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ADSORPTION OF CRYSTAL VIOLET DYE FROM AQUEOUS SOLUTION USING *JATROPHA TANJORENSIS* LEAF POWDER IN A FIXED–BED COLUMN

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Abstract: Discharging effluents containing dyes into water bodies pose serious environmental problems such as destruction of aquatic lives and food web, deterioration of water quality etc. Adsorption is an efficient method to remove dyes from these effluents but has a challenge of high cost of adsorbent. The adsorption of Crystal Violet dye from aqueous solution onto a low–cost *Jatropha tanjorensis* leaf powder was investigated using a fixed bed column. Breakthrough curves were used to study the performance of the fixed bed column by varying the initial concentration (10–50 mg/L), flowrate (10–20 mL/min) and bed height (5–15cm). The maximum bed capacity of 174.478mg/g was obtained when the column bed height was kept at 15 cm, initial concentration of 30 mg/L and flow rate of 10 mL/min. The experimental data were analysed using three fixed–bed adsorption column models namely, Thomas, Adams–Bohart and Yoon and Nelson column models and the results fitted well into Thomas and Yoon and Nelson column models with a high correlation coefficient ($R^2 >$ 0.964) at different conditions. The activated *Jatropha tanjorensis* leaf powder was shown to be suitable adsorbent for adsorption of CV dye using fixed–bed adsorption column.

Keywords: *Jatropha tanjorensis,* crystal violet, fixed–bed, breakthrough curves

1. INTRODUCTION

Water pollution poses threats on the lives of human and animals and preservation of natural ecosystems (Lopez–Cervantes, *et al*., 2018). Many industries discard their wastewater into water bodies without any or proper treatment, which ultimately deteriorate the quality of water (Lei, *et al.,*2021, Khamparia, *et al*.,2015). Textile, pulp and paper, colouring, printing, cosmetics, leather and tanning and food industries use dyes and the effluents released from these industries bear large quantity of coloured wastes (Banerjee and Chattopadhyaya, 2017).

Dye is one of the most severe pollutant to water bodies (Bhatia, *et al*., 2017). The presence of dye in wastewater even at a very minute quantity is highly visible and undesirable (Albayati, *et al*., 2016). When wastewaters containing dyes are discharged into water bodies pose serious environmental problems especially the destruction of aquatic lives and food web (Kilic and Janabi, 2017, Ma, *et al*., 2017). These dyes resist light, washing, and microbial invasion and cannot biologically degrade easily in water (Saed, *et al*., 2014, Tkaczyk, *et al*., 2020). (Mosoarca, *et al*., 2020) stated that pigments in dyes absorb and reflect sunlight, which hinders microbial growth and photosynthesis in aquatic plants.

Dyes are toxic, carcinogenic, mutagenic and tetratogenic (Afroze, *et al*., 2016, Liu, *et al*., 2012, Liu, *et al*., 2013). Taking up of dyes in water path ways through food chain in aquatic organisms may cause various physiological disorders like hypertension, sporadic fever, renal damages and cramps in human and animals (Nidheesh, *et al*., 2012). Alardhi, *et al*., 2020 reported that basic and diazo direct dyes have the highest rate of toxicity. Hence, the removal of dyes from wastewater is necessary.

Literature has shown that various conventional methods have been used to remove dyes from wastewater, such methods include ion exchange, electrocoagulation/electroflocculation (Pathania, *et al*., 2017), ultrafiltration (Khodabandehloo, *et al*., 2017), reverse osmosis (Iqbal, *et al*., 2021), oxidation (Rajkumar and Muthukumar, 2017) and adsorption (Dawood and Sen, 2012). These methods have many limitations such as relatively high cost of operation, generation of sludge, complicated procedures and designs and inefficiencies (Radhika, *et al*., 2018) except adsorption (Albayati, *et al*., 2016). Adsorption process has been adopted as an efficient industrial method to remove dye from aqueous waste due to its initial cost, simplicity of design and operation, low sludge formation and insensitivity to toxic substances (Radhika, *et al*., 2018).

Activated carbon has been extensively employed as conventional adsorbent for adsorption process because it has a good adsorptive capacity to remove pollutants and contaminants from wastewater

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(Banerjee and Chattopadhyaya, 2017). However, commercial activated carbon remains an expensive material due to high cost of treatment and difficulty in regeneration (Lopez–Cervantes, *et al*., 2018) especially in a developing country like Nigeria. Thus, the use of low–cost, locally available, highly efficient and eco–friendly materials as alternative to commercial activated carbon to remove dye from wastewater has become increasingly popular (Bello, *et al*., 2013), this technology is called biosorption.

The feasibility of using orange peel (Lakshmipathy & Sarada, 2013), wheat bran (Chowdhury, *et al*., 2018), neem powder (Radhika, *et al*., 2018, Patel & Vashi, 2015a), agricultural waste (Sulyman, *et al*., 2017), biomass (Yagub, *et al*., 2012) and palm ash (Debamita, *et al*., 2020) as non–conventional adsorbents for adsorption process have been investigated. These biomaterials can be used as adsorbents with little or no pre–treatments and can be made with lost methodologies (Jayganesh, *et al*., 2017).

Jatropha tanjorensis is an edible plant majorly cultivated in the southern Nigeria. Residents and farmers in this region use *Jatropha tanjorensis* for fencing their homes and farmlands (Egbon, *et al*., 2013, Oboh, and Masodje, 2013). They are often trimmed to keep surroundings neat. (Ochulor, *et al*., 2018) investigation on *J. tanjorensis* showed that it has the following composition: 51.784% carbohydrate, 6.991% protein, 6.195% moisture content and 12.172% crude fibre and some functional groups such as carboxyl, hydroxyl and amines. These functional groups, fibre and protein contained in *J. tanjorensis* leaf powder make it a possible good adsorbent (Han, *et al*., 2014).

Breakthrough curve is used to describe the performance and dynamics of a fixed–bed column (Han, *et al*., 2018). Continuous adsorption study with a fixed–bed column is often desired, more practical and efficient to remove pollutants from real wastewater and from industrial point of view because of its simplicity in terms operation, good adsorption capacity and the usefulness of data from its laboratory process which can be scaled–up to design a pilot adsorption column (Vairavel and Murty, 2017). In a column adsorption technique, the adsorbate continuously enters and leaves a packed bed of adsorbent where separation occurs. Continuous adsorption does not operate under equilibrium conditions because there is no enough contact time between the adsorbate and the adsorbent. When the aqueous solution goes up the packed column, the feed zone which is at the bottom of the packed column becomes exhausted, the mass transfer zone then moves up the column, the concentration of adsorbate becomes low and contacts fresh adsorbent material at the top of the packed column (Patel and Vashi, 2015b).

In this work, the removal efficiency of activated *Jatropha tanjorensis* leaf powder for the adsorption of Crystal Violet dye using fixed–bed column was investigated. The important design parameters such as initial concentration of dye solution, flow rate of fluid and column bed height (Han, *et al*., 2014) were investigated using a laboratory scale fixed–bed column. The breakthrough curves for the adsorption of CV dye were analyzed using Adams–Bohart, Thomas and Yoon–Nelson. Modeling on the column dynamics of the fixed bed was presented as well as the correlation between the model and the experimental data.

2. METHODS AND MATERIALS

Preparation of Aqueous Solution

Crystal Violet (CV) used in this study was purchased from Sigma–Aldrich, Malaysia. It has a molecular formula of $C_{25}H_{30}N_3Cl$ and molar mass of 407.99 g/mol. The dye stock solution was prepared by dissolving accurately weight dye in distilled water to the concentration of 1 g/L. The dye solution was agitated to form a homogeneous solution. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to the required working solutions (initial dye concentrations).

Adsorbent Preparation

J. tanjorensis leaves were collected and washed several times with clean water to remove dirts and dried under the sun for two days to remove excess water from the washings. The leaves were further dried in the oven at 60^{o}C until the leaves become crisp. The dried leaves were then crushed with a commercial Heavy Duty blender to powder and then was sieved obtain a mesh size of 500 µm (0.50 mm). The sample powder was further washed with distilled water till the washings were free from green colour and turbidity. The washed powder was dried in the oven at 60^{o}C for 7 hours to remove water and stored. 0.1 N sulphuric acid (Sigma–Aldrich, Malaysia) was prepared for the activation process. The *J. tanjorensis*

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leaf powder was stirred in a beaker containing considerable amount of 0.1 N sulphuric acid to form a pulp for 30 minutes. Thereafter, it was washed with de–ionized water to remove untreated acid. The wet activated *J. tanjorensis* leaf powder was then dried in an oven at 60°C and stored in a container at room temperature for adsorption experiment.

Characterization of the Adsorbent

The characteristics of the leaf powder were studied under Fourier Transform Infrared (FTIR) Analysis, Scanning Electron Microscopy (SEM) Analysis, Surface Area, Bulk Density.

— Scanning Electron Microscopy (SEM) Analysis

Scanning Electron Microscopy (SEM) Analysis used scanned beam to analyze the surface structure and chemical composition of test samples. Scanning Electron Microscopy (SEM) Analysis was conducted for *J. tanjorensis* leaf Powder before and after adsorption. The powders were dried to remove any moisture present. The sample powders were mounted on a stub of metal with adhesive, coated with a layer of gold metal, and then observed under the microscope. The results were recorded and printed.

— Fourier Transform Infrared (FTIR) Analysis

Fourier Transform Infrared (FTIR) Analysis is used to identify organic, polymeric and some inorganic materials in test samples. FTIR spectrophotometer was used to analyse *J. tanjorensis* leaf powder before and after adsorption. About 0.25–0.50 teaspoons of potassium bromide (KBr) were mixed with 0.1g *J. tanjorensis* leaf powder. The mixture was placed in sample holder and then placed in the spectrophotometer for recording of spectra. The range (wave number) of spectra was 350 to4000cm^{-1}.

— Determination of pH

The pH of the activated *J. tanjorensis* leaf powder was determined. 2.0 g of the biosorbent was weighed and transferred into a conical flask containing 100 mL of distilled water and then stirred with a stirring rod for 1 hour. The mixture was filtered using a Whatman filter paper and pH of the filtrate was measured with an electronic pH meter.

— Determination of Bulk Density

The bulk density of the *J. tanjorensis* leaf powder was determined according to the tapped density procedure by (WHO, 2012). 5.0 g of was weighed *J. tanjorensis* leaf powder and transferred into a 100 mL clean, dry graduated cylinder. The cylinder was tapped 10 times with a rubber pad on the surface of a work bench, thereafter its volume was noted and recorded. The procedure was continuous until there was no further settling of the *J. tanjorensis* leaf powder in the cylinder. The bulk density expressed in (g/cm^3) was calculated using Equation 1.

$$\text{Bulk density } (g/cm^3) = \frac{\text{Weight of the sample (g)}}{\text{volume occupied by the sample } (cm^3)} \quad (1)$$

— Determination of Surface Area

The surface area of the *J. tanjorensis* leaf powder was determined by gas adsorption. 1 g of *J. tanjorensis* leaf powder was placed in a glass cell and heated under a vacuum. The heated sample was brought to a constant temperature by means of an external bath containing a cryogen like liquid nitrogen. Then, small amounts of gas were admitted in steps into the evacuated sample chamber. The absorbate molecules quickly found their way to the surface of every pore in the solid sample. Gas molecules that stuck to the surface were said to be absorbed.

Fixed bed experiment

J. tanjorensis leaf powder was packed into the column to desired bed heights of the adsorbent 5, 10 and 15 cm (equivalent to 4.95, 9.80 and 14.70g of *J. tanjorensis* leaf powder). A layer of cotton wool was placed at the top of the packed bed to keep it stationary during the experiment. Distilled water was passed through the packed column to dampen the packed bed and remove void from the bed of adsorbent. The aqueous solution was pumped to the top of the packed column with the aid of a peristaltic pump at three different flow rates (10, 15 and 20 mL/min) with different initial dye concentrations (10, 30 and 50 mg/L). The samples of the effluent at the outlet of the column were taken at regular time interval (1 hour) and the concentration of CV dye in the effluent was measured using an UV–visible spectrophotometer at wavelength of 584 nm. Fixed bed experiment were terminated when the initial column concentration equals exit column concentration reached.

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Determination of Adsorption Capacity

The performance of a fixed–bed column is described through the concept of the breakthrough curve. The breakthrough appearance time and its shape are very important characteristics for determining the operation and the dynamic response of an adsorption fixed–bed column. The breakthrough curves are usually expressed in terms of adsorbed dye concentration (C_{ad}), initial concentration (C_o), outlet CV concentration (C_t) or normalized concentration defined as the ratio of outlet CV concentration to initial CV concentration (C_t/C_o) as a function of time or volume of effluent for a given bed height. The effluent volume was calculated by using Equation 2

$$V = Qt_{total} \tag{2}$$

where *V* is the effluent volume collected in mL, Q is the volumetric flow rate in mL/min and t_{total} is the total flow time in min.

The area under the breakthrough curve (A) is obtained by integrating the adsorbed concentration (C_A) mg/L versus t (min) plot can be used to find the total adsorbed CV dye quantity (maximum column capacity). Total adsorbed CV quantity q_{total} (mg) in the column for a given feed concentration and flow rate is calculated as shown in (3)

$$q_{total} = \frac{QA_c}{1000} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} C_A\, dt \tag{3}$$

The maximum adsorption capacity ($q_{o,}$) at the exhaustion time was calculated by using (4)

$$q_o = \frac{q_{total}}{m} \tag{4}$$

where *m* is the amount of *J. tajorensis* leaf powder packed in column. Total amount of CV sent to column (M_{total}) was obtained from (5)

$$M_{total} = \frac{C_o Qt_{total}}{1000} \tag{5}$$

Equilibrium CV uptake q_{max} (mg/g) or maximum capacity of the column in the column is defined by equation (6) as the total amount of adsorbed (q_{total}) per gram of adsorbent (w) at the end of total flow time (Luo, *et al*., 2011).

$$q_{max} = \frac{q_{total}}{w} \tag{6}$$

Dynamic adsorption model

The data obtained from experiments were fitted into four Column Adsorption models namely: Adams–Bohart, Thomas, Yoon and Nelson and Bed Depth Service Time (BDST) models as seen in Table 3 to evaluate the efficiency and applicability of the column models for large–scale operations. The applicability of data to these models were explained by observing the values of the correlation coefficients, R^2. According to the regression analysis, the higher the R^2 value (closer to unity), the better is the model for scale–up parameters (Nidheesh, *et al*., 2012, Yang, *et al*., 2018). These mathematical models are used to predict the transient behaviour of the concentration and temperature profiles for any defined changes in the initial parameters such as feed concentration, temperature, and flow rate (Hwang, *et al*., 1995, Shafeeyan, *et al*., 2014).

Table 3: Dynamic adsorption model

Column Model	Equation	References
Adams–Bohart	$\ln\left(\frac{Ct}{C_0}\right) = \left(k_{AB}C_0 t - k_{AB}N_0\frac{Z}{U}\right)$	Adhami and Mirzaei, 2018
Thomas	$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{TH}q_0 M}{Q} - \frac{K_{TH}C_0}{Q}t$	Jain and Gogate, 2017
Yoon–Nelson	$\ln\frac{C_t}{C_0 - C_t} = (k_{YN}t - \tau k_{YN})$	Olivares, et al., 2013
Bed Depth Service Time	$t = \frac{N_0}{C_0 F}Z - \frac{1}{K_a C_0}\ln\left(\frac{C_0}{C_t} - 1\right)$	Kishor and Rawal, 2019

Where C_t and C_0 are the initial and final concentration of the adsorbate (mg/L) respectively, k_{AB} is the kinetic constant (L/g. min), N_0 is the capacity of the adsorption (g/L), Z is the bed height in the column (m), t is the time (min) and U is the velocity of fluid out (m/min), the kinetic coefficient k_{TH} and the adsorption capacity of the column q_o, K_a is the rate constant of adsorption (L/ mg min), k_{YN} is the rate constant (min^{-1}), τ is the time required for 50% asdorbate breakthrough (min), k_{AB} is the kinetic constant (L/g. min), N_0 is the capacity of the adsorption (g/L). Thus, the parameters of different kinetic models were obtained using nonlinear regressive analysis by employing the use of General Reduced Gradient (GRC) in Microsoft Excel Solver Protocol.

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3. RESULTS AND DISCUSSION

Characterization of *J. tanjorensis* leaf powder

Table 1 shows the bulk density, pH value and specific surface area of *J. tanjorensis* leaf powder. The bulk density is 0.204 g/cm^3 which was relatively low implies that the *J. tanjorensis* leaf powder is porous and has the ability to retain the absorbed CV molecules onto its surface (Patel and Vashi, 2015a). The value of internal surface area obtained before and after activation from the analysis of the powder (adsorbent) were 116.55 m^2/g and 121.40 m^2/g respectively. This shows that *J. tanjorensis* leaf powder has a higher surface area than blast furnace slug which is a good adsorbent that was used in the adsorption of malachite green dye in a column adsorption experiment (Ali, *et al*., 2012). The difference in the internal surface area of the *J. tanjorensis* leaf powder before and after activation is due to the presence of sulphuric acid (H^{2+} ions) which was used in the activation process of the powder. The presence of acid increased the internal specific surface area by enlarging the pores openings and increasing the number of pores present in the powder (adsorbent) (Bhatnagr, *et al*., 2006). The greater number of pores and pore openings, the more the number of adsorption sites for adsorption process. Hence, the activation of *J. tanjorensis* leaf powder increased the internal surface area of the powder.

Table 1: Physical properties of *J. tanjorensis* leaf powder.

Physical properties	J. tanjorensis leaf powder
Surface area (before activation) (m^2/g)	116.55
Surface area (activated) (m^2/g)	121.40
Bulk density (g/cm$^{3)}$	0.204
pH	5.4

In order to confirm CV adsorption in *J. tanjorensis* leaf powder packed column, *J. tanjorensis* leaf powder was analysed with Scanning Electron Microscopy (SEM) systems to determine the chemical structure of the adsorbent before and after adsorption. The SEM photograph of adsorbents before and after adsorption are shown in Figures 1and 2 respectively. From these pictures, it is clear that there was significant difference in the appearance of the adsorbent surfaces. The surface of the adsorbent after adsorption had white particles spread across it, in other words, the surface appeared the adsorbent surface before adsorption. The white materials or particles or whitening of the *J. tanjorensis* leaf powder surface after adsorption represents the adsorbed CV onto the surface (Bharathi and Ramesh, 2012).

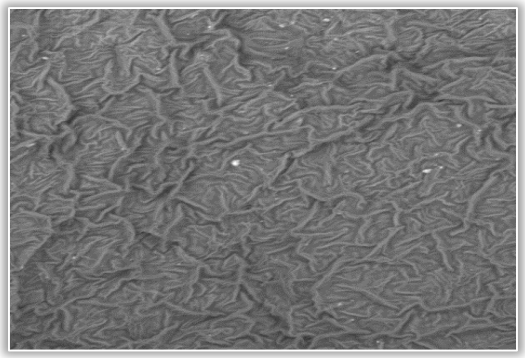

Figure 1: SEM photograph of *J. tanjorensis* leaf powder before adsorption

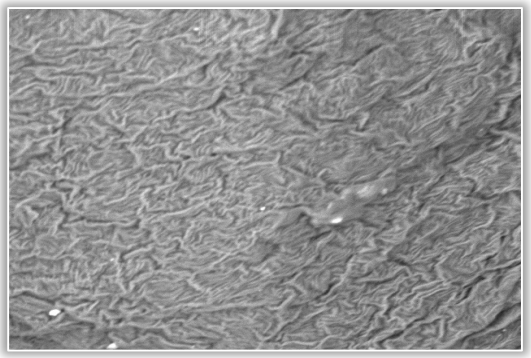

Figure 2: SEM photograph of *J. tanjorensis* leaf powder before adsorption

The FT–IR spectra of the *J. tanjorensis* leaf powder before adsorption was illustrated in Figure 3 revealed a broad and strong adsorption peak between 1058.00 cm^{-1} and 1148 cm^{-1} which represented the presence of –OH bond stretching of alcohol group. The medium intense adsorption peak from 1058.00 cm^{-1} and 1244.66 cm^{-1} corresponds to –NH stretching of amine group. The peaks between 1320.78 cm^{-1} and 1379. 00 cm^{-1} were attributed to the presence of sulphonic acid. A medium intense adsorption peak from 1379 cm^{-1} to 1446.18 cm^{-1} indicated the presence of S=O bonds stretching of the sulphate compound and also an adsorption peaks 1320 cm^{-1} and 1446.18 cm^{-1} represented the sulphonyl chloride. A medium adsorption peaks stretching from 1559 cm^{-1} to 1640 cm^{-1} represented the amines group (NH_2). A strong and very broad adsorption peaks from 2363.83 cm^{-1} to 2926.81 cm^{-1} was found to indicate the presence of –OH stretching of carboxylic group and also a very strong and broad adsorption peak between 3425.00 cm^{-1} and 3749.63 cm^{-1} was observed to be associated with O–H stretching of the alcohol group. The presence of carboxylic group, hydroxylic group and amine groups in the *J. tanjorensis* leaf powder proves that it is suitable adsorbent for adsorption process (Soni, *et al*., 2012)

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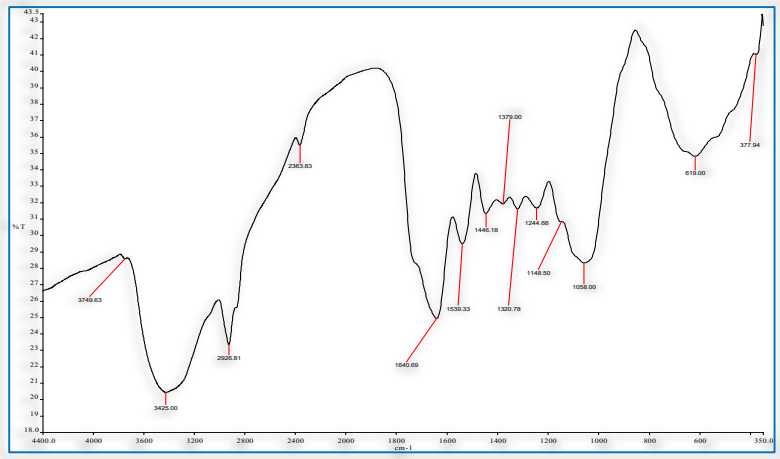

Figure 3: FTIR spectra of *J. tanjorensis* leaf powder spectrum before adsorption.

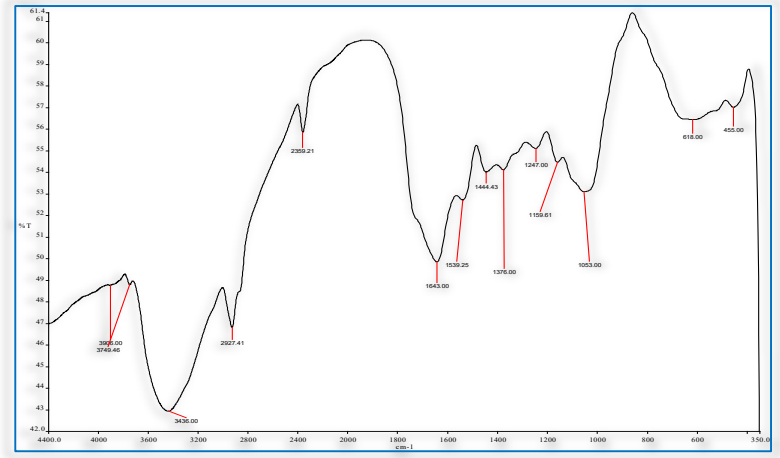

Figure 4: FTIR spectra of *J. tanjorensis* leaf powder spectrum after adsorption

The FT–IR spectra of the *J. tanjorensis* leaf powder after adsorption was displayed in Figure 4, it revealed that the broad and strong adsorption peak between 1058.00 cm^{-1} and 1159.61 cm^{-1} which represented the presence of –OH bond stretching of alcohol group has dropped to 1053.00 cm^{-1} and 1148.50 cm^{-1} (Patel and Vashi, 2015a) which indicated that adsorption took place. The medium intense adsorption peak from 1058.00 cm^{-1} and 1244.66 cm^{-1} which correspond to –NH stretching of amine group increased to 1053.00 cm^{-1} and 1244.66 cm^{-1}.

The adsorption peaks between 1376.00 cm^{-1} and 1444.43 cm^{-1} were attributed to the presence of sulphonic acid. A medium intense adsorption peak from 1379 cm^{-1} to 1446.18 cm^{-1} indicated the presence of S=O bonds stretching of the sulphate compound and also an adsorption peaks 1320 cm^{-1} and 1446.18 cm^{-1} represented the sulphonyl chloride. A strong broad adsorption peaks was observed between 1539.25 cm^{-1} and 1643 cm^{-1} to be associated with C=C stretching the aromatic group (alkene compound). A medium adsorption peaks stretching from 1559 cm^{-1} to 1640 cm^{-1} represented the amines group (NH_2). A strong and very broad adsorption peaks from 2359.21 cm^{-1} to 2927.41 cm^{-1} was found to indicate the presence of –OH stretching of carboxylic group. A very strong and broad adsorption peak between 3749.46 cm^{-1} and 3906.00 cm^{-1} was observed to be associated with O–H stretching of the alcohol group.

The reduction and changes in intensities and positions of peaks for the carboxylic groups, hydroxylic groups, amines groups that are present in the *J. tanjorensis* leaf powder proves that adsorption took place and these groups took part in adsorption process because they constitute the binding sites (Soni, *et al*., 2012).

Table 2: Column data parameters obtained at different CV dye initial concentrations, bed heights and flow rates

Concentration (mg/L)	Bed height (cm)	Flowrate (mL/min)	q_{total} (mg/g)	m_{total} (mg)	q_{eq} (mg/g)
10	5	10	824.550	1260	166.576
30	5	10	732.750	1026	148.030
50	5	10	699.810	824	141.374
30	10	10	1504.990	1656	153.570
30	15	10	2564.820	2574	174.478
30	5	15	633.085	978	127.896
30	5	20	589.880	907	119.168

Effect of Bed Height

Figure 1 shows the effect of bed height on breakthrough curve obtained for CV adsorption on the *J. tanjorensis* leaf powder. The fixed bed study was carried out at bed heights of 5, 10 and 15 cm with a constant initial CV concentration of 30 mg/L and flow rate of 10 mL/min. Figure 1 shows that the breakthrough and exhausting or saturation times decreased with increasing bed height thereby

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increasing the number of adsorption sites on the adsorbent and the residence time of the CV in the column, thus increasing the removal efficiency of CV in the fixed bed system.

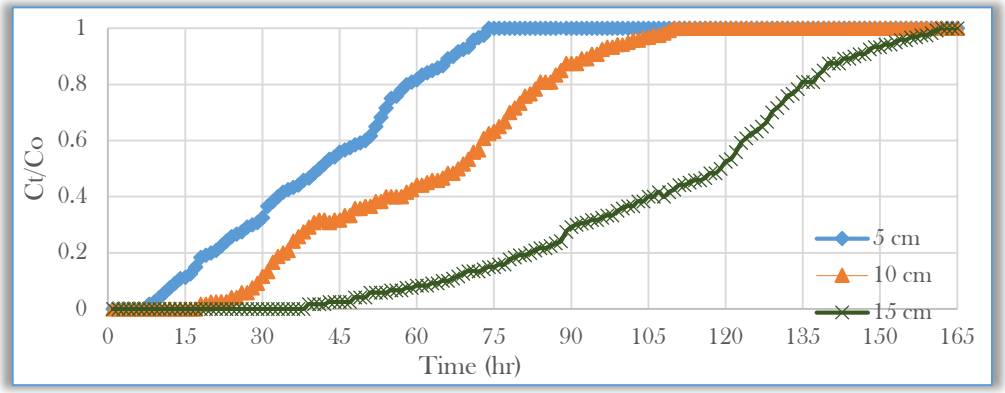

Figure 1: Effect of bed height on breakthrough curves

The slope of breakthrough curve decreased with increasing bed height, which resulted in a broadened mass transfer zone (Luo, *et al*., 2011). A high adsorption capacity was seen at the highest bed height due to an increase in the binding sites of the adsorbent for the adsorption (de Franco, *et al*., 2018). The throughput volume of dye solution was increased with the increase in bed height due to the increase in surface area of adsorbent which brought about more binding sites and a greater number of adsorption sites for the adsorption (Futalan, *et al*., 2011). The highest bed capacity of 174.478 mg/g was obtained at flow rate of 10 mL/min, 10 mg/L initial dye concentration and 15cm bed height.

Effect of Initial Concentration of CV

Figure 2 shows the breakthrough curve obtained for CV adsorption on the *J. tanjorensis* leaf powder for different initial CV concentration of 10 mg/L, 30 mg/L and 50 mg/L at a constant bed height of 5 cm and 10 mL/min flow rate. It was observed that the adsorption capacity increased with increasing initial concentration of the aqueous solution because a high concentration difference provided a high driving force for the adsorption process. The breakthrough curves became steeper and breakthrough volume decreased when dye concentration increased because of the lower mass–transfer system from the bulk solution to the adsorbent surface while at lower CV dye concentrations, breakthrough curves were dispersed and breakthrough time occurred slower (Girish and Murty, 2015). The time the dye broke through the column decreased from 960 to 420 minutes while the time the bed was exhausted were deceased from 4440 to 2580 minutes because the adsorbent got saturated faster at higher initial CV dye concentrations than at lower initial concentration.

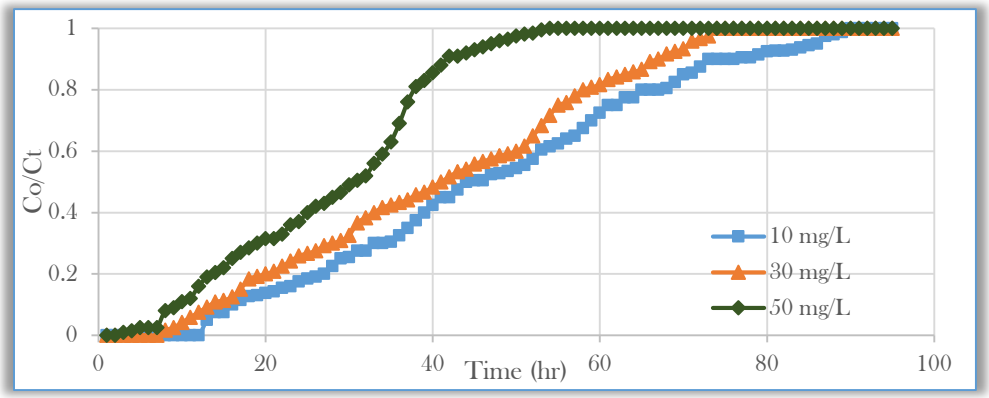

Figure 2: Effect of initial concentration of CV on breakthrough curves.

Effect of Flowrate on Breakthrough Curve

The effect of the flow rate on the adsorption of CV using the *J. tanjorensis* leaf powder was investigated by varying the flow rate of the initial (10, 15 and 20 mL/min) using 30 mg/L initial CV concentration and 5 cm bed height as shown by the breakthrough curve in Figure 3. It was seen that the breakthrough curve occurred faster at higher flow rate due to the lower residence time of the CV dye in the column. The adsorption capacity was lower at higher flow rate, due to short residence time of the CV dye in the

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column and its rate of diffusion into the pores of the adsorbent. Also at higher flowrate, the mass transfer rate increased with increasing flow rate which led to faster adsorbent bed saturation at higher flow rate (Chafi, *et al*., 2015). Hence, the CV ions left the column at a shorter time. At a lower flow rate, the adsorption capacity was higher due to sufficient residence time of the CV dye in the column and diffusion of the solute into the pores of the adsorbent (*J. tanjorensis* leaf powder), thus, making the dye to exit the column after longer period of time. The breakthrough and exhaustion times reduced at higher flow rate and increased at lower flowrates. The breakthrough and saturation times decreased from 3600 to 2940 minutes and 720 to 360 minutes respectively.

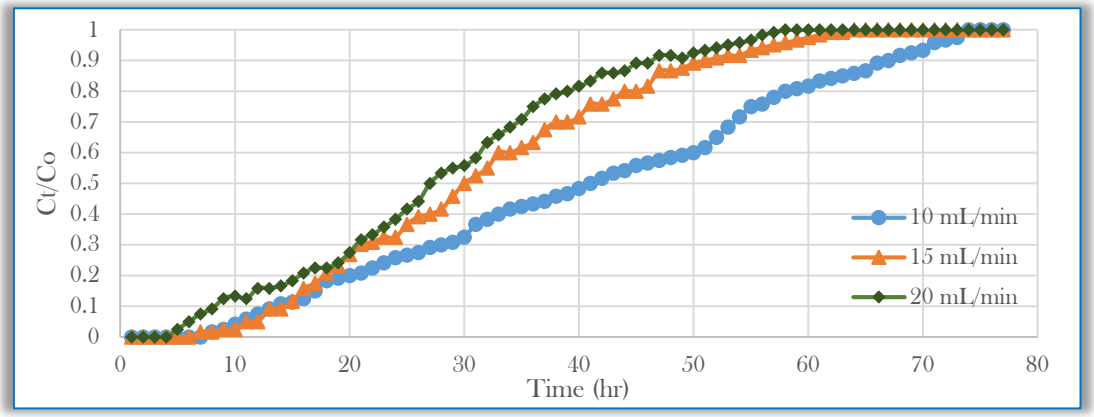

Figure 3: Effect of flowrate on breakthrough curves.

Adams–Bohart

The Adams–Bohart adsorption model was applied to experimental data for the description of the initial part of the breakthrough curve. For all breakthrough curves shown above, respective values of N_o, and k_{AB} were calculated and presented in Table 4 together with the correlation coefficients ($R^2 > 0.75$). From Table 4, it can be seen that the values of N_o increased with both initial CV concentration and bed height, but it decreased with flowrate increase but the values of k_{AB} decreased with both initial CV concentration and flow rate increase, but it increased with bed heights increase. This showed that the overall system kinetics was dominated by external mass transfer in the initial part of adsorption in the column (Adhami and Mirzaei, 2018).

Table 4: Adams–Bohart parameters at different conditions using non–linear regression analysis.

Initial concentration (mg/L)	Bed height (cm)	Flowrate (mg/L)	k_{AB} X 10^3 (L/mg.min)	N_o (mg/L)	R^2
10	5	10	0.025	2435.036	0.899
30	5	10	0.037	1940.3278	0.874
50	5	10	0.045	1091.583	0.753
30	10	10	0.050	2745.873	0.806
30	15	10	0.081	2830.984	0.882
30	5	15	0.012	1454.954	0.837
30	5	20	0.011	1105.240	0.815

Thomas model

The column data were fitted to the Thomas model to determine the Thomas rate constant (k_{TH}) and maximum solid–phase concentration (q_o) using non–linear regression analysis. From Table 5, the determined coefficients (R^2) ranged from 0.955 to 0.998; the initial concentration of increased the value of q_o decreased but the value of k_{TH} increased. The reason is that the driving force for adsorption is the concentration difference between the dye adsorbed on the adsorbent and the dye in the aqueous solution (Adhami and Mirzaei, 2018, Debamita, *et al*., 2020). With flow

Table 5: Thomas parameters at different conditions using non–linear regression analysis.

Initial concentration (mg/L)	Bed height (cm)	Flow rate (mg/L)	k_{TH} X 10^3 (L/mg.min)	q_o (mg/L)	R^2
10	5	10	0.012	147.748	0.964
30	5	10	0.011	147.804	0.958
50	5	10	0.041	170.746	0.955
30	10	10	0.034	823.602	0.989
30	15	10	0.044	807.236	0.990
30	5	15	0.064	147.713	0.995
30	5	20	0.068	147.714	0.998

Table 6: Yoon and Nelson parameters at different conditions using non–linear regression analysis.

Initial concentration (mg/L)	Bed height (cm)	Flow rate (mg/L)	k_{YN} (1/min)	τ (min)	R^2
10	5	10	0.002	2771.779	0.994
30	5	10	0.002	2431.757	0.987
50	5	10	0.004	1690.388	0.990
30	10	10	0.001	3743.374	0.989
30	15	10	0.001	6717.231	0.989
30	5	15	0.003	1844.85	0.995
30	5	20	0.004	1656.055	0.998

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rate increasing, the value of q_o decreased but the value of k_{TH} increased. As the bed heights increased, the value of q_o increased while the value of k_{TH} decreased.

From Table 6, the rate constant k_{YN} increased and the 50% breakthrough time, τ decreased with increasing both flow rate and CV initial concentration. As the bed height increased, the values of τ increased while the values of k_{YN} decreased. the value of correlation coefficients (R^2) ranged from 0.987 to 0.998. Thomas and Yoon–Nelson models, had their values of correlation coefficients (R^2) to be greater than (R^2 > 0.955) and this shows that these two models are better fit to data obtained from the adsorption experiment at various conditions Thus, Thomas and Yoon–Nelson models can be used to describe the behaviour of adsorption of CV dye in a fixed–bed column. The value of R^2 was obtained from fitting experimental data in to the Adams–Bohart model were lower than that of the Thomas and Yoon–Nelson models under the same experimental conditions. This is so because the Adams–Bohart model is only used for the description of the initial part of the breakthrough curve (Han, *et al*., 2014).

4. CONCLUSION

This study showed that the activated *Jatropha tanjorensis* leaf powder with 0.1N of sulphuric acid was a promising technique for removing CV dye from aqueous solutions using fixed–bed adsorption column. lower CV dye initial concentration, lower feed flow rate and higher bed height favoured the adsorption system. The column data were fitted into three fixed–bed adsorption column models namely, Thomas, Adams–Bohart and Yoon and Nelson column models but they fitted well into Thomas and Yoon and Nelson models. Adams–Bohart model well described the initial region of breakthrough curve at all experimental conditions studied.

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