ISSN 2320-5407 International Journal of Advanced Research (2015), Volume 3, Issue 7, 521-529

ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Fixed Bed Column Study and Adsorption Modelling on the Adsorption of Malachite Green dye from wastewater using Acid Activated Sawdust

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Manuscript Info

Manuscript History:

Received: 15 May 2015
Final Accepted: 22 June 2015
Published Online: July 2015

Key words:

Adsorption, Acid Activated Sawdust, Breakthrough Curve, Fixed Bed Column, Malachite Green

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Abstract

The sorption capability of Acid Activated Sawdust for removing Malachite Green from wastewater was evaluated in a fixed bed column. The column experiment was conducted by varying the bed height, initial dye concentration and solution flow rate. An increase in bed depth extended the life of the column while an increase in flow rate and initial concentration exhausted the column earlier. Several column adsorption models were applied to the experimental data. The adsorption capacity using the Thomas model was found to be 10.06 mg/g. Among the various models applied the Bohart-Adam model fitted the experimental data well with an r^2>0.9. The Yoon–Nelson model also estimated the 50% breakthrough curve and provided the estimate break-through time for the column systems. The results indicated that Acid Activated Sawdust could be used for adsorption of Malachite Green containing waste water.

INTRODUCTION

Dyes are chemical substances which are used during the manufacturing process to impart value to the final product. Industries such as tanneries, food, paper and pulp use dyes and pigments to colour their products. Colour is an observable pollutant whose presence in even a very minute amount of colouring substance makes it undesirable due to its appearance [1]. Besides this the dye effluent from industries has high Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) values. Also, the reduction in light penetration leads to the instability of the biotic component of the receiving body [2]. They may also be a complication if their partial deterioration takes place under anaerobic conditions by the bacteria leading to creation of toxic amine [3]. Therefore the threats posed by dyes have not gone unnoticed and over the past several years many different techniques have been researched for the effective removal of dye from the industrial effluent.

The conventional methods adopted by industries for the removal of colour were froth flotation, coagulation and flocculation [4]. However these techniques were inefficient and thus the attention shifted on innovating new techniques which were not only highly efficient but were also less capital extensive. Recently researchers have shifted their focus on the use of adsorption technique for the removal of dye pollutants from industrial effluent. A survey of the available literature reveals a large number of waste products which have been successfully used for the adsorption of various pollutants [5-11].

The present paper attempts to investigate the usability of acid treated sawdust of Tectona Grandis for the removal of Malachite Green (MG), a tri-phenyl methane dye from the industrial effluent. MG has long been used as colouring agent for leather products, cotton and wool [12]. In addition, as an external applicant, its use as an antiseptic and antifungal has been clearly established in literature [13-14]. However the presence of nitrogen makes it toxic, hazardous and carcinogenic if consumed orally [15]. Sawdust is a waste material produced during manufacture of woodwork. It is an undesirable material which is collected and dumped in landfills. Even though considerable research has been done on the use of acid activated sawdust (AAS) for the removal of various dyes and metals, none has established a relationship between the removal capabilities of MG by AAS.

Furthermore, batch adsorption processes may not be convenient during the industrial operations with high flow rates. Fixed bed columns can be used continuously at higher flow rates for effective adsorption. In this study column study has been performed to understand the adsorption capability of MG by AAS.

2. Materials and Methods

2.1 Adsorbent Preparation

Sawdust of Tectona Grandis was collected from a local wood market based in Keshav Puram, New Delhi and washed under tap water to remove any dust and impurities on the sawdust surface. The sawdust was then sun dried for 2 days to remove the moisture content after which the dried sawdust was ground in a crushed to obtain finer aggregates prior to transportation to the laboratory. In the laboratory, the dried sawdust was mixed with 1.2 N conc. H_2SO_4 (35 % w/v) and the mixture was allowed to react for a period of 24 hours at room temperature. The reacted mixture was extracted and washed with 0.1N $NaHCO_3$ solution to neutralize the solution pH. The sawdust was then washed with distilled water and finally dried in an oven at 105° C till dry. The dried sawdust was subsequently passed through a sieve to obtain an average grain size of 500 µm.

2.2 Preparation of dye solution

Analytical grade chemicals and reagents were used throughout the course of the experiment. The stock solution of MG was obtained by dissolving predetermined amounts of MG in distilled water to obtain a concentration of 1000 mg/L. Different concentration solutions of MG were obtained by dilution the stock solution with distilled water.

2.3 Column Experiments

For the column experiments, a PVC column with an inner diameter of 3.85 cm and a length 22.5 cm was used. The bottom of the column was sealed off with a plastic cap to prevent the loss of adsorbent during the infiltration process. The design of the column experiment is illustrated in fig 1. AAS of known quantity was filled in the column and wetted with distilled water in the downward direction in order to remove any air trapped between the particles. The dye working solution was continuously fed in the downward direction using a peristaltic pump. At different pre-defined intervals samples were collected in a test tube and measured for residual dye concentration in a spectrophotometer at 618nm wavelength.

2.3.1 Effect of Initial Dye Concentration

Working solutions of 200 and 500 mg/L were used as an influent to study the ability of sawdust to remove the MG dye of different concentrations. The flow rate during the experiments was controlled at 100 cc/hr while the bed depth remained at 7.5 cm. The effluent was collected at pre-defined intervals to measure the residual dye concentration.

2.3.2 Effect of Flow Rate

The contact period between the dye and the sawdust surface is directly influenced by the rate of flow of the influent. During this study, the flow rate of influent dye was varied from 100 to 200 cc/hr. The initial dye concentration remained at 500 mg/L. The effluent was collected at pre-defined intervals to measure the residual dye concentration.

2.3.3 Effect of Bed Height

To evaluate the effect of bed height, different amounts of sawdust is filled in 3 separate columns up to a height of 7.5, 15 and 22.5 cm respectively. The working MG dye solution of 500 mg/L was fed into the columns separately with a flow rate of 100 cc/hr. At different pre-defined intervals the effluent was collected for analysis.

3. Results and Discussion

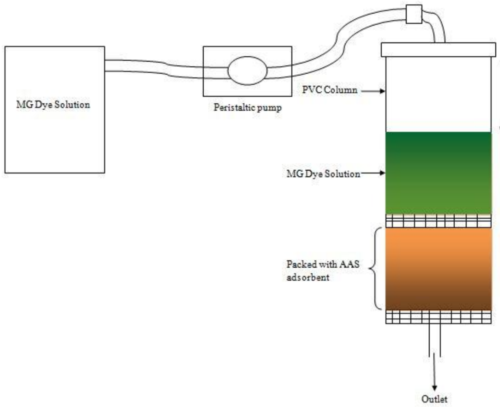

Fig 1. Continuous column bed Diagram

3.1 Effect of bed Study

3.1.1 Effect of initial dye concentration

In order to establish optimum conditions for the adsorption of MG dye in a column by AAS, the initial dye concentration is varied to 200 and 500 mg/L. Fig. 2 illustrates the breakthrough curve between C_t/C_o (Concentration at time t/ initial concentration) and time t. With an increase in initial concentration from 200 to 500 mg/L, the value of C_t/C_o increases from 0.3 to 0.45. This represents a steeper slope in case of 500 mg/L dye concentration. The breakthrough time decreases from 120 min to 70 min with an increase in initial dye concentration which is due to a larger mass transfer coefficient. The presence of more dye ions provided an increased competition for the lesser available biding sites on the adsorbent [16]. Therefore it is concluded that the adsorption process is concentration dependent. Similar results were obtained for biosorption of reactive black by bamboo waste based activated carbon [17].

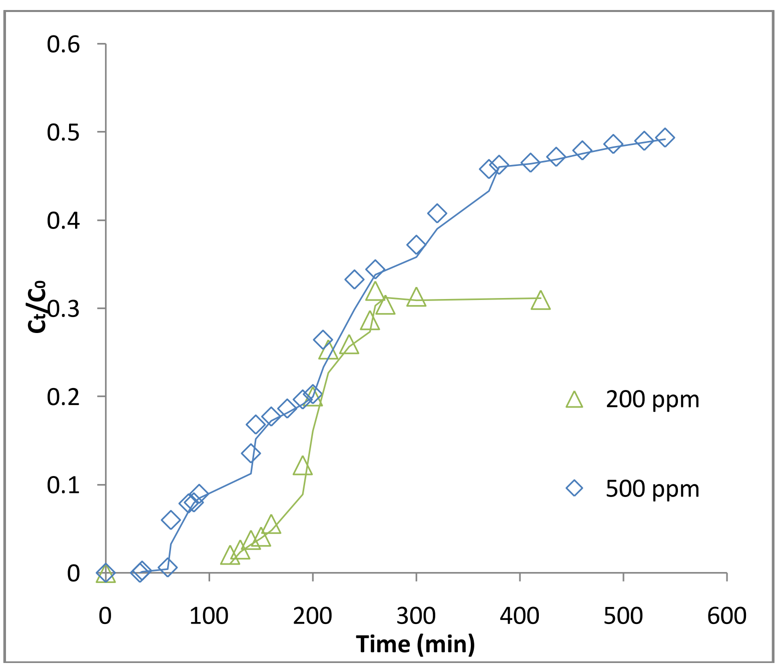

Fig 2. Breakthrough curve for adsorption of MG by AAS at different initial MG concentrations.

3.1.2 Effect of the solution flow rate

The influent flow rate as seen from Fig 3. has a significant effect on malachite green adsorption in the fixed bed column. The flow rates were varied from 100 to 200 cc/hr with a constant bed height and initial concentration of 500 mg/L. The breakthrough is achieved faster at a higher influent flow rate which is visible from the fact that the breakthrough time decreases from 75 min to approximately 25 min as flow rate increases from 100 to 200 cc/hr. The inadequate time experienced by the adsorbent strips the dye solution the privilege of diffusing into the adsorbent pores which consequently decreases the adsorbent's adsorption capacity. The high flow rates didn't allow for sufficient time to achieve equilibrium conditions before the exit of dye from the column leading to a faster breakthrough at higher flow rate.

3.1.3 Effect of bed height

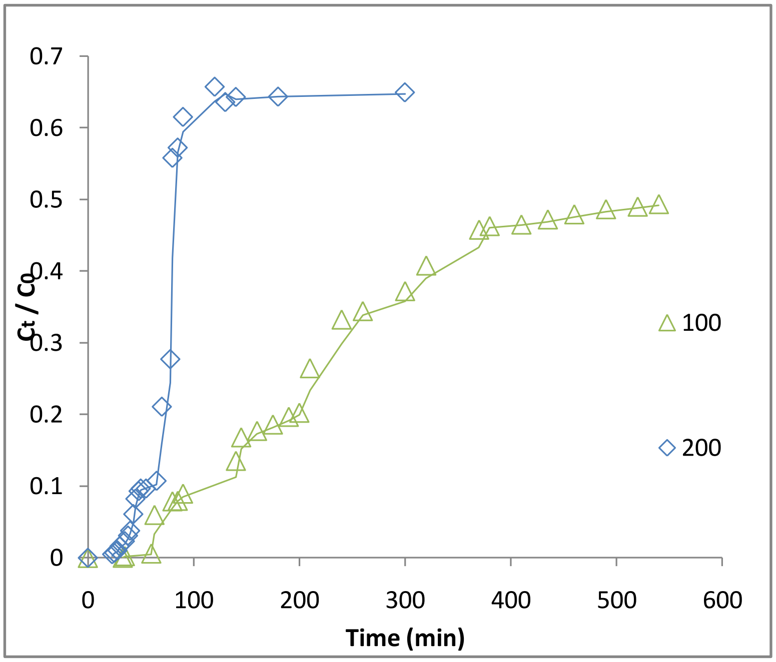

Fig 3. Breakthrough curve for adsorption of MG by AAS at different solution flow rates.

To determine the breakthrough of MG dye, various bed heights i.e. 7.5, 15, 22.5 cm were applied and the results are represented in Fig 4. It is observed from the breakthrough curve that with an increase in bed depth, slope of breakthrough curve decreases [18]. An increase in breakthrough time from 50 min at 7.5 cm to 210 min at 15cm depth and subsequently to 570 min at 22.5 cm is observed from the graph. The variation may be due to an increase in bed height which offers more of the surface area to MG ions resulting in more contact time with AAS which in turn results into lower concentration of dye in the effluent. Higher surface area of AAS generates more active sites for adsorption to take place and it also broadens the mass transfer zone length [17-19].

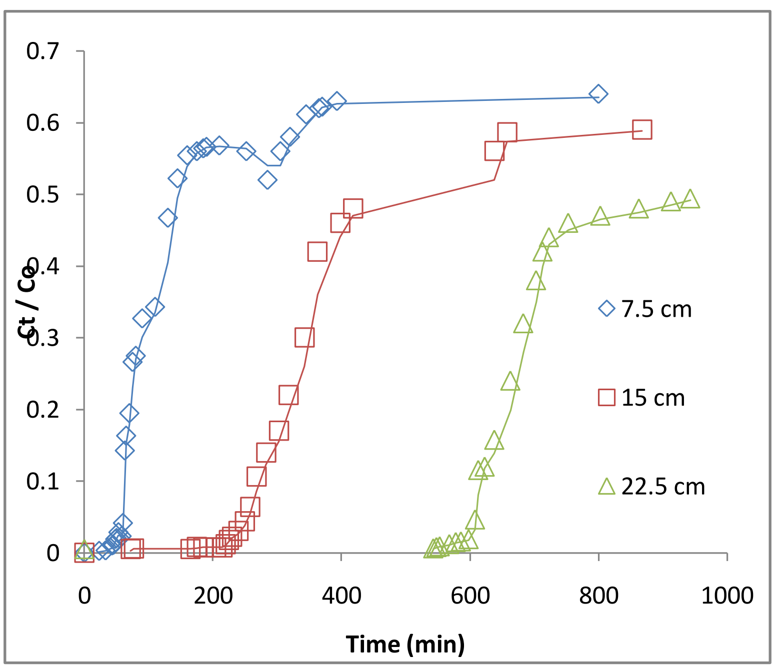

Fig 4. Breakthrough curve for adsorption of MG by AAS at different bed heights.

3.2 Analysis of Fixed Bed Models

3.2.1 Bohart- Adams Model

Bohart Adams Model is assumed to follow "step isotherm" in which the rate of adsorption is found to be proportional to the fractional adsorption capacity available at the surface of an adsorbent [17] . This concept also follows the basic principle of surface reaction theory [20-21]. The linear expression of the model provides characteristic parameters such as kinetic constant (k) and adsorption capacity (N_o). The following is the expression:

$$t_b = \frac{N_o Z}{C_o v} - \frac{\ln(\frac{C_o}{C_b} - 1)}{k_{AB} C_o} \quad (1)$$

Where, k_{AB} is the Bohart Adams rate constant (L/mg-min), C_o and C_b are the initial and breakthrough concentration in mg/L respectively, N_o is the adsorption capacity of adsorbent (mg/l), v and t_b are linear velocity and breakthrough time respectively (min), Z is the bed depth in cm. The above equation can be generalised in a simpler form as

$$t_b = aZ + b \quad (2)$$

$$a = \frac{N_o}{C_o v} \quad (3)$$

$$b = \ln[\left(\frac{C_o}{C_b}\right) - 1] * \frac{1}{C_o k_{AB}} \quad (4)$$

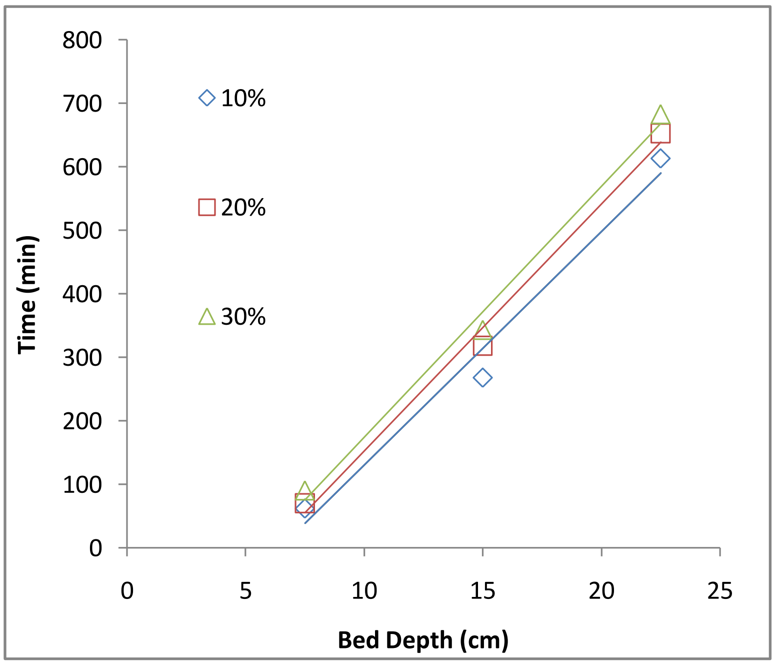

Fig 5. Bohart Adams Linearized Model

A linear plot between time and bed depth representing iso-removal points of different bed depths at constant flow rate and initial malachite green concentration is shown in Fig 5. Values of slope and intercept are further used to calculate the rate constant and adsorption capacity as depicted in Table 1.

Adsorption capacity (N_o) lies in the range of 671.88 -721 mg/L for iso- removal lines (10%, 20% and 30%). A slight decrease in the value of kinetic constant from $1.86*10^{-5}$ to $0.77*10^{-5}$ is observed with increase in removal percentage. Further, it is clear from the high value of Regression constant that Bohart – Adams model explains the sorption process in a better way.

Table 1. Bohart-Adams model constants for the adsorption of MG on AAS in a fixed bed column

Iso –Removal Percentage	A_i (min/cm)	B_i (min)	N_o (mg/L)	K_{ab} (L/min.mg)	R^2
10	36.73	-236.6	671.88	$1.86*10^{-5}$	0.979

20	38.86	-236	710.5	$1.17*10^{-5}$	0.992
30	39.53	-221	722.72	$0.77*10^{-5}$	0.992

3.2.2 Clark model

This model is based on Freundlich isotherm model where Freundlich constant n=2.06 is used for the calculation of Clark model parameters A and r (min^{-1}) [17] [22-23] .The linearized form of the model is represented as:

$$\ln[(\frac{C_o}{C_t})^{n-1} - 1] = -rt + \ln A \quad (5)$$

The predicted Clark model parameters calculated are depicted in Table 2. It is observed from Table 2, that the value of rate constant decreases and the value of A increased with an increase in bed height.

Table 2. Clark model constants for the adsorption of MG on AAS in a fixed bed column

Intial Concentration (mg/L)	Bed Height (cm)	Flow Rate (cm^3/hr)	Rate constant (L/min)	A	R^2
500	7.5	100	0.065	1396.8	0.811
500	15	100	0.024	2881.3	0.937
500	22.5	100	0.019	1745	0.808
500	7.5	200	0.006	17.3	0.903
200	7.5	100	0.02	476.27	0.903

3.2.3 Thomas model:

Thomas model which follows the Langmuir kinetics of adsorption and desorption [24] is widely used to calculate the performance of a column and predict its breakthrough curves [18]. It is based on the assumption of negligible axial dispersion. Its main limitation is that the model is based on second order kinetics and hence doesn't restrict the sorption by a chemical reaction and is controlled by mass transfer at the surface [25]. The model is represented by the following formula:

$$\ln\left[\frac{C_O}{C_t} - 1\right] = \frac{k_{th} q_0 m}{Q} - k_{th} C_o t \quad (6)$$

Where K_{th} is the Thomas rate constant (mL min^{-1} mg^{-1}), Q_o is the equilibrium Malachite green uptake per g of the adsorbent (mg/ g). X is the amount of adsorbent in the column (g), C_o is the influent malachite green concentration (mg/L), C_t is the concentration of effluent at time t (mg/L), v is flow rate (ml/min). C_t/C_o is the ratio of effluent and influent malachite green concentrations. Thomas constant Q_o and K_{th} can be obtained through graph plotted between ln [(C_o/C_t)-1] against t [26].

Table 3. Thomas model constants for the adsorption of MG on AAS in a fixed bed column

Bed Height (cm)	Flow Rate (ml/min)	Initial dye Conc. (mg/L)	Q_o (mg/g)	K_{th} (L/mg min)	R^2
7.5	100	500	4.5	9.2*10-5	0.8
15	100	500	10.06	5*10-5	0.947
22.5	100	500	7.4	4.6*10-5	0.88

The predicted Thomas parameters are given in Table 3. Here, the value of K_{th} decreases with an increase in bed depth. Value of K_{th} decreases from 9.2 x 10^{-5} to 4.6 x 10^{-5} as the bed depth increases from 7.5 to 22.5 cm.. Adsorption capacity is found to be in range of 4.5-10.06 mg/g which is much better than the various adsorbents used till now for malachite green.

3.2.4 Yoon-Nelson:

This model is applied to a range of concentrations of the effluent between the breakthrough and saturation time of the column and is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and probability of adsorbate breakthrough on the adsorbent [25].The equation of Yoon-Nelson model can be given as:

$$\ln\left[\frac{C_t}{C_o - C_t}\right] = k_{YN}t - \mathcal{J}k_{YN} \quad (7)$$

Where K_{YN} is the rate constant (per minute) and τ is the time required for 50% adsorbate breakthrough (min). The approach involves a plot of $C_t/(C_o\text{-}C_t)$ versus sampling time (t)[24].The parameters of k_{YN} and $\mathcal{J}$ can be obtained using the non-linear regressive method[26].

Table 4. Yoon-Nelson model constants for the adsorption of MG on AAS in a fixed bed column

Concentration (mg/L)	Bed Height (cm)	Flow Rate (cm^3/hr)	k_{YN}($Lmin^{-1}$)	t(min)	R^2
500	7.5	100	0.062	110.7	0.813
500	15	100	0.025	313	0.947
500	22.5	100	0.018	271	0.81
500	7.5	200	0.006	459..5	0.919
200	7.5	100	0.023	284.8	0.941

It is observed from Table 4 that value of rate constant increases from 0.006 $Lmin^{-1}$ to 0.023 $Lmin^{-1}$ with a subsequent decrease in concentration of dye from 500 mg/L to 200 mg/L. A proportional relationship was seen between rate constant and Bed Height. The results obtained were similar to the results of Dutta et al [17].

4. Conclusion

The chemically treated sawdust prepared from sawdust of Tectona Grandis is found to be effective in removal of Malachite green from aqueous solution. The removal efficiency of dye was found to be strongly dependent on flow rate, initial concentration and bed depth. It was established that exhaustion of column increased with increase in flow rate and initial concentration and decreased with increase in bed depth. The models studied gave good approximations of experimental data amongst various models applied to analyze the data obtained. The adsorption capacity got by Thomas Model was found to be up to 10.06 mg/g which is comparatively good amongst various adsorbents available for removal of Malachite green dye. The bed sorption capacity (N_o) obtained from Bohart Adams Model is in the range of 671.88 – 722 mg/L. The Yoon–Nelson model also estimated the 50% breakthrough curve and provided the estimate break-through time for the column systems. The Clark model is found suitable to describe column adsorption obeying the Freundlich isotherm. Therefore information obtained from the fixed bed column study suggested that the treated sawdust could be used as an efficient and economical adsorbent for treatment of malachite green dye from waste water.

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