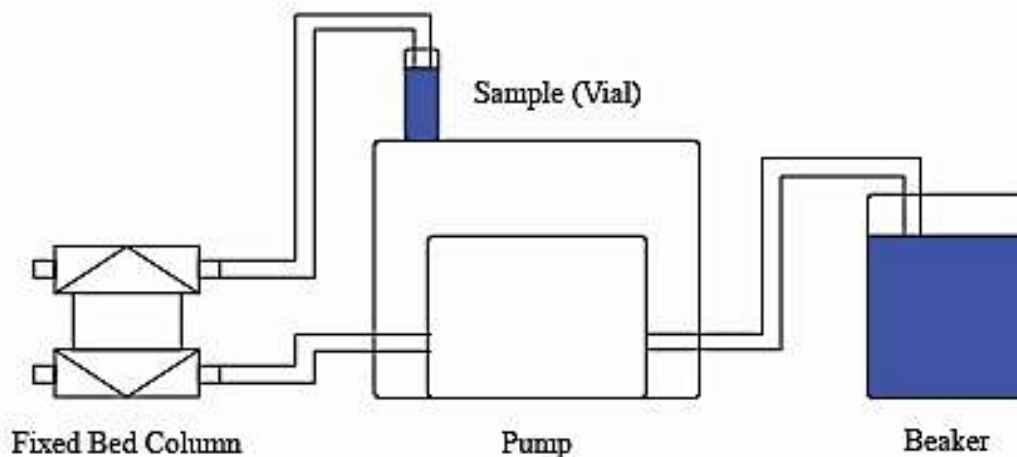


Figure 1. Fixed-bed experimental set up with column diameter at 30 mm and column length at 50 mm.

Fig. 1 shows the set up for the fixed-bed column experiment. A fabricated column with a height and diameter of 50mm and 30mm respectively was used as fixed bed column. Moreover, a pump was connected to the fixed-bed in order to control or set the flow rate.

Table 1. Applied MB Concentration, flowrate and calculated porosity for the column experiments.

<i>System</i>	<i>C_o (mg solute/L solution)</i>	<i>Flow rate (mL/min)</i>	<i>Porosity</i>
A	150	30	0.96
B	125	30	0.96
C	100	30	0.96
D	100	6.6	0.59
E	100	12.4	0.58
F	150	19.8	0.58

For the first set of fixed bed column experiments, washed coco peat was placed in the column with a diameter of 30 mm and length of 50 mm at a bulk density of 0.098 g/mL (porosity = 0.96). A constant flow rate of 30 mL/min was set for three different MB concentrations (100, 125, 150 mg/L). The concentrations of the effluent collected at various times were plotted for the calibration of the developed model. These are the test cases *A*, *B*, and *C* (see Table 1).

Another set of column experiments was conducted by varying the flow rates at 6.6, 12.4, and 19.8 mL/min with two different MB concentrations (100 and 150 mg/L). The dry bulk density of the column was 0.292 g/mL (porosity = 0.58). The concentrations of the effluent collected at various times were plotted for the calibration of the developed model. These are the test cases *D*, *E*, and *F* (see Table 1).

Effluent samples were taken every five minutes and its concentration is measured using spectrophotometer. A sample was also taken directly from the prepared solution to measure the influent concentration. Breakthrough curves (C/C_o versus elapsed time) was generated, where C is the concentration at a particular time and C_o is the influent solution concentration. The breakthrough curve is an indication of how fast or slow the adsorbent becomes saturated with the adsorbate. The experiment can be considered finished if the graph approaches a C/C_o value of 1. The temperature was set to 25°C.

4. RESULTS AND DISCUSSION

Removal efficiency

The removal efficiency was calculated from the batch experiments based on the equation below.

$$\% \text{ removal} = \frac{\text{initial concentration} - \text{final concentration}}{\text{initial concentration}} * 100\% \quad (41)$$

Figure 2 shows that for all initial concentrations investigated, removal efficiency ranged from 99.49% - 99.65%. It can be concluded from this that coco peat is a very good adsorbent of MB.

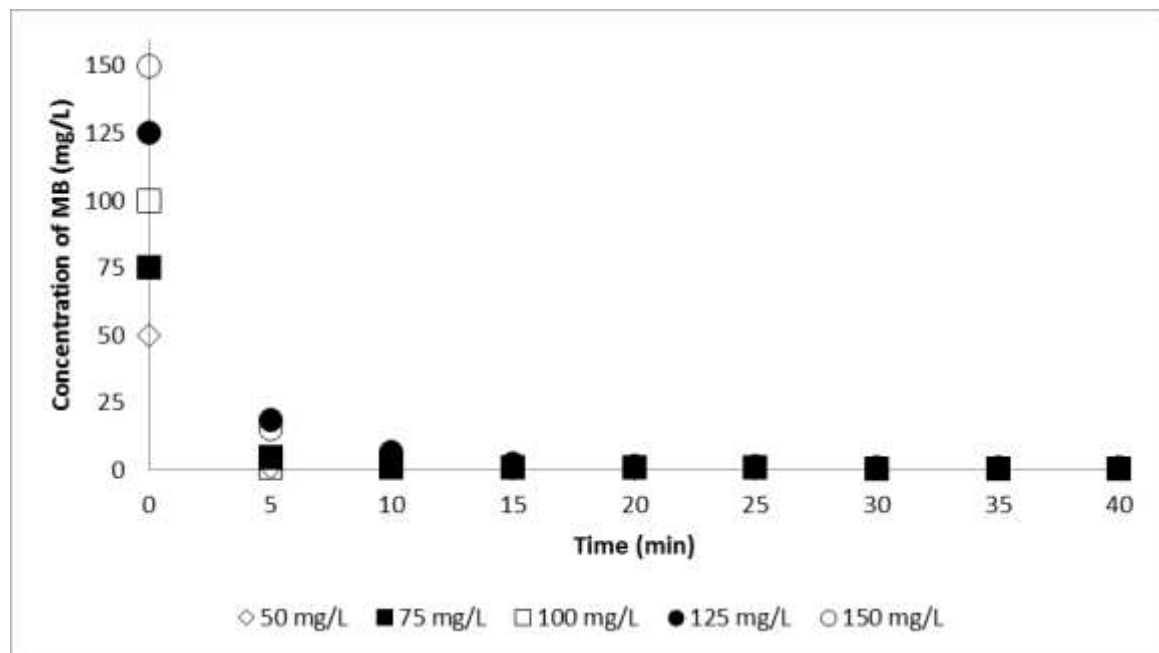


Figure 2. Dye removal efficiency at 25°C with varying initial MB concentration.

Adsorption equilibrium

The sorption isotherm of MB onto coco peat was established and is presented in Fig. 3. The equilibrium data can be modeled using the Langmuir isotherm equation:

$$\frac{1}{q_e} = \frac{1}{Kq_m} \frac{1}{C_e} + \frac{1}{q_m} \tag{42}$$

The values of the Langmuir parameters are given in Table 2. The model was fitted to the experimental equilibrium data using nonlinear least squares method. With a coefficient of determination (r^2) of 0.927587, the Langmuir model fitted well the experimental data. These obtained Langmuir parameters were used as adsorption parameters describing the dynamic sorption of MB onto coco peat in column experiments in the transport model.

Table 2. Langmuir isotherm parameters.

Parameters	Values
q_m (mg/g)	0.6474
K_L (L/g)	100.32
R^2	0.927587

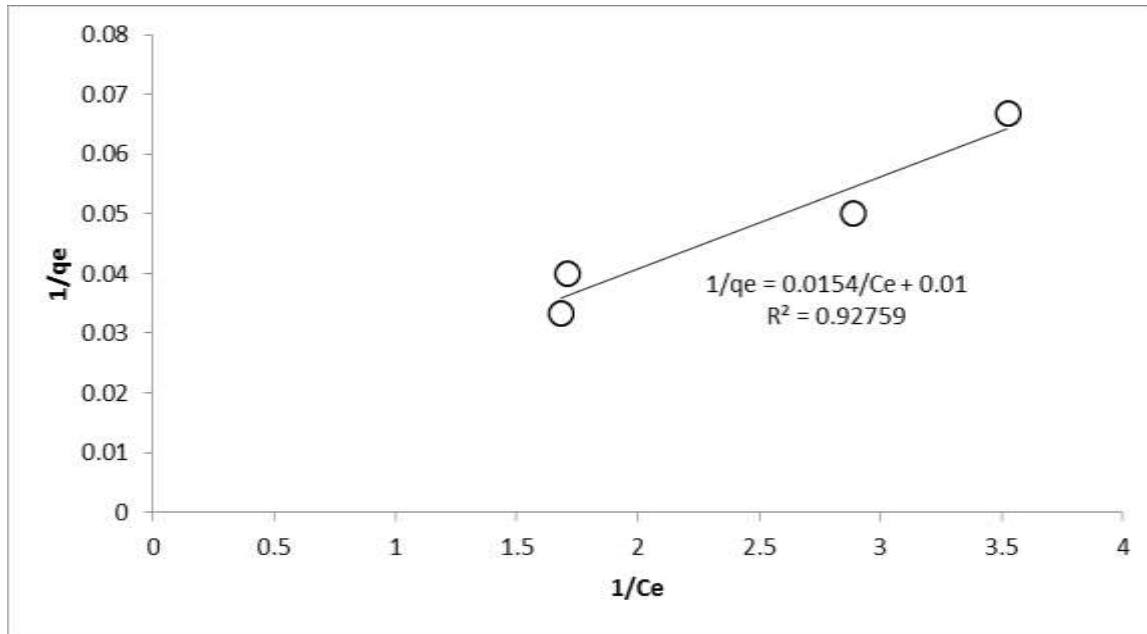


Figure 3. Langmuir model for the adsorption of MB onto coco peat at 25°C.

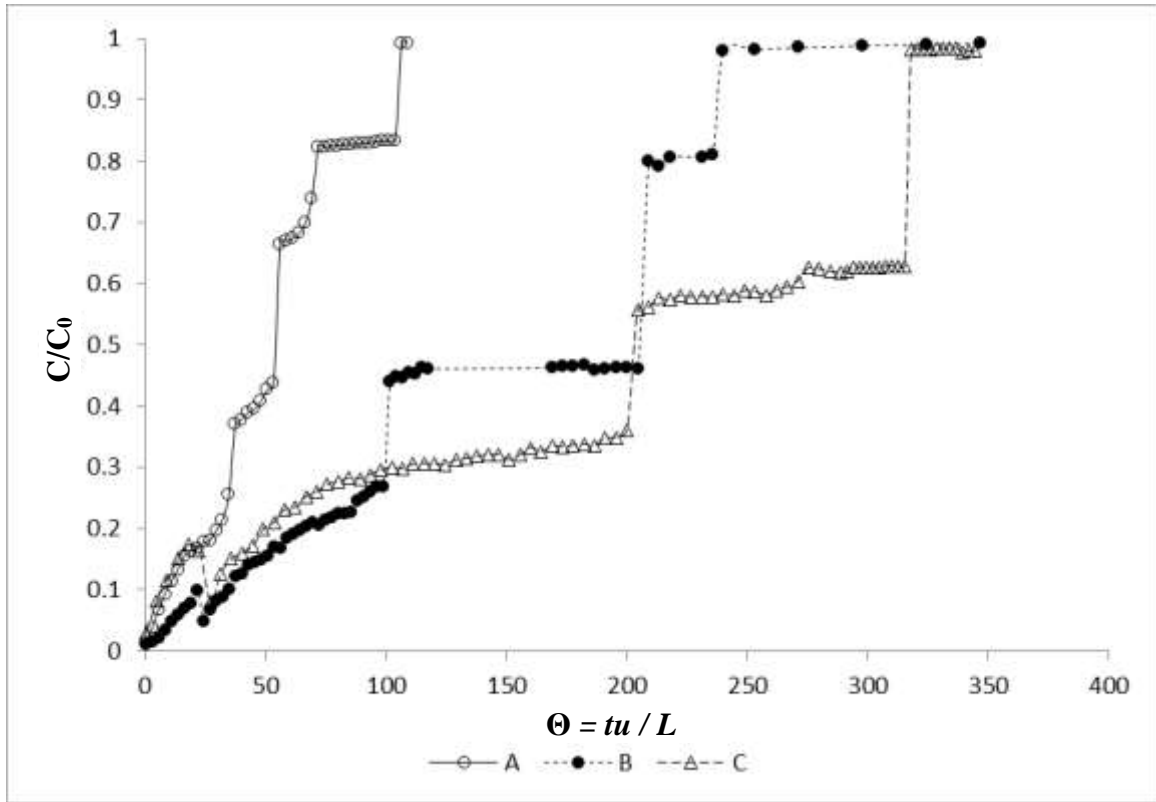


Figure 4. Breakthrough curves for MB-coco peat system at different initial solute concentrations at 30 mL/min and 25°C.

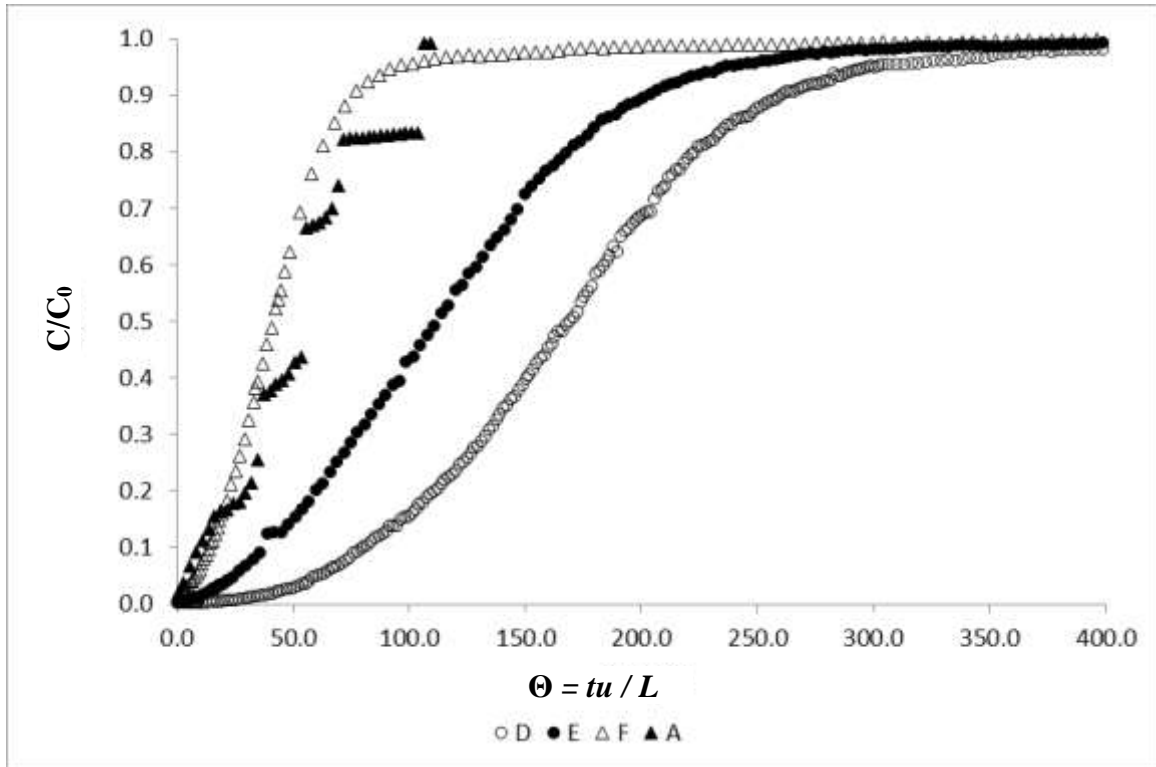


Figure 5. Breakthrough curves at 25°C at different initial MB concentrations and flow rates.

Breakthrough curves

Breakthrough experiments are done to predict the shape of the adsorption wave front, which determines the lifespan of the adsorbents in the bed and the regeneration times. The breakthrough curves of MB onto coco peat in various conditions as described in Table 1 for the different experimental runs are given in Fig. 4 and Fig. 5.

The initial dye concentration of the inlet is significant because a given amount of adsorbent can only adsorb a fixed or maximum amount as is theoretically calculated by the Langmuir isotherm. Therefore, increasing the initial dye concentration should lessen the volume that the column can process. This is observed in Fig. 5 where the slope of the breakthrough curve increases with increasing initial MB concentration until the bed reaches saturation, the breakthrough time is decreased and, for the same flow rates the volume of the processed solution is decreased.

The flow rate of the inlet is also important since it is used to adjust process times of the wastewater for better scheduling and economy. The higher the flow rate, the faster the same amount of solution can be processed. This is shown in Fig. 4 where the slope of the breakthrough curve increases with increasing flow rate.

Model fitting of breakthrough curves

The main goal of this study is to determine the parameters that govern adsorption of a single solute (MB) onto a granulated adsorbent (coco peat). The effects of k_f , the external mass transfer coefficient of the film, D_L , the axial dispersion coefficient, and D_s , the solid diffusion coefficient, on the breakthrough curves were explored.

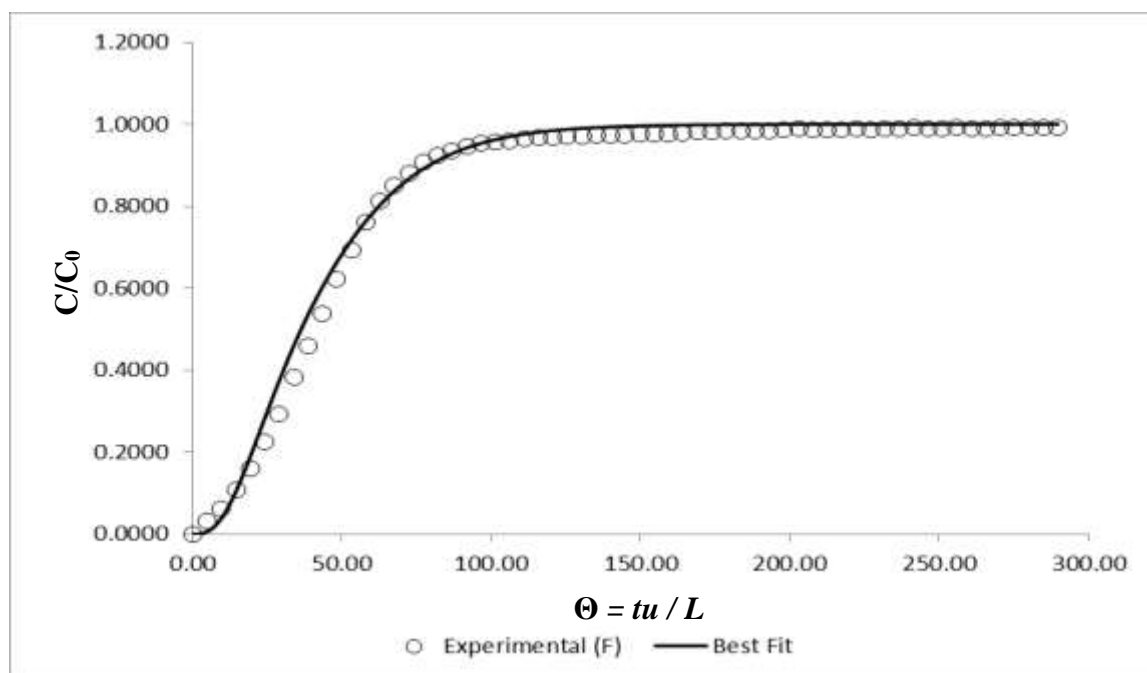


Figure 6. Application of the model on the breakthrough curves for MB-coco peat system F (RMSE = 0.0009).

Table 3. Model parameter test values of the external liquid film mass transfer coefficient, k_f , axial dispersion coefficient, D_L , and solid diffusion coefficient, D_s , for the sensitivity analysis.

Test System	k_f ($m\ s^{-1}$)	D_L ($m^2\ s^{-1}$)	D_s ($m^2\ s^{-1}$)
I-A	7.2798E-04	3.9564E-05	3.3487E-07
I-B	7.2798E-04	3.9564E-05	3.3487E-08
I-C	7.2798E-04	3.9564E-05	3.3487E-09
II-A	3.6399E-03	3.9564E-05	3.3487E-07
II-B	3.6399E-03	3.9564E-05	3.3487E-08
II-C	3.6399E-03	3.9564E-05	3.3487E-09
III-A	7.2798E-03	3.9564E-05	3.3487E-07
III-B	7.2798E-03	3.9564E-05	3.3487E-08
III-C	7.2798E-03	3.9564E-05	3.3487E-09
IV-A	7.2798E-04	7.9128E-06	3.3487E-07
IV-B	7.2798E-04	7.9128E-06	3.3487E-08
IV-C	7.2798E-04	7.9128E-06	3.3487E-09
V-A	3.6399E-03	7.9128E-06	3.3487E-07
V-B	3.6399E-03	7.9128E-06	3.3487E-08
V-C	3.6399E-03	7.9128E-06	3.3487E-09
VI-A	7.2798E-03	7.9128E-06	3.348E-07
VI-B	7.2798E-03	7.9128E-06	3.3487E-08
VI-C	7.2798E-03	7.9128E-06	3.3487E-09
VII-A	7.2798E-04	3.9564E-06	3.3487E-07
VII-B	7.2798E-04	3.9564E-06	3.3487E-08
VII-C	7.2798E-04	3.9564E-06	3.3487E-09
VIII-A	3.6399E-03	3.9564E-06	3.3487E-07
VIII-B	3.6399E-03	3.9564E-06	3.3487E-08
VIII-C	3.6399E-03	3.9564E-06	3.3487E-09
IX-A	7.2798E-03	3.9564E-06	3.3487E-07
IX-B	7.2798E-03	3.9564E-06	3.3487E-08
IX-C	7.2798E-03	3.9564E-06	3.3487E-09

The model was fitted into the breakthrough curve of System C based on the dynamic experimental parameters on Table 1. Fig. 6 shows the model captured the experimental results with the following values of the three variables:

$$D_L = 5.5467E-06\ m^2\ s^{-1}$$

$$k_f = 7.3462E-0\ m\ s^{-1}$$

$$D_s = 3.1126E-09\ m^2\ s^{-1}$$

Sensitivity analysis was performed in this study by changing the value of one parameter while maintaining the values of the other two parameters. The shape of the breakthrough curves changed depending on the values of these three parameters (see Figure 7).

Effect of D_L

The axial dispersion coefficient is a function of the flow rate and the particle size of the adsorbents; physical properties of the system. It is independent of the chemical properties of the solutes. Figure 8 shows the effect of D_L on the breakthrough curve. The smaller the D_L of the system, the higher the slope of the breakthrough curve. This translates to less processing time.

Effect of k_f

The magnitude of the external mass transfer coefficient is inversely proportional to the thickness of the film boundary that the solute has to cross to reach the surface of the adsorbent. It is an essential parameter in the adsorption process that is dependent on the interactive forces of the solution and the adsorbent material. Figure 9 shows the effect of varying the k_f of the system on the breakthrough curve. As the k_f value increases, so does the slope of the breakthrough curve. The higher the value of k_f , the lower the mass transfer resistance. This means that the sorption happens at a faster rate.

Effect of D_s

The solid diffusivity, D_s , describes the molecular transport of the solute into the internal pores of the adsorbent particles. This value is chiefly dependent on the surface properties of the adsorbent and the interactive forces between this surface and the solution. If the solid diffusivity has a very significant influence on the breakthrough curve of the system studied, then this would indicate that the system is largely controlled by external mass transfer or an intraparticle diffusion controlled process. Figure 10 suggests that the lower the D_s , the faster breakthrough happens.

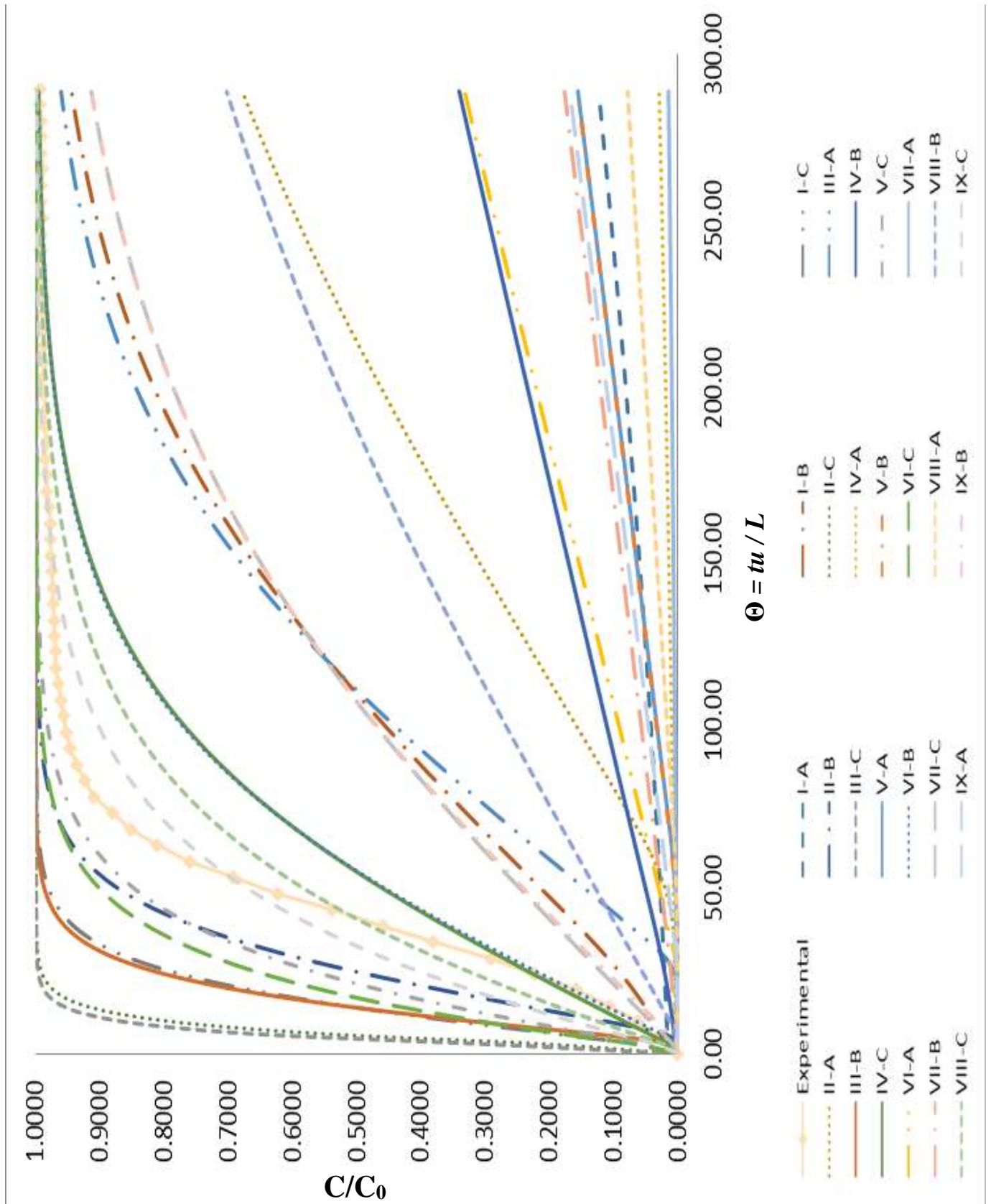


Figure 7. Summary of the sensitivity analysis of the three parameters as described in Table 3 for Sytem C of Table 1.

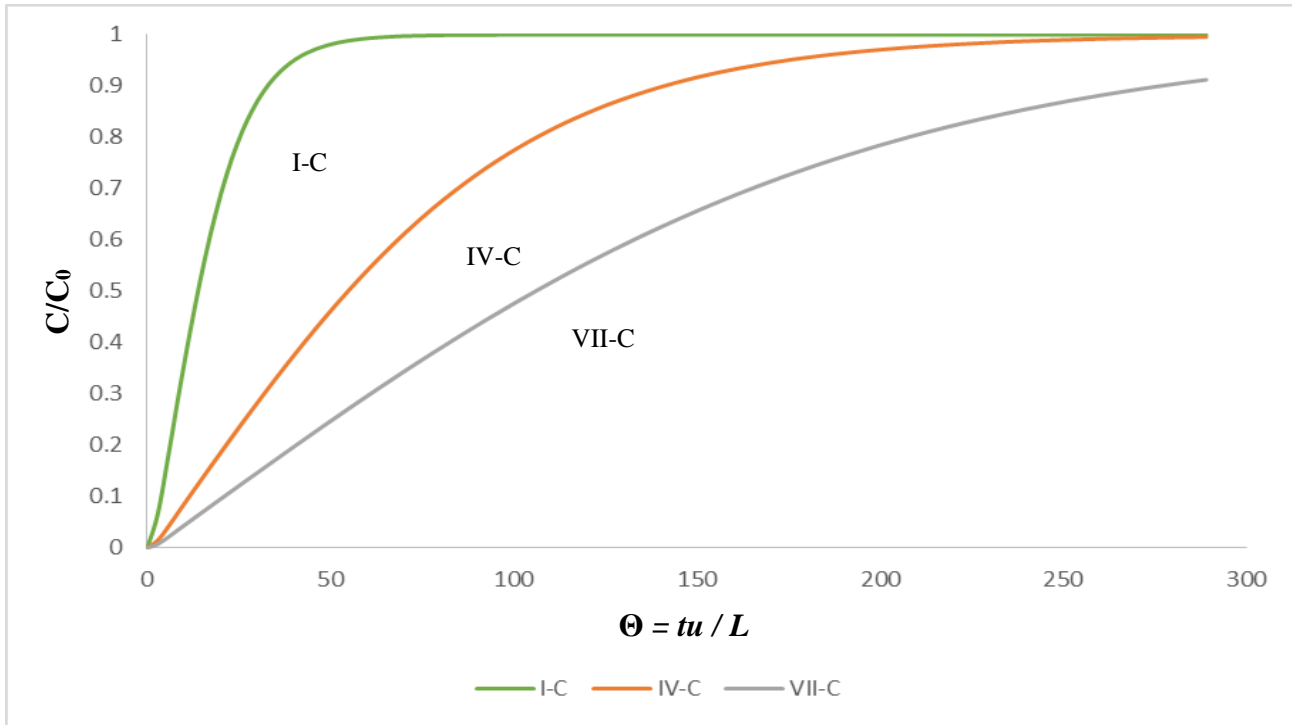


Figure 8. Influence of axial dispersion coefficient, D_L , on the breakthrough curves for MB-coco peat System C.
 I-C - $D_L = 3.95642E-05 \text{ m}^2 \text{ s}^{-1}$; IV-C - $D_L = 7.91283E-06 \text{ m}^2 \text{ s}^{-1}$; VII-C - $D_L = 3.95642E-06 \text{ m}^2 \text{ s}^{-1}$

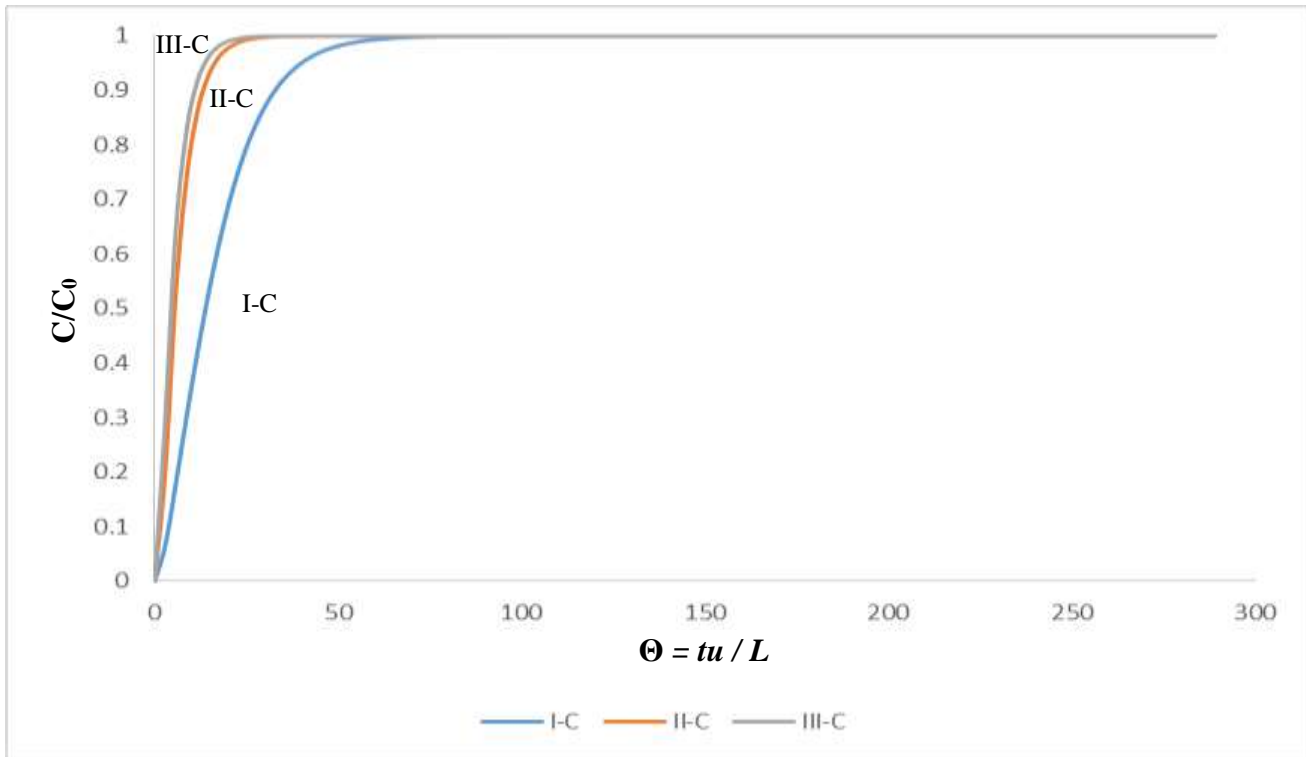


Figure 9. Influence of external mass transfer coefficient, k_f , on the breakthrough curves for MB-coco peat System C.
 I-C - $k_f = 7.2798E-04 \text{ m s}^{-1}$; II-C - $k_f = 3.6399E-03 \text{ m s}^{-1}$; III-C - $k_f = 7.2798E-03 \text{ m s}^{-1}$

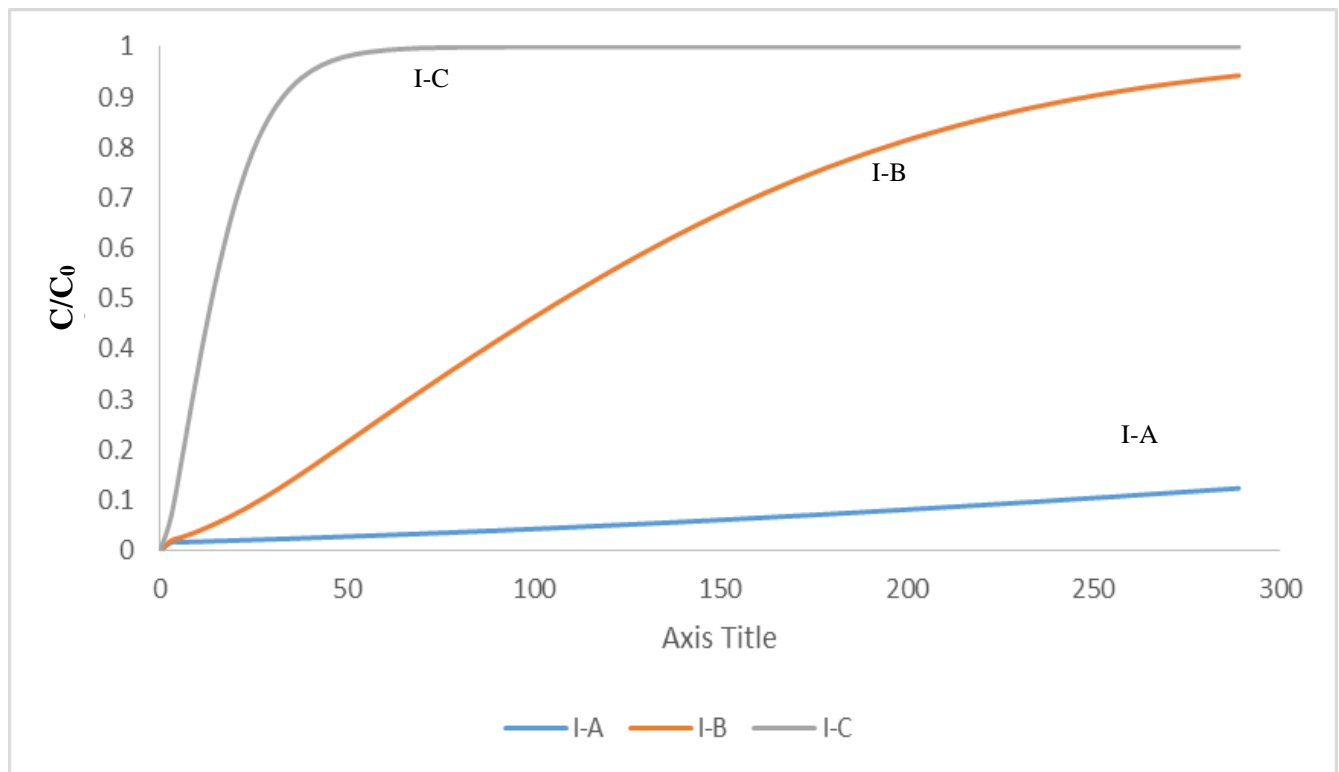


Figure 10. Influence of the solid diffusion coefficient, D_s , on the breakthrough curves for MB-coco peat System C.
 I-A - $D_s = 3.3487E-07 \text{ m}^2 \text{ s}^{-1}$; I-B - $D_s = 3.3487E-08 \text{ m}^2 \text{ s}^{-1}$; I-C - $D_s = 3.3487E-09 \text{ m}^2 \text{ s}^{-1}$

5. CONCLUSIONS

The adsorption of MB onto coco peat in batch and fixed bed column was studied. Batch studies revealed that coco peat is a very good adsorbent of MB with a removal efficiency of 99.61%. The adsorption process follows a monolayer Langmuir isotherm adsorption. The theoretical Linear Driving Force kinetic model coupled with a solid diffusion model was successfully applied to the experimental results. They showed that the system is dependent on the external mass transfer coefficient, k_f , and is controlled by the external film resistance rather than by the solid diffusivity, D_s , or intraparticle diffusion. The effect of the axial dispersion coefficient, D_L , a physical parameter dependent on flow rate and particle size, was also determined. A higher D_L , provides slower breakthrough thus a longer processing time. All three parameters are essential in designing a fixed bed column adsorption system to determine the capacity, run times, and economy of processing wastewater.

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7. NOTATION

C	concentration of the solute in the bulk phase, mg/L
C_o	inlet solute concentration, mg/L
\bar{C}	solute concentration in the liquid in the pores of the particles, mg/L
C_s, C_{ε}	liquid phase solute concentration in equilibrium with q_s on the surface, mg/L
D_L	axial dispersion coefficient, m ² /s
D_s	solid diffusion coefficient, m ² /s
K_L	Langmuir isotherm parameter, L/g
k_f	external mass transfer coefficient, m/s
q	concentration of the solute inside the particle, mg/g
\bar{q}	average concentration of the solute inside the particle, mg/g
q_m	Langmuir isotherm parameter, mg/g
q_s, q_{ε}	solute concentration on the surface of the particles, mg/L
r_p	radius of the particle, cm
t	time, min
u	average interstitial velocity, cm/min
z	distance in flow direction, cm
Z	dimensionless distance variable in flow direction
ε	bed porosity
ε_p	particle porosity
ρ	particle density, g/L
θ	dimensionless time variable

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