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Adsorption of Malachite Green from Aqueous Solution using Hen Feathers -Application of Different Mathematical Models to Continuous Biosorption

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Abstract

Proper remediation of aquatic environments contaminated by toxic organic dyes has become a major research focus for environmental and chemical engineers in recent years. The focus of this study was to evaluate the adsorption of malachite green from an aqueous solution in a continuous fixed-bed column system. Waste materials like hen feathers, a biosorbent was proven to remove the water-soluble malachite green dye from wastewater. This study evaluates the adsorption potential of malachite green dye ions in a continuous flow adsorption column. The performance of the hen feathers was evaluated in the fixed bed column at various operating conditions such as bed height (6-10cm), flow rate (4-12ml/min), and initial concentration (10-30 mg/l). The bed height (8cm), flowrate(12 ml/min), and highest inlet concentration (20mg/l) resulted in the highest malachite green uptake of 2.829mg/g compared to other experimental conditions. The column experimental data obtained at different conditions were analyzed using three different models viz., Bohart-Adams model, Yoon-Nelsons model, BDST model, which provided a good breakthrough curve prediction. However, the results obtained from the Yoon-nelson model and BDST model were more satisfactory. The various characteristics of the hen feathers were studied using FTIR studies. The activated hen feather powder was a successful potential bio sorbent for the malachite green from the aqueous phase.

Keywords: pH, Adsorption, Hen feathers, Dye, Breakthrough curve, Fixed bed column

1 Introduction

The complex aromatic molecular structure and synthetic origin of dyes make them more stable and more difficult to separate from the effluents. Today there are more than 10,000 dyes available commercially. Dyes are mostly used in textiles, paper, rubber, plastic, leather, cosmetics, and pharmaceutical and food industries [1]. The industries discharge a massive quantity of dye wastewater into the aquatic system. The effluent must be treated before discharging into the aquatic system as it harms the aquatic life. Also, it cannot be used directly for the resource of water without treatment. Dyes ask the organic substances to enable the strong coloring of fiber and a few other materials. There are various kinds of dyes and are divided into natural dyes (such as vegetable dyes, animal dyes, mineral dyes, etc.) and artificial dyes. According to the molecular structure, they are often divided into azo dyes, anthraquinone dyes, phthalocyanine dyes, aromatic dyes, and nitro dyes. They are also divided based on the application methods into acid dyes, basic dyes, sulfur dyes, reactive dyes, disperse dyes, direct dyes, and so on. Natural dyes are obtained from animals, plants, and minerals. According to sources, they will be divided into plant dyes; dyes extracted from the roots, stems, leaves, and fruit of some plants like indigo extracted from the leaves of indigo (blue); curcumin extracted from turmeric (yellow); alizarin extracted from madder (red) and so on; animal dyes; dyes extracted from the animal body such as carmine extracted from cochineal, etc; mineral dyes; dyes extracted from the colored inorganic substance of mineral-like chrome yellow, ultramarine, brown and other manganese. Synthetic dyes, also referred to as "artificial dyes." are specially made through the chemical processing of pitch (or oil processing) fractionation products (such as benzene, naphthalene, anthracene, carbazole, etc.), sometimes also are referred to as pitch dyes. Due to its effects on the immune system and reproductive system, and also due to its genotoxic and carcinogenic potentials, MG has generated a major environmental concern in recent times [2,3,4]. Due to the carcinogenic, m.utagenic, and teratogenic properties of MG and its metabolites, discharge of MG-loaded

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wastewaters into the environment reduces light penetration in the water bodies and affects the living organisms [5,6,7]. MG is toxic to mammalian cells and has been shown to cause cancer in different organs including the liver and thyroid of experimental animals. For the treatment of these wastewaters, numerous conventional methods such as oxidation, coagulation, precipitation, ozonation, and adsorption were employed [8]. Due to its easy implementation and availability of a large number of adsorbents, adsorption is proved to be highly efficient and simple [9,10]. In recent years, the use of naturally available biomass under the name of bio sorbents has gained a lot of popularity because of its reduced cost and no pre-treatment expenses.

Recently, our laboratory explored the use of hen feathers, as a bio sorbent to remove the toxic triphenylmethane dye, Brilliant Blue FCF, and found it to be quite successful and economical. Not much literature was found to use chicken feathers as adsorbents. Only a few reports were available, which only describe the removal of metal impurities from wastewater [11-14]. Thus, the idea to use hen feathers as adsorbents to remove hazardous dyes seems to be an innovative one for the appropriate, valuable and necessitous utilization of such a waste material for mankind. The present objective of the research is to research the sensible applicability of the bio sorbent during a continuous column operation. Various operational parameters such as bed depth, feed flow rate, and inlet dye concentration have been analyzed to study their influence. Further, the fit of the experimental data to various models such as bed depth service time (BDST), Adams–Bohart and Yoon–Nelson was subjected to describe the breakthrough curves.

2 Materials and Methods

2.1 Preparation of the Biosorbent

Collected hen feathers were of about approximately 1 cm in length, which was first agitated and rinsed thoroughly within the pool of double water so dried. Soft barbs of every dried feather were now digging small pieces of about but 0.1 mm length and hard middle rachis was removed and discarded. Barbs were then treated with peroxide (30%, v/v) for about 24 h to oxidize the adhering organic material. The fabric thus obtained was kept during an oven at 60 0C for 12 h for the removal of moisture and eventually stored in a vacuum desiccator**.**

2.2 Characteristics of the Biosorbent

A spectrum GX (Perkin Elmer, USA) spectrophotometer from 400-4000 cm with a resolution of 1cm using four scans with background subtraction was used to characterize the bio sorbent. The peaks were noted from the spectra by comparing them with literature-reported spectra.

2.3 Preparation of the malachite green dye stock solution

Malachite green dye stock solution of 1000 mg/L is prepared by dissolving 1 g of Malachite green dye in 1000 ml of water. This solution is used as the source of stock solution. All the specified solutions are prepared with analytical reagents and double-distilled water. By following appropriate dilutions, synthetic samples of different concentrations of the dye were prepared from this stock solution. 20 mg/L stock solution is prepared by diluting 20 mL of 1000 ppm stock solution with distilled water in a 1000 mL volumetric flask up to the mark. The required pH of the aqueous solution is obtained by adding 0.1 M HCl and 0.1M NaOH. Prepared dye solutions are analyzed using a UV spectrophotometer, Systronics at a λmax=617 nm.

2.4 For fixed bed

For the fixed bed experiments, a glass column has 3 cm internal diameter of 20cm height. The parameters chosen for the present study are bed height, flow rate, and initial dye concentration. To avoid any loss of the bio sorbent material glass wool is placed at the inlet and outlet of the column. The malachite green solution was fed through the top of the column with the help of a peristaltic pump and output was collected from the bottom of the column at regular intervals for analysis. The flow rate was checked regularly and the pumping was continued till there was no further biosorption of malachite green i.e, inlet and outlet concentration of malachite green became the same. Table 1 shows column experimental conditions during the adsorption of MG dye onto activated hen feathers

Table 1: Column Experimental Conditions during the Adsorption of MG Dye onto Activated Hen Feathers

Initial concentration (mg/l)	Bed height (cm)	Flow rate (ml/min)
10	8	8
20	6, 8, 10	4, 8, 12
30	8	12

2.5 Breakthrough curve (BTC) and mass transfer zone (MTZ)

The form of the BTC has been estimated accurately to design a hard and fast bed column and therefore the appearance of the breakpoint, which is a crucial thing to access the feasibility of using the adsorbent in real applications. BTC is known as the plot of exit concentration versus time-lapse or volume throughput reacted, for a given column bed height [15]. Through BTC, the performance of a packed bed is obtained. The characteristic shape of the BTC along the time axis varies due to various parameters like the inlet flow rates, concentration, and other properties like column diameter and bed height. Hence, prediction of the concentration-time profile from BTC for the effluent discharged from the column is required for the successful design of an adsorption column. For a given bed height, the typical BTC is usually expressed by plotting Ceffluent (C_t) or Ceffluent/Cinfluent (C_o) versus treated volume V or service time t. Figure 3 depicts an ideal BTC where the column capacity is fully utilized [16]. The concentration at the breakthrough point is arbitrarily chosen at some low value, C_b. When the effluent concentration Ct is approaching 99.5 % of Co (influent adsorbate concentration), then the adsorbent is considered to be essentially exhausted [17,18]. For a given feed concentration, the area under the BTC gives the total quantity of absorbed adsorbate. For column data analysis, the subsequent parameter calculations are applicable. Time equivalent to total or Stoichiometric Capacity is [19]:

$$t_t = \int_{t=0}^{t=\infty} \left(1 - \frac{c_t}{c_0}\right) dt = A_1 + A_2 \quad (1)$$

Time equivalent to usable capacity is:

$$t_u = \int_{t=0}^{t_b} \left(1 - \frac{c_t}{c_0}\right) dt = A_1 \quad (2)$$

Usable capacity of bed up to the breakthrough time point t_b and A_2 area calculation give unused bed height.

$$t_u \approx t_b \quad (3)$$

The value of t_t (total time) is given by the area under the curve $\int_{t=0}^{t=\infty}\left(1-\frac{c_t}{c_0}\right)dt$, whereas the area under the curve $\int_{t=0}^{t_b}\left(1-\frac{c_t}{c_0}\right)dt$ gives the t_u value. Total bed capacity or length utilized up to breakpoint is given by t_u/t_t. The area under the curve can be calculated either graphically or by numerical integration. Mass transfer zone (MTZ) is made at the front of the column where adsorption takes place. The controlling factors for the depth of MTZ are, for instance, the character of adsorbate, characteristics of adsorbent, mass (or bed-depth) of adsorber, particle size of adsorbent, adsorbate inlet concentration, solution pH, and solution flow rate [20]. Among these parameters, bed-depth, solute concentration, and flow rate considerably affect the lifetime of the column [21]. The unused bed length ($HUNB$) or MTZ can be calculated as:

$$H_{UNB} = \left(1-\frac{t_u}{t_t}\right)H_T = \left(1-\frac{t_b}{t_t}\right)H_T \quad (4)$$

where H_T is total bed height (cm) MTZ = H_{UNB}. The used bed length H_B can be calculated as

$$H_B = \left(\frac{t_b}{t_t}\right)H_T \quad (5)$$

The volume of the effluent, V_{eff} (mL), can be calculated using:

$$V_{eff} = Qt_{total} \quad (6)$$

where Q is the volumetric flow rate (mL/min) and t_{total} is the total flow time (min). The total mass of dye adsorbed, q_{total} (mg), can be calculated from the area under the breakthrough curve:

$$q_{total} = \frac{Q}{1000}\int_{t=0}^{t=total} C_{ad}dt \quad (7)$$

where C_{ad} is the concentration of dye removal (mg/l). Equilibrium metal uptake or maximum capacity of the column, $q_{e,exp}$, (mg/g), in the column, is calculated as follows:

$$q_{e,exp} = \frac{q_{total}}{m} \quad (8)$$

where m is the dry weight of adsorbent in the column (g). The total amount of metal ion entering the column (m_{total}) is calculated from the following equation:

$$m_{total} = \frac{C_0 Q t_{total}}{1000} \quad (9)$$

and the removal percentage of MG can be obtained using the following equation:

$$\mathrm{Y}(\%) = \frac{q_{total}}{m_{total}} * 100 \quad (10)$$

2.6 Breakthrough curve modeling

Precise prediction of the concentration-time profile from the breakthrough curve of discharged effluent from the column is required to design the adsorption column. The breakthrough time and curve shape (or slope) are the main parameters to determine the operations and dynamic response of adsorption in the plug flow system. Bohart-Adams, BDST, and Yoon–Nelson equations were used to analyze the experimental data.

2.6.1 Bohart-Adams model

The Bohart and Adams[22] model was derived based on the surface reaction theory, assuming that the equilibrium is not instantaneous. Therefore, the adsorption rate is proportional to the residual capacity of the adsorbent and the concentration of adsorbate. The relationship between $\frac{C_2}{C_1}$ and t in a plug flow system for the sorption of chlorine on activated charcoal is described using this model [23]. The correlation between time and bed depth of the column and expressed as

$$ln\frac{C_2}{C_1} = k_{AB}C_1 t - k_{AB}N_0\frac{z}{U_0} \quad (11)$$

where k_{AB} is the Bohart–Adams kinetic coefficient (L mg^{-1} min^{-1}), N_0 is the saturation concentration (mg l^{-1}), U_0 is the superficial velocity (cm min^{-1}), and z is the bed depth (cm).

2.6.2 The Yoon-Nelson Model

Another model was also developed by Yoon and Nelson (1984) for analyzing the column's breakthrough performance. The model is based on the assumption that the decreasing rate of the adsorption for each of the adsorbate particles is directly proportional to both the adsorbate adsorption and the adsorbate breakthrough on the adsorbents [24].

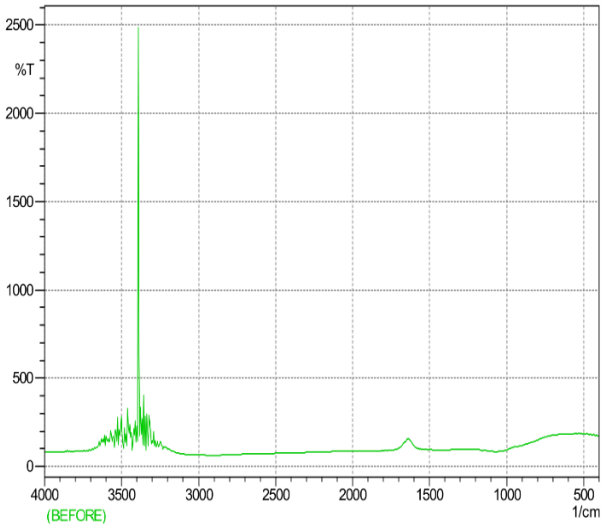

Figure 1: FTIR plot before activation

Yoon-Nelson model required no elaborate details or data concerning the characteristics of adsorbate, type of adsorbent, or its physical features. It is given by

$$\ln\left(\frac{C_2}{C_1-C_2}\right) = k_{YN}t - \tau k_{YN} \quad (12)$$

where k_{YN} is the rate constant (min^{-1}) and τ is the time required for 50% adsorbate breakthrough (mins).

2.6.3 BDST model

The breakthrough data in terms of bed depth and service time is predicted using this simple and convenient method. This model assumes that adsorption is governed by reaction that takes place between adsorbate and unused adsorbent with

respect to time of interaction between them. A linear plot of Z (bed depth, cm) versus t (min) gives the value of N_0 adsorption capacity and K_a (rate constant). A general relationship of the BDST model is given below [25].

$$t = \frac{N_0 z}{C_1 u} - \frac{1}{kC_1}\ln\left(\frac{C_1}{C_2} - 1\right) \quad (13)$$

where C_1 and C_2 are inlet and outlet concentration respectively, k is the adsorption rate constant (l/mg min), No is the adsorption capacity (mg/l) z is the bed depth (cm) and t is the service time to breakthrough(min). The dynamic adsorption model parameters were determined by fitting the three models with experimental data through linear regression. Using the coefficient determination (R^2) and analysis of error, the superiority or suitability of each model was measured. The effect of various parameters on the adsorption of Malachite Green was first analyzed graphically and then attempted theoretically to justify the observation made from the graphical analysis. The range of variables covered is compiled.

3 Results and Discussions

3.1 Characterization of Hen feathers

1) Fourier Transform Infra-Red Spectroscopy (FTIR): Infrared spectroscopy belongs to the group of molecular vibration spectroscopy's which are molecule-specific and give direct information about the functional groups, their kind of interactions, and orientations. Its sampling requirements allow the gain of information from liquids/gases and in particular from solid surfaces. The shift of bands and changes in signal intensity allows the identification of the functional groups involved in dye sorption.

2) FTIR spectrum of untreated powder: FTIR spectrum of untreated Hen Feathers powder is presented in Fig.1 the peak at 1157 cm^{-1} denotes the involvement and participation of =CH bend alkenes mode in adsorption. The band at 3230 cm^{-1} and 3273 cm^{-1} indicates Hydroxyl, Alcohol, and Phenol groups. The peak at 3591 cm^{-1} and 3622 cm^{-1} indicates O-H (Alcohol) group.

3) FTIR spectrum of treated powder: FTIR measurements for MG dye loaded with Hen Feathers are shown in Fig. 2 the peaks at 680 cm^{-1} indicate Alkyl halides (C-Cl). The peak at 1465 cm^{-1} indicates Alkyl C-H stretch mode. The peak at 3217 cm^{-1} indicates Asymmetric -CH_2-, Symmetric CH_3, and -CH_2 stretching vibrations. The peak at 3286 cm^{-1} indicates the Amine N-H group. The bands at 3759 cm^{-1}, 3801 cm^{-1}, and 3817 cm^{-1} indicate Non bonded O-H stretch Hydroxyl group. The peak at 3992 cm^{-1} indicates the O-H group as well as Amine N-H stretch modes.

3.2 Fixed Bed Column Adsorption Study on BTC

Continuous flow columns are used by most separation and purification processes that employ sorption technology. In biosorption applications, a packed bed column is effective process equipment for continuous wastewater treatment, as it makes the best use of the concentration difference known to be a drive for biosorption and allows more efficient utilization of biosorption capacity, and leads to a better quality of the effluents. In the present study, a fixed bed is operated to generate biosorption data. Activated hen feathers powder has exhibited higher MG uptake in batch biosorption experiments. So, the fixed bed is formed with Activated hen feathers powder. A continuous flow-packed bed column is employed to investigate MG biosorption as a function of the flow rate of an aqueous solution, initial MG concentration, and bio sorbent bed height. The performance of the packed bed column is analyzed using breakthrough curves. The experimental results and application of various models are discussed below.

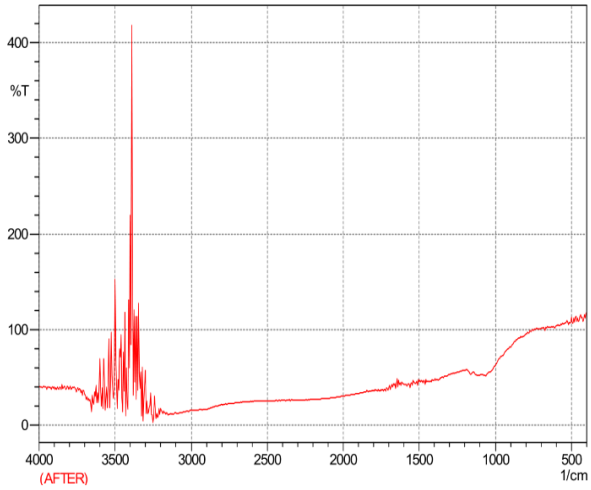

Figure 2: FTIR plot after activation

3.2.1 Effects of adsorbate Flow rate

In a continuous mode study, the flow rate has a significant effect on the performance of the column, and this is often a crucial parameter for evaluating the efficiency of adsorbent during a continuous treatment process of effluents on the pilot or industrial scale. Columns were run at different flow rates such as 4, 8, and 12 ml/min with a fixed bed height of 8cm at an initial concentration of 20 mg/L to study the effect of flow rate in the performance of activated Hen feathers powder bed. Initially, the pH of the aqueous solution is maintained at 4. Fig 3.3 represents the breakthrough curves for the flow rates of 4, 8, and 12 ml/min. The breakthrough and exhaust times correspond to C2/C1=0.1 and C2/C1=0.9 respectively. In this effort, the flow rate was varied so that we can achieve the maximum removal of MG dye adsorbate, and the maximum uptake was found to be achieved at a flow rate of 4 ml/min. The percentage removal of MG dye was achieved at about 56.603-51.067% at this flow rate (4–12 ml/min) and the removal % decreased with increasing flow rate. For the flow rates of 4, 8, and 12 ml/min, with a constant bed height of 8cm and inlet malachite green dye adsorbate concentration of 20mg/l. the breakthrough times are 165,120 and 105 min respectively while the exhaust times are 450, 330, and 270 min respectively. The time taken to achieve breakthrough has reduced with the increase of the flow rate. Similarly, the exhaustion times were increased with reduced flow rate contact with bio sorbent, which showed a greater removal of MG, in insufficient residence time of the solute in the column and diffusion of the solute into the pores of the bio sorbent is less, and therefore the solute left the column before equilibrium occurred. The maximum uptake capacities for flow rates of 4, 8 and 12 min/min are found to be 1.67, 2.21 and 2.829 mg/g respectively. The BTCs showed that originally the adsorption was very rapid for all three flow rates (4, 8 and 12 ml/min), which can be related to the supply of reaction sites ready to capture dye molecules around or inside the cells. In the next stage, the uptake became less effective because of the gradual occupancy of those sites. Even though at a progressively lower efficiency, the column was capable of accumulating MG dyes even after breakthrough occurs. It was found that the BTC became steeper when the flow was increased, with which the break point time and adsorbed dye concentration was

decreased. The reason for this is explained as that when the residence time of MG adsorbate in the column was not long enough for adsorption equilibrium to be reached at that flow rate, the front of the adsorption zone quickly reached the top of the column, which saturated the column early, and the MG solution left the column before equilibrium occurred [26]. Thus, a reduction in removal efficiency occurs as the contact time of MG dyes with Hen Feathers is very short at the higher flow rate. At a low rate of influent, MG had more time to contact the activated Hen feather powder which resulted in a shallow adsorption zone as well as higher removal of MG dye molecules in the column. Hence, from Table 2, it can be seen that the dye removal percentage of the column is decreased with an increase in the flow. As shown in Table 2, the breakthrough time can be observed to be decreased from 165 to 105 min for the flow rates between 4 and 12 mL/min respectively. Mass transfer fundamentals can be used to explain the variation within the slope of the BTC and adsorption capacity. At higher flow, the speed of mass transfer increases, i.e., the quantity of dye adsorbed onto the unit bed height (MTZ) increases with increasing flow, resulting in faster saturation at a higher flow rate [27]. The theory was further supported by the results of MTZ or unused beds (HUNB) presented in Table I.

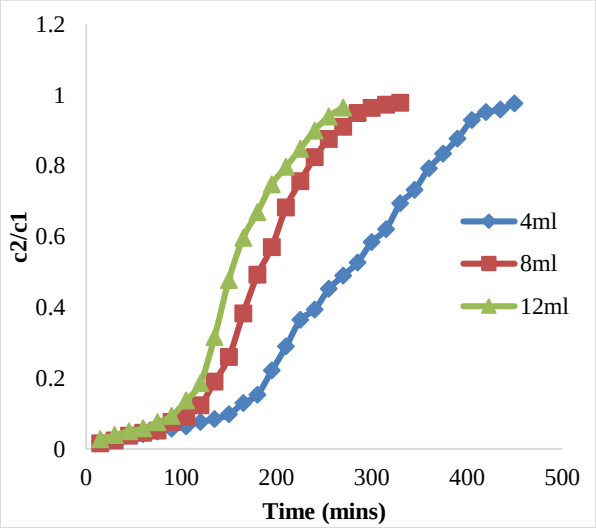

Figure 3: Plot for varying flow rate of Adsorption of Malachite Green using Hen Feathers

3.2.2 Effect of adsorbate inlet concentration

One of the limiting factors is the effect of initial dye concentration in the inlet flow and it is also the main process variable. Since a given mass of adsorbent can only absorb a limited amount of dye, the initial dye concentration of the effluent is very important. As a result, the more concentrated an effluent gets, the quantity of effluent that a hard and fast mass of adsorbent can purify is decreased. To study the effect of adsorbate concentration on the performance of the BTC, the MG dye concentration was varied between 10 and 30 mg/l in the column experiments. Other parameters like bed height (8 cm) and flow rate (8ml/min) were kept constant during the experiment. Fig.3 shows the sorption BTCs obtained for adsorbate concentrations of 10, 20, and 30 mg/L. As seen in Fig.3, for low inlet concentrations of MG dye, the surface of the adsorbent was saturated with MG dye after a long time and the breakthrough also occurred late, whereas, in the case of higher MG concentration, the breakthrough occurred in a less amount of time. At lower inlet MG concentration, the breakthrough was flatter which indicates a relatively wide MTZ and film-controlled process. On the contrary, the BTCs were sharp at high inlet MG concentration which indicates a relatively smaller MTZ and intra-particle diffusion-controlled process. The results were found to be similar to other researchers [28-30]. Figure 5 shows that the breakthrough time was reduced with the increasing influent MG concentration. These results show that the change of concentration gradient affects the saturation rate and breakthrough time [31]. The possible explanation is that, as the MG concentration increased, more adsorption sites were being covered. The more the influent concentration is, the steeper the slope of BTC and the smaller the breakthrough time. Reduced inlet MG dye concentrations gave delayed BTCs and the treated volume was also more since the lower concentration gradient caused slower transport due to reduced diffusion coefficient [32,33]. The binding sites of the hen feathers bed saturated more quickly leading to earlier breakthrough and exhaustion time at the highest MG concentration (30 mg/l) which can be seen in table 2. In Table 2, different BTCs parameters of packed bed column for the removal of MG by hen feathers at different MG solution concentrations were shown. Table 2 shows that there is an increase in the amount of total sorbed dye, equilibrium dye uptake, and MTZ, whereas the total percentage of removal is reduced with increasing inlet MG dye concentration. The total amount of MG dye adsorbed was found to increase from 17.2649 to 28.3985mg with an increase in initial MG dye concentration from 10 to 30 mg/L, and at the same time, the percentage MG removal decreased from 53.287 to 49.3% when the inlet MG concentration increased from 10 to 30 mg/l (Table 1). Due to high inlet MG concentration providing the higher driving force for the transfer process to overcome the mass transfer resistance there is an increase in uptake capacity of the adsorbent. Similarly, at lower concentrations, all dye molecules present within the solution interact with the binding sites of the adsorbent, facilitating higher adsorption. However, all adsorbents have a limited number of binding sites, which become saturated at a certain concentration [34]. Therefore, more dye molecules are left unadsorbed in the solution at higher concentrations, due to the saturation of binding sites resulting in reduced adsorption efficiency.

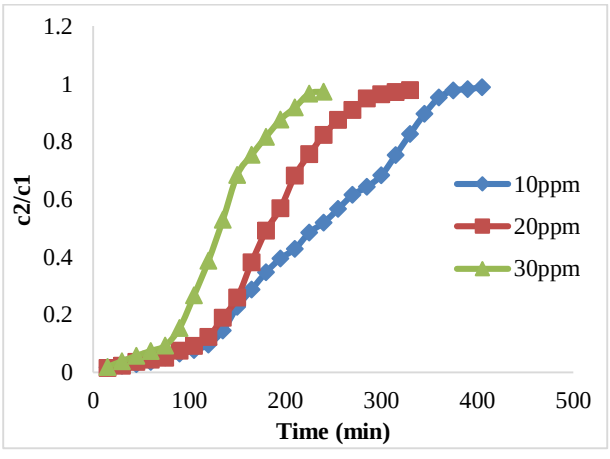

Figure 4: Experimental breakthrough curves (BTC) for adsorption of MG dye onto activated hen feather powder at different initial MG dye concentrations (conditions: MG dye flow rate = 8 ml/min, bed height = 8 cm, temperature = 28 ± 1 C)

3.2.3 Effect of adsorbent bed height

Bed height is one of the important parameters for the performance of the biosorption process, particularly in the continuous column process. The experiments were conducted for three different bed heights 6, 8, and 10 cm using 9.147, 12.196, and 15.245 g of bio sorbent. The steepness of all the BTCs may be a strong function of bed height as the accumulation of adsorbate in a fixed-bed column depends on the number of adsorbents inside the column. Dye solution having influent MG concentration 20 mg/l, pH 4, and flow 8 ml/min was skilled the column by varying the bed height in order to get the effect of bed height on the BTC. Figure 4 shows the performance of BTCs at different bed heights of 6,8 and 10 cm. As shown in Fig.4, the breakthrough time varies with the bed height. The results showed that as the bed height was increased from 6 to 10 cm, the breakthrough time increased from 75 min to 135 min. The bed capacity and biosorption efficiency were also found to be increased with increasing bed height. As the bed height increased, the residence time of MG solution inside the column increased, allowing the dye molecules to diffuse deeper into the activated hen feather powder which resulted in the higher dye removal efficiency [35,36]. Due to an increase in the surface area of hen feathers, higher uptake was observed at the highest bed height, which in turn caused increased availability of binding sites for the attachment of MG dye molecules for the adsorption process [37]. With the rise in bed height, the volume of treated effluent, breakthrough time, and exhaustion time was also increased (Table 3). As the breakthrough time determines the parameter of the process, the more the breakthrough time is, the better the intra-particulate phenomenon and also the higher the adsorption capacity of the column will be [38]. This can be attributed to the fact that when there was an increase in bed height, the axial dispersion was decreased in the mass transfer, and as a result, the diffusion of the dye molecules into the adsorbent got increased. Thus, the solute got enough time to diffuse into the whole of the adsorbent, staying in the column for a long time and treating a greater volume of effluents [39].

The successful design of a column biosorption process requires the prediction of a concentration-time profile. Various mathematical models have been used to describe fixed bed biosorption. Among these, many studies have been reported on the testing of the kinetics of biosorption in the column using the Bohart-Adams model. The other models which were tested for fixed-bed column biosorption data include BDST, Thomas, and Yoon-nelson. In the present study, an attempt was made to find out the best model describing the biosorption kinetics in the column.

3.3.1 Application of Bohart-Adams model

Bohart-Adams model was applied to the experimental data for description of the initial part of the breakthrough curve.

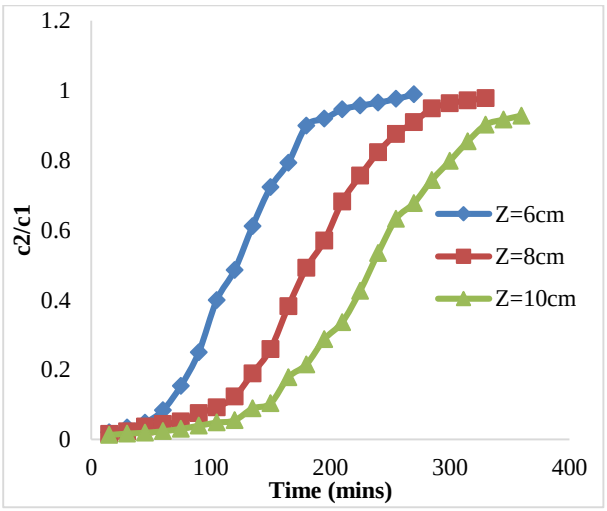

Figure 5: Experimental breakthrough curves (BTC) for adsorption of MG dye onto activated hen feather powder at different initial MG dye concentrations (conditions: MG dye flow rate = 8 ml/min, initial MG dye concentration = 20mg/l , temperature = 28 ± 1 C)

3.3. Application of Different Breakthrough curve Models

Table 2: Fixed bed parameter studies

Flow rate, ml/min	Time, min	Volume of effluent, ml	m_{total} mg	q_{total} mg	$q_{e,exp}$ g/g	%Y	MTZ	H_B
4	450	1.815	36	20.3772	1.67	56.603	3.17	4.829
8	330	2.660	52.8	26.9634	2.21	51.067	2.694	5.306
12	270	3.258	64.8	34.508	2.829	53.25	2.6208	5.3796
Initial concentration, mg/l								
10 mg/l	405	3.264	32.4	17.2649	1.415	53.25	3.3552	4.6448
30 mg/l	240	1.933	57.6	28.3985	2.328	49.3	2.4848	5.5152
Bed height, cm								
6 cm	270	2.176	43.2	17.4031	1.902	40.285	2.2392	3.7608
10 cm	360	2.892	57.6	35.0467	2.2988	60.845	3.51	6.49

Table 3: Bohart-Adams model parameters

Flow rate, ml/min	Time, min	The volume of effluent, ml	m_{total} mg	q_{total} mg	$q_{e,exp}$ mg/g	%Y	MTZ	H_B
4	450	1.815	36	20.3772	1.67	56.603	3.17	4.829
8	330	2.660	52.8	26.9634	2.21	51.067	2.694	5.306
12	270	3.258	64.8	34.508	2.829	53.25	2.6208	5.3796
Initial concentration, mg/l								
10mg/l	405	3.264	32.4	17.2649	1.415	53.25	3.3552	4.6448
30mg/l	240	1.933	57.6	28.3985	2.328	49.3	2.4848	5.5152
Bed height, cm								
6cm	270	2.176	43.2	17.4031	1.902	40.285	2.2392	3.7608
10cm	360	2.892	57.6	35.0467	2.2988	60.845	3.51	6.49

The mathematical equation of the model can be written as:

$$ln\frac{C_2}{C_1} = k_{AB}C_1t - k_{AB}N_0\frac{z}{U_0} \quad (14)$$

where C_1 and C_2 are the inlet and outlet adsorbate concentrations respectively in mgL-1, z is the bed height (cm), U_0 is the superficial velocity (cm/min), N is the saturation concentration (mg/L) and K_{AB} is the kinetic constant (L/mg min). The characteristic parameters such as saturation concentration (N_0) and the kinetic constant (K_{AB}) were to be assumed in this approach. In the present study, the range of time considered is shown in the table. Time considered (linear portion) for calculation of model parameters. Values of $\ln(C_2/C_1)$were plotted against t at different flow rates, initial MG concentration, and bed heights are shown in Fig below. The kinetic constant (K_{AB}) and saturation concentration (N_0) values were calculated from the slope and intercept of the curves, respectively, and are given in the table. From this table 3, it is observed that the kinetic constant, K_{AB} increased with an increase in flow rate, decrease in initial concentration, and bed height. This shows that the overall system kinetic was dominated by external mass transfer in the initial part of biosorption in the column. Although the Bohart-Adams model provides a simple and comprehensive approach for running and evaluating sorption-column test., its validity is limited to the range of conditions used.

3.3.2 Application of the bed depth service time (BDST) model

Experimental data obtained from colin studies were used to plot the BDST curve. The BDST model is expressed as:

$$t = \frac{N_0z}{C_1u} - \frac{1}{kC_1}\ln(\frac{C_1}{C_2} - 1) \quad (15)$$

where C_1 and C_2 are inlet and outlet concentration respectively, k is the adsorption rate constant (l/mg min), No is the adsorption capacity (mg/L) z is the bed depth (cm) and t is the service time to breakthrough (min). K and No values were calculated from the slope and intercept of the plot between $\ln(C_1/C_2\text{-}1)$ versus time t at different biosorption parameters such as flow rate, inlet adsorbate concentration, and bed height were shown. The estimated values of characteristic parameters like k and N_0 are presented in Table 4.

Table 4: BDST model parameters

Flow rate, ml/min variable, z= 8cm, C_1 =20 mg/l			
Q, ml/min	Kab*10^-4	No, mg/l	R2
4ml	8.35	375.4981	0.9855
8ml	13.14	514.8478	0.9954
12ml	13.95	673.6306	0.9886
Initial malachite green concentration, mg/l variable, Q=8ml/min, z=8cm			
10mg/l	20.59	317.6645	0.9723
30mg/l	11.23	566.0297	0.9949
Bed height, cm variable, Q=8ml/min, C_1=20mg/l			
6cm	16.48	480.6794	0.9904
10cm	10.68	534.6242	0.9939

3.3.3 Application of the Yoon-Nelson model

A simple theoretical model developed by Yoon-Nelson was also tested to investigate the breakthrough behavior of MG on Hen feathers powder. The linearized model for a single component system is expressed as:

$$\ln\left(\frac{C_2}{C_1-C_2}\right) = k_{YN}t - \tau k_{YN} \quad (16)$$

where k_{YN} is the rate constant (1/min), t is the time required for 50% adsorbate breakthrough (min). The values of k_{YN} and t was estimated from the plots drawn between $\ln\left(\frac{C_2}{C_1-C_2}\right)$ versus time t at different flow rates, bed heights, and initial concentration are shown in figs. With the increase in flow rate and initial MG concentration, thek_{YN} values increased whereas the t showed the reverse trend. The increase in bed height decreases the k_{YN} and reverse trend on t was observed. The predicted uptake values from the model, experimental uptake values along with values of $k_{YN}$and t and statistical parameters are listed in the table from Table 5 it can be seen that in most of the cases theoretical uptake capacity is very close to those predicted by the Yoon-Nelson model.

Table 5: Yoon-Nelson model parameters

Flow rate, ml/min variable, z= 8 cm, C_1 =20 mg/l			
Q, ml/min	k_{YN}	t	R^2
4ml	0.0165	265.1152	0.9855
8ml	0.0262	181.6985	0.9954
12ml	0.0276	158.6667	0.9886
Initial malachite green concentration, mg/l variable, Q=8 ml/min, z=8cm			
10 mg/l	0.02	225.07	0.9723
30 mg/l	0.0335	133.4179	0.9949
Bed height, cm variable, Q=8 ml/min, C_1=20 mg/l			
6cm	0.0326	127.3436	0.9904
10cm	0.0212	236.6368	0.9939

4 Conclusions

The present work aims to guage the suitability of activated hen feathers as bisorbents for the removal of Malachite Green from aqueous solutions during a continuous process. Fixed bed studies. From these studies, the subsequent conclusions are drawn

- The breakthrough time (165 to 105 min) and exhaust time (450 to 270 min) have decreased with an increase in flow from 4 to 12 ml/min.
- The breakthrough time (135 to 90 min) and exhaust time (405 to 240min) have decreased with an increase in initial malachite green concentration from 10 to 30 mg/l.
- The breakthrough time (75 to 135 min) and exhaust time (270 to 360 min) have increased with an increase in bed height from 6 to 10 cm respectively.
- Bohart-Adams, BDST model, Thomas, and Yoon-Nelson are applied to predict breakthrough curves and determine the characteristics of parameters of the column.
- Prominent and unique characteristics of features of the respective models like service time (Hutchins BDST model), biosorption capacity (Bohart-Adams model), and 50% breakthrough (Yoon-Nelson model) were determined.

Based on the precise characteristics BDST and Yoon-Nelson model best described the kinetics of malachite green biosorption in the column.

Ethical issue

Authors are aware of and comply with, best practices in publication ethics specifically about authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. Authors adhere to publication requirements that

submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that no conflict of interest would prejudice the impartiality of this scientific work.

Authors' contribution

All authors of this study have a complete contribution to data collection, data analyses, and manuscript writing.

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