Modelling of the removal of crystal violet dye from textile effluent using *Murraya koenigii* stem biochar

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ABSTRACT

Dye-based industries, particularly small and medium scale industries, release their effluents into waterways without treatment due to cost considerations. *Murraya koenigii* stem is an agricultural waste that is present in various vegetable markets. To produce a value-added product from this agricultural waste, it is proposed to convert this waste into activated carbon for the removal of crystal violet dye from the aqueous medium. Therefore, the biochar was prepared from the curry tree bark. Batch adsorption experiments were conducted as a function of variables such as adsorbent dosage, time, temperature and dye concentration and subsequently, the optimum conditions were determined. The optimum operational parameters such as adsorbent dosage were found to be 100 mg L^{-1}, time (60 min), temperature (35°C) and dye concentration (50 mg L^{-1}). The equilibrium adsorption of dye on the adsorbent (q_e) was found to be 50 mg g^{-1} and the removal efficiency was about 70%. The structure and morphology of curry tree carbon (CTC) before and after adsorption were characterized by Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy. FTIR analysis indicated a change in peak. The results were analyzed using Langmuir and Freundlich isotherm model and it best fitted with the Langmuir model. Kinetic studies were assessed and were found to follow the pseudo-second-order model. We investigated the use of biochar produced from agricultural waste and our results provide novel perception into the potential of biochar to remove crystal violet from textile effluents.

Keywords: Curry tree carbon; Crystal violet; Textile effluent; Decolourization

1. Introduction

1.1. Textile effluents

Amidst the major water crisis in India these days, a decline in the quality of water due to effluent discharge from industries is a prime concern. The effluents have various amounts of chemicals, Dyes are the most common and troublesome ones that are the most difficult to treat due to its chemical structure [1]. Dyes from textile, leather, pulp, paper, rubber, printing and cosmetic industries are led into the water bodies. Besides dyes, industrial wastewater also contains other contaminants such as inorganic and organic material, surfactant, salts, additives, etc. that affect the quality of water. These contaminants if not treated have a deleterious effect on living organisms and human beings in an indirect way such as fertility disorders and DNA damages [2]. A study reported by Iqbal [3] suggests the removal of heavy metals by *Vicia faba* bioassay in order to monitor the environmental toxicity. The usage of dyes and chemicals for

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the manufacture of textiles generates an enormous amount of sludge, fibers and chemically polluted water as wastes. When this polluted water mixes with natural resources, it degrades the quality of soil and water and also affects the habitat and environment [4]. As a result, this industry is facing a major problem in environmental pollution. An enormous amount of water is being utilized for bleaching, dyeing and screen printing. The second-largest exporter of dyestuffs after China is India. It is determined that about 2% of dyes produced are released into the water effluent and 10% is lost during the process of coloration [5,6]. Industries such as textile, leather, tannin, paper, pharmaceuticals, cosmetics, hair coloring, wood staining, agricultural, biological, chemical research, light-harvesting arrays and photochemical cell industries utilize dyes [7].

1.2. Permissible limits

The industries, therefore, must reduce the number of contaminants being left into the water bodies and thus there are permissible limits set for the effluents chosen by the Department of National Environmental Protection from the Central Pollution Control Board. It is also important to treat the effluents and then dispose of the water bodies so that they remain un-reactive to the marine ecosystem. Standards for the effluent is given in Table 1 [1]

The prime sources of water pollution are textile industry effluents that release dyes, detergents and other contaminants. They are considered as a major source because they consume dissolved oxygen, undergo chemical and biological changes, destroy the aquatic life and pose a threat to human health as many of these contaminants are highly toxic in nature [8].

1.3. Dyes in the effluents

Colour can be considered as a primary pollutant to be detected in wastewater. A very small amount of synthetic dyes less than 1ppm can be detected [9]. Classes of dyes include acidic dyes, basic dyes, direct dyes, dispersive dyes, reactive dyes, sulfur dyes and vat dyes [10]. About 10%–50% of polluted water is contributed by the dyeing section [11].

During dyeing, all the dyes are not fixed on to the fabric. A portion of the dye is always present that is unfixed

and is released into the freshwater. These unfixed dyes are found to be in enormous amounts in the textile industry effluents [12]. The amount of water that is utilized and unleashed in the process is also dependent on the type of fabric produced [13].

Crystal violet (CV) also known as Gentian violet or Basic violet 3 is a synthetic dye that is classified under the cationic triphenyl methane dyes. This is the most common dye used in the paper and textile industry. It has been concluded that this dye can cause harmful effects on flora and fauna and therefore must be treated before it is discharged [14]. In general, the triphenyl methane dyes are difficult to remove from effluents due to their structural complexity [15]. Thus the treatment of highly colored complex pollutants in effluent water is a major concern. The structure of crystal violet is shown in Fig. 1 [16].

To date different physical, biological and chemical techniques are in practice to treat the wastewater [17,18], adsorption is one of the promising techniques. In the adsorption process, different adsorbents have been used and the cost of the adsorbent is one of the important factors [19,20]. Activated carbon is a form of carbon derived from charcoal and is processed to have low volume pores and large surface area [21,22]. Hence, they are highly applicable in the treatment of effluent water where they are served as an adsorbent in adsorbing heavy metals, dyes and other contaminants [23]. The problem with commercially available activated carbon is that it is obtained majorly from coal. Coal is a non-renewable fossil fuel and it might cease to exist very soon. The growing inclination in biotechnology led to the emergence of bioadsorbents and its key source is the agrowaste materials. Agricultural materials being easily available, low cost and due to its renewability, the activated carbon is prepared from them for the remediation of dyes such as Methylene blue as reported by Rafatulla et al. [24]. Many agricultural and forestry wastes have been used as adsorbents such as peanut husk, banana peel, sawdust, coconut coir dust, internal almond shell, walnut shell, etc. [25]. The suggested mechanism for the removal of crystal violet dye is electrostatic interaction and chemical interaction between the dye and surface functional groups of the adsorbent [26]. In this study, a novel bio-adsorbent was prepared from curry tree bark and used for the adsorption of crystal violet dye. As the biochar is cost-effective and environmentally friendly, it can be used as an alternate source of the adsorbent.

Table 1
Standards for the effluents

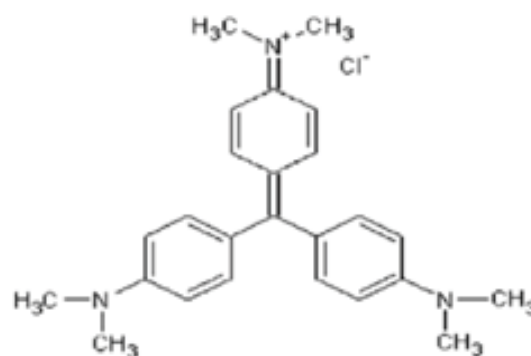| Parameter	Standards
pH	5.5–9.0
Total suspended solids	100 mg L^{-1}
Biochemical oxygen demand	30 mg L^{-1}
Chemical oxygen demand	250 mg L^{-1}
Total residual chlorine	1 mg L^{-1}
Oil and grease	10 mg L^{-1}
Total chromium	2 mg L^{-1}
Sulphide	2 mg L^{-1}
Phenolic compounds	1 mg L^{-1}

Fig. 1. Structure of crystal violet.

2. Aim

The aim of the present study is to synthesize the biochar from *Murraya koenigii* for textile effluent treatment and to study the adsorption of crystal violet dye. The importance of this study is mainly due to the abundance of this low biodegradable agricultural waste that can be utilized as biochar in the removal of pollutants, which is cost-effective and eco-friendly also.

2.1. Objectives

The objective of this study is to investigate the adsorption effectiveness of *Murraya koenigii* based biochar in the removal of crystal violet dye from aqueous solution and to study the effect of various parameters like equilibrium time, temperature, initial concentration and adsorbent dosage through suitable experiments. The equilibrium isotherms as well as kinetic parameters of the adsorption process are evaluated.

3. Materials and methods

3.1. Materials

Curry tree carbon (CTC) was collected from a local vegetable market as a biowaste. Crystal violet was obtained from Kem light Laboratories Private Limited, Mumbai, India. Sulphuric acid was purchased from M.V Krishnaaram Laboratories Chemicals Company Perungudi, Chennai, India. The chemicals used were of analytical reagent grade and were used as received without further purification. Double distilled water was used throughout the experiments.

3.2. Preparation of CTC

The barks of curry tree plants were collected as vegetable waste from the local market and are cut into small pieces after removing the rinds. It was dried at 110°C for about 1 h in a hot air oven as shown in Fig. 2. The dried pieces (50 g) were treated with concentrated sulphuric acid (1:1 w/v).

The barks were taken in small quantities and mixed with concentrated sulphuric acid by continuous stirring. This caused the charring of the material and was followed by the evolution of heat and fumes. The mixture was cooled to room temperature and washed with distilled water in order to remove the free acid completely, filtered and dried at 110°C. This was further heated at 170°C for 90 min in a muffle furnace to complete carbonization and activation. The material was washed with distilled water until the slurry reached a constant pH and dried at 110°C for 1 h in hot air oven as shown in Fig. 3. The dried carbon was finely ground and sieved. The resulting carbon from the curry leaf tree was abbreviated as CTC shown in Fig. 4 [27].

3.3. Batch adsorption study

In this experiment, the batch adsorption technique was used. In order to study the effects of various important parameters such as adsorbent dosage, contact time, temperature and dye concentration. It was conducted at different conditions viz., adsorbent dosage (50–200 mg L^{-1}), time

Fig. 3. Acid treated curry tree barks.

Fig. 2. Dried curry tree barks.

Fig. 4. Powdered biochar.

(20–100 min), temperature (25°C–55°C) and dye concentration (10–80 mg L⁻¹). The sample was filtered after analysis using the Whatman No.42 filter paper. The dye concentration was estimated spectrophotometrically at the wavelength of 580 nm using a UV spectrophotometer. The amount of dye uptake at equilibrium is calculated using the equation.

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where q_e is the dye uptake capacity of the adsorbent (mg g⁻¹); C_0 is the initial concentration of dye (mg L⁻¹); C_e is the equilibrium concentration of dye after (mg L⁻¹); W is the mass of the adsorbent taken (g); V is the volume of the dye solution taken from Eq. (l):

The percentage removal of the dye is calculated using the equation:

$$\% \text{ Removal} = \frac{(C_0 - C_e) \times 100}{C_0} \tag{2}$$

4. Results and discussions

4.1. Effect of adsorbent dosage

The effect of adsorbent dosage was analyzed at neutral pH with the initial dye concentration of 30 mg L⁻¹ and at a constant time of 1 h, varying the biochar dosage from 50 to 200 mg L⁻¹. The adsorbent dosage vs. removal of crystal violet dye is shown in Fig. 5. The increment in adsorption capacity as the dosage increases is expected. But as the dosage increases the removal efficiency of the dye decreases after reaching a maximum which may be due to the requirement of an increase in the contact time as the adsorbent dosage increases. The present study reveals that optimum adsorbent dosage was found to be 100 mg L⁻¹, which provided the maximum color removal efficiency of 98.33%.
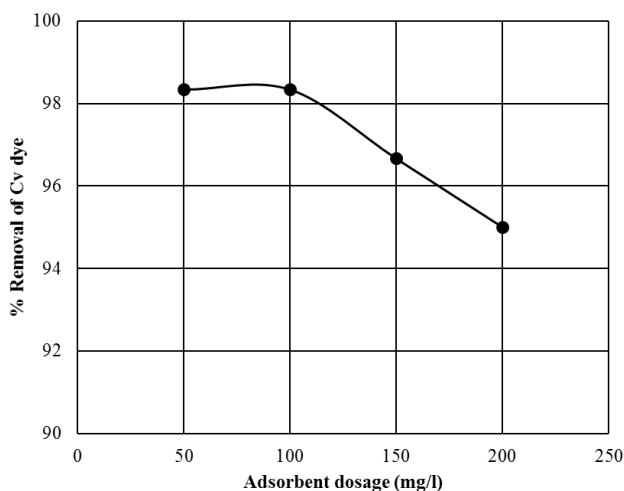
4.2. Effect of contact time

Fig. 6 shows the effect of contact time on the adsorption of CV on CTC. The equilibrium adsorption percentage increases with an increase in contact time and approaches to equilibrium after 60 min. Therefore, 1 h was taken as the optimum time for adsorption of CV on CTC because the further increase in contact time did not show an increase in biosorption. A similar trend was reported by Ibisi and Asoluka [28] where the removal rates of heavy metals on bio-adsorbent remained at equilibrium after 60 min. Due to a large number of vacant sites available at the beginning of the adsorption process, the rate is high and hence the % removal of dye was increasing. As time increases, due to adsorption, the vacant sites are occupied, the rate slows down due to the limited mass transfer of the adsorbate from bulk liquid to the external surface of adsorbents. Further increase in time duration will not support anymore adsorption due to unavailable vacant sites for the adsorbate.

4.3. Effect of temperature

The adsorption of crystal violet dye using CTC is carried out in the temperature ranging from 25°C–55°C and the removal efficiency is shown in Fig. 7. When the temperature increases to 35°C, the removal of the dye increased from 86.6%–96.6%. Further, an increase in temperature from 35°C–45°C caused a decrease in adsorption. As the temperature increases, the physical interaction between the dye and the adsorbent weakens and also the bonding between the dye and solvent becomes stronger which becomes tedious for the interaction of dye and biochar [29]. A similar trend was reported by Alshabanat et al. [29] for the adsorption of CV on date palm fibers. Further increase in temperature to 55°C, the removal efficiency remained constant as 88.35%. Therefore, this suggests that at 35°C there is a maximum removal efficiency of CV dye.

Fig. 5. Effect of varying adsorbent dosage for the removal of CV dye (dye concentration = 30 mg L⁻¹; time = 60 min; temperature = 35°C).
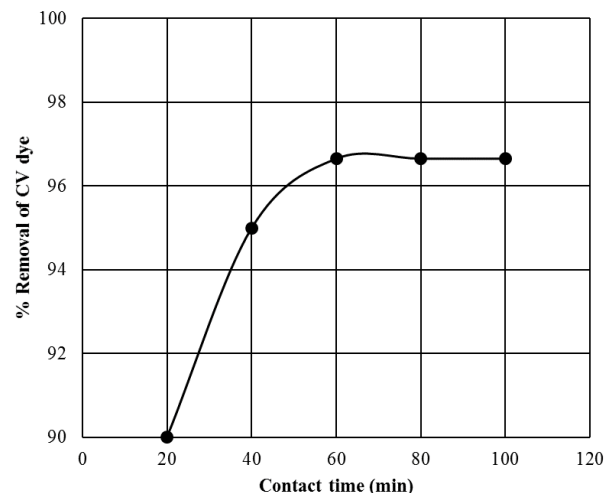
Fig. 6. Effect of contact time on CV decolourisation (adsorbent dosage = 100 mg L⁻¹; dye concentration = 30 mg L⁻¹; temperature = 35°C).
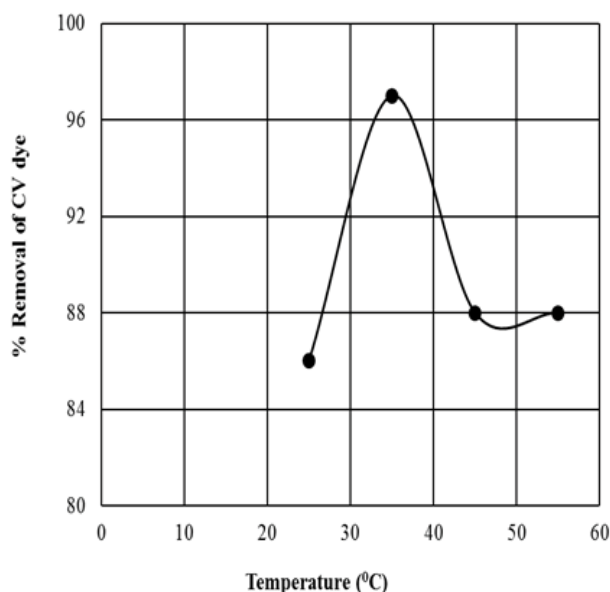
Fig. 7. Effect of varying temperature on CV decolourisation (adsorbent dosage = 100 mg L^{-1}; dye concentration = 30 mg L^{-1}; time = 60 min).

Fig. 8. Effect of varying CV dye concentration (adsorbent dosage = 100 mg L^{-1}; time = 60 min; temperature = 35°C).

4.4. Effect of CV dye concentration

The adsorption capacity fluctuates as the dye concentration increases from 10–40 mg L^{-1} as shown in Fig. 8. At 60 mg L^{-1}, the removal efficiency was found to be maximum. On further increase in the dye the concentration of the removal efficiency decreased. This is due to the decrease in the availability of active sites on adsorbent to adsorb the CV dye. The same pattern was observed in the removal of cadmium and lead, where the removal efficiency decreased as the concentration of metal ion increases [28]. It was observed that the optimum maximum dye concentration for adsorption on CTC was found to be 50 mg L^{-1} where the removal efficiency was 70%. Therefore, as the dye concentration increases it is required to increase the adsorbent dosage to achieve maximum removal efficiency.

4.5. Characterisation of CTC

The characterization of CTC before and after adsorption of CV dye using Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were analysed.

4.5.1. Fourier-transform infrared spectroscopy

The infrared spectra of CTC were tested using the KBr technique. This measurement showed the presence of the following groups in Fig. 9. The absorbance bands at 1,701.24 and 1,601.91 are due to C=C bond. In the region (1,200–1,100 cm^{-1}), there is a peak at 1,154.42 cm^{-1} refers to the C–H bending vibrations. Two peaks observed in the range (500–700 cm^{-1}) are due to the C–H out of the plane bending vibration. This type of bending is commonly found on various surfaces of activated carbon.
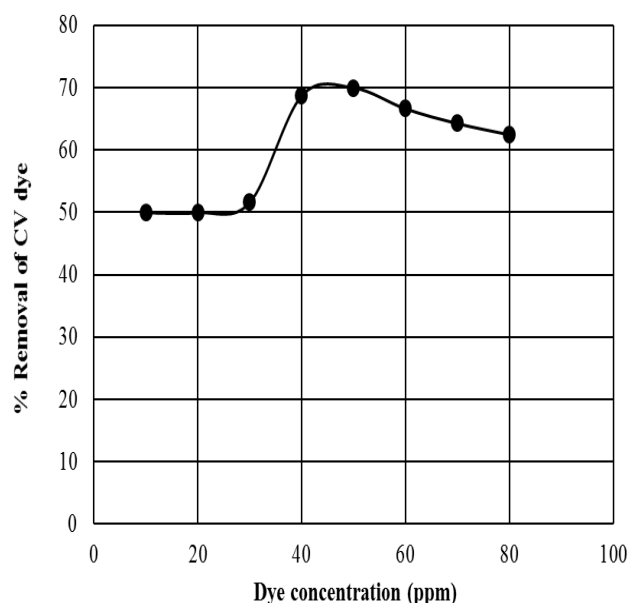
The FTIR spectrum for CTC after adsorption of CV is shown in Fig. 10. The broadband in the range 3,600–3,100 cm^{-1} is due to NH and OH^{-} stretching vibration, is deformed in comparison to CTC before adsorption and the band around 2,900–2,500 cm^{-1} shows a C–H stretching vibration [30]. The bands in 2,300–2,100 cm^{-1} corresponds to the symmetric (NH^{3+}) stretching frequency which is the main characteristic peak of crystal violet dye. The broad peak at 2,100 can be assigned to allene group (C=C=C). In the region 1,400–1,600 cm^{-1} a cluster of complex bands may be due to the presence of aromatic bands and other substitution modes of aromatic rings. The peak at 1,200.35 can be C–X bond where X is a halide. In the case of crystal violet, it is chlorine. The band at 1,585.51 indicates the C=C stretching of the benzene ring.

4.5.2. Scanning electron microscopy

The surface morphology of CTC before and after adsorption was analyzed by SEM image as shown in Fig. 12. It is clear from the image that the adsorbent has rough surface morphology with a number of micropores. As seen in Fig. 11a. It has uneven cavities and fine open pores. Thus it is easy for the CV dye molecules to adsorb on the porous surface. The holes are seen to be covered appearing fibrous in nature as shown in Fig. 11b. Thus the treatment with sulphuric acid increases the porous nature and is also responsible for high surface area for CV dye to adsorb on the CTC.

4.6. Mechanism of adsorption of crystal violet onto CTC

The crystal violet, also known as tris[4-(dimethylamino)phenyl]methylium chloride has a negatively charged chlorine held by the positively charged R=N(CH$_3$)$_2^+$ in the dye structure. The chlorine ion dissociates in the aqueous
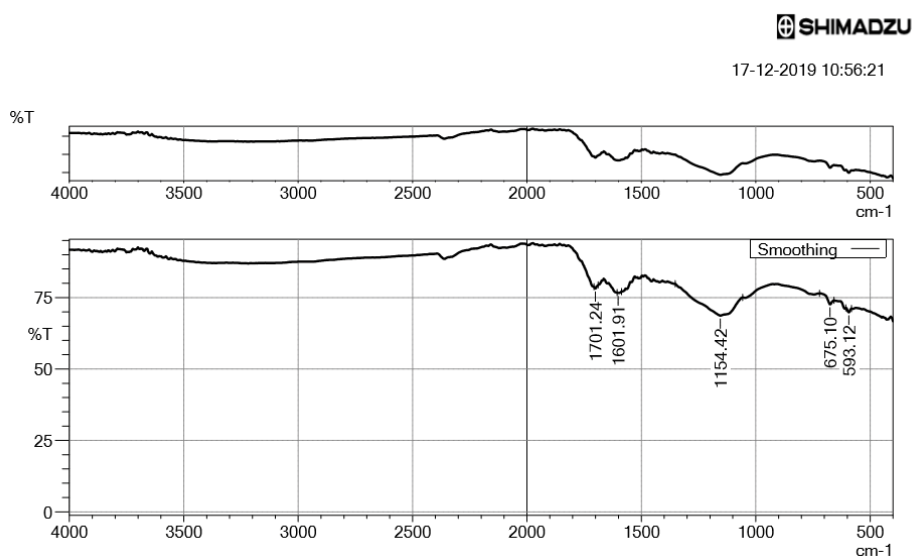
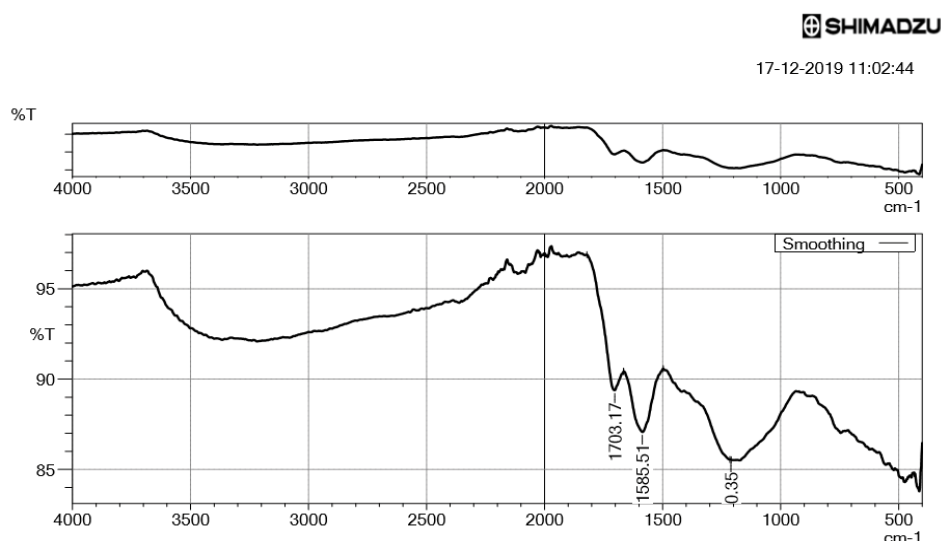Fig. 9. FTIR spectrum of CTC before adsorption of CV dye.

Fig. 10. FTIR spectrum of CTC after adsorption of CV dye.

solution of biochar containing free and protruding –C–H bonds, in a manner similar to halide substitution, following which the partially charged water molecule dissociates into Arrhenius base, Arrhenius acid and modifies the chlorine substituted biochar. As a sequel of which the Arrhenius base hydroxyl group OH⁻ attacks the –C–Cl bond in biochar and forms –C–OH on the surface of biochar, where –C–H was originally present. The Arrhenius acid attacks the double bond nitrogen in $R=N(CH_3)_2^+$ and yields an imine product, $R–NH(CH_3)_2^+$. This mechanism has been deconstructed from the FTIR result wherein the presence of OH⁻ and –NH– group has been detected, in the sample post adsorption. From the FTIR result and the mechanism mentioned above, the charges are redistributed as follows. The crystal violet structure with the imine group has a positive charge while the hydroxylated biochar tends to exhibit a partial negative charge due to the highly electronegative oxygen atom. The charge difference between these two moieties facilitates surface adsorption of crystal violet on biochar in an aqueous medium. During this process, this process the pH tends to decrease slightly, however, the post adsorption sample pH remained near neutral, suggesting the concentration of HCl was minimal and thus did not significantly influence the pH of the process. The effective adsorption based on the charge distribution and differences has been proved through the batch adsorption studies and FTIR results.

4.7. Adsorption isotherm studies

The adsorption isotherm is important in designing the adsorption system. It is used to study the interaction of adsorbent with adsorbate and also provides information
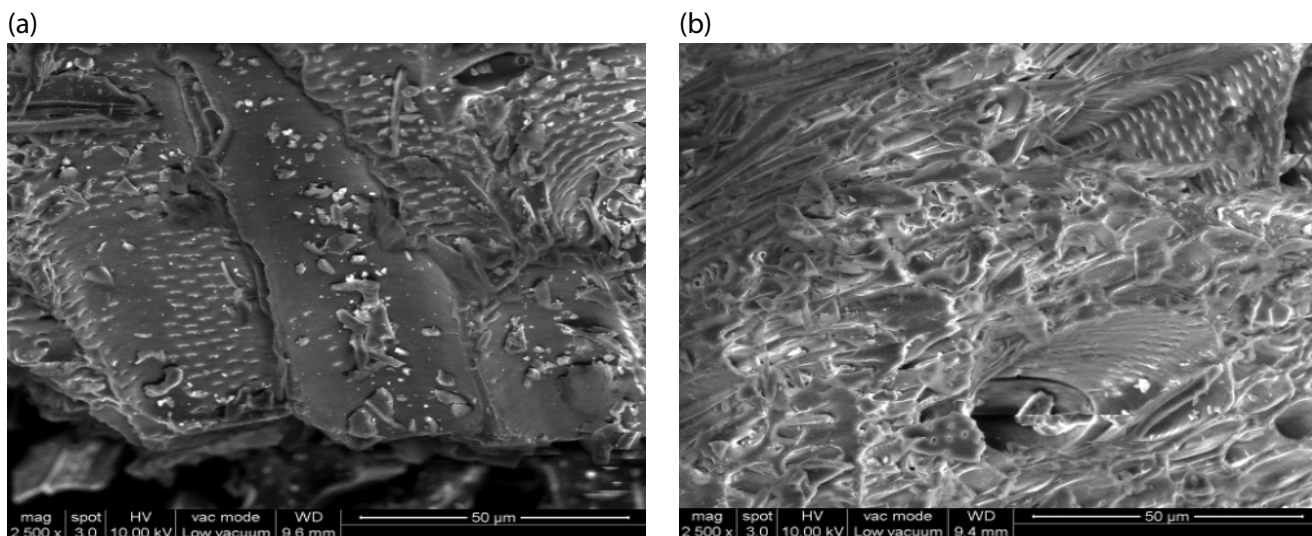
(a)

(b)

Fig. 11. SEM image of untreated CTC (a) and CV loaded CTC and (b) with 20 µM magnification.

about the heterogeneity or homogeneity of the adsorbent [31]. The adsorption equilibrium data in this study were modeled with two isotherms: Langmuir isotherm and the Freundlich isotherm model.

4.7.1. Langmuir isotherm

Langmuir Isotherm refers to a single homogenous layer of adsorption [32]. This model predicts the maximum monolayer adsorption capacity of CV on CTC. Based on this assumption Langmuir isotherm can be subsequently obtained from the below equation.

$$q_e = Q_0 \frac{K_L C_e}{1 + K_L C_e} \tag{3}$$

The linearized form of the above Langmuir isotherm equation is represented as:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \tag{4}$$

where C_e = equilibrium concentration of dye (mg L^{-1}); q_e = amount of CV on (CTC) at equilibrium (mg g^{-1}); Q_0 = maximum monolayer coverage capacity (mg g^{-1}); K_L = Langmuir isotherm constant (L mg^{-1}).

The values of Q_0 and K_L are obtained from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$ as shown in Fig. 12. The isotherm was found to be linear over a range of dye concentrations with a correlation coefficient (R^2 = 0.939). The value of Q_0 is found to be 35.71 mg g^{-1}. A comparison of Q_0 values with respect to different adsorbents used in adsorbing dyes is given in Table 2. As the dye concentration in this experiment ranges from 10–80 ppm, the value is found to be low. K_L implies the binding affinity of the adsorbent to the adsorbate, and its value is found to be 0.0289 (L mg^{-1}).

The essential property of this isotherm is a dimensionless constant separation factor, R_L or equilibrium parameter [33,34]. It is defined by the equation:
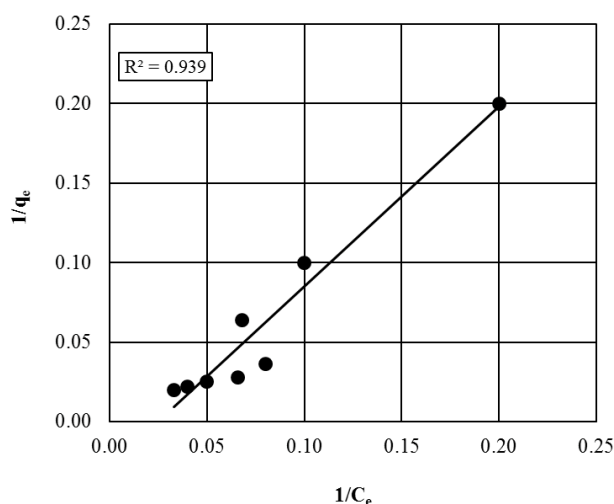

Fig. 12. Langmuir adsorption isotherm for the removal of CV by CTC.

$$R_L = \frac{1}{1 + \left(1 + K_L C_0\right)} \tag{5}$$

A plot between C_0 and R_L is shown in Fig. 13. It is inferred that as the dye concentration increases, the separation factor decreases due to the less availability of active sites of the biochar. The separation factor can be increased by increasing the dosage of the adsorbent.

4.7.2. Freundlich isotherm

Freundlich isotherm model is used to describe the adsorption equation. Unlike the Langmuir model, this isotherm explains the multilayer adsorption on heterogeneous surfaces [35]. The empirical equation proposed by Freundlich is given by the below equation:

Table 2
Comparison of adsorption capacity of crystal violet on Curry tree bark using Literature

Adsorbent	Dye	Q_0 (mg g^{-1})	References
Bentonite clay	Reactive black 5	34.01	36
Tricalcium phosphate	Reactive yellow 4	40.85	37
Apatiticoctocalcium phosphate	Reactive yellow 4	61.65	37
Atermit factory solid wastes	Reactive red 45	35.771	38
Soybean hull	Safranin	29.49	39
Corncob modified with epichlorohydrin	Crystal violet	71.43	40
Curry tree bark	Crystal violet	35.71	This study
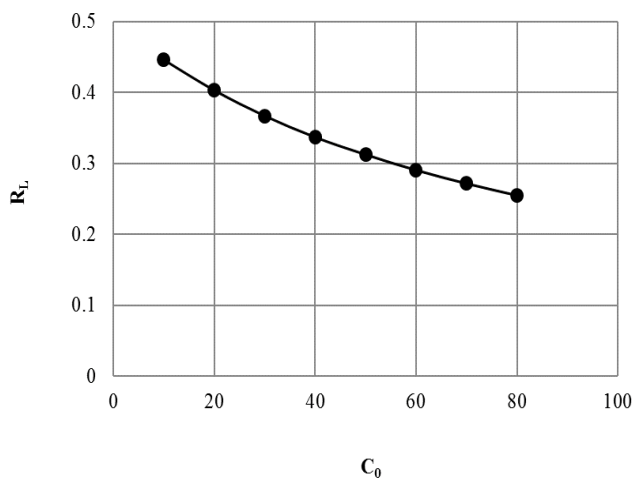
Fig. 13. R_L for CV removal by CTC.

Fig. 14. Freundlich adsorption isotherm for the removal of CV by CTC.

$$Q_e = K_f C_e^{\frac{1}{n}} \tag{6}$$

where K_f = Freundlich isotherm constant (L mg^{-1}); n = adsorption intensity; C_e = equilibrium concentration of adsorbate (mg L^{-1}); Q_e = amount of CV dye adsorbed per gram of the adsorbent at equilibrium (mg g^{-1}).

By linearizing the above equation:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{7}$$

where K_f is an approximate indicator of adsorption capacity; $1/n$ is a function of the strength of adsorption in the adsorption process.

K_f and n are obtained from the intercept and slope of the plot of $\ln Q_e$ vs. $\ln C_e$, as shown in Fig. 14. If $n = 1$, then the partition between the two phases are independent of the concentration. If the value of $1/n$ is below one, it indicates normal adsorption. On the other hand, $1/n$ above one indicates cooperative adsorption. In this study, the value of n calculated using the Freundlich model was 0.7336. Therefore, the value of n illustrated that the adsorption bonds between CV and CTC green waste activated carbon were by cooperative adsorption. The adsorption isotherm parameters are given in Table 3.
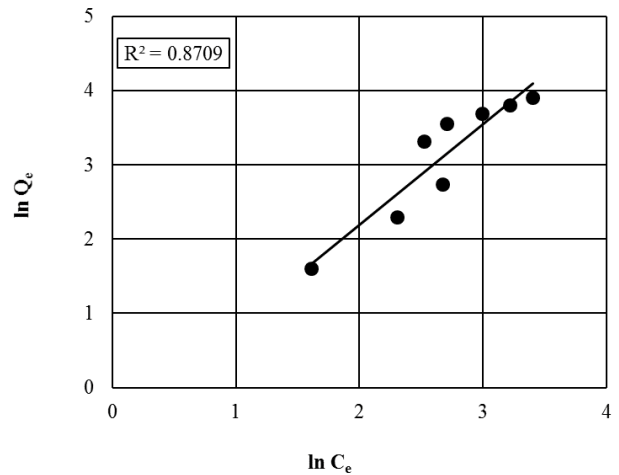
4.8. Kinetic studies

Adsorption kinetics are used to assess the rate of the adsorption process.

The Lagergren first-order equation [41] is given as:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{8}$$

where q_e and q_t are the amount of crystal violet adsorbed (mg g^{-1}) on the adsorbent at equilibrium and at any time t respectively and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). The Lagergren pseudo-first-order is plotted between $\log(q_e - q_t)$ and time t and the constants for the adsorption of crystal violet on CTC is given in Table 4.

The Lagergren pseudo-second-order equation is expressed below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

where the q_e and q_t are mass of crystal violet dye adsorbed at equilibrium and at any time t, respectively. k_2 is the rate constant of pseudo-second-order (g mg^{-1} min^{-1}) is obtained from the intercept of the graph that is plotted between 't' and t/q_t. The kinetic constants for the second-order are given in Table 4.

Table 3
Langmuir and Freundlich model parameters

Adsorbate	Q_0 (mg g^{-1})	Langmuir			Freundlich		
		K_L (L mg^{-1})	R^2		K_f (L mg^{-1})	n	R^2
CV	35.71	0.0247	0.939		0.536	0.7336	0.870

Table 4
Kinetic constants for the adsorption of crystal violet on curry tree bark

Adsorbent	Curry tree bark
Pseudo-first-order kinetics	$q_e = 2.447$
	$k_1 = 2.303 \times 10^{-3}$
	$R^2 = 0.691$
Pseudo-second-order kinetics	$q_e = 30.303$
	$k_2 = 0.0205$
	$R^2 = 0.999$

The q_e from pseudo-second-order kinetics is found to be 30.303 mg g^{-1}. The R^2 values obtained from pseudo-first-order and second-order models, pseudo-second-order hold the best fit with the adsorption data. This shows that the chemisorption process controls the adsorption process [42].

5. Conclusion

In this study, biochar was prepared from low-cost agricultural waste (*Murraya koenigii* stems) and has demonstrated the potentiality to decolorize crystal violet dye from aqueous solution in batch mode. The optimum adsorption parameters of the study were, the optimum adsorbent dosage (100 mg L^{-1}), Time (60 min), temperature (35°C) and optimum dye concentration (10 ppm). The removal efficiency was pH-independent and adsorption equilibrium was obtained within 60min. The removal efficiency of the dye was found to be >70%. The experimental data obtained from the isotherm studies fit well with the Langmuir isotherm model due to the increase in correlation coefficient which was higher in comparison to R^2 of Freundlich Isotherm. The maximum adsorption capacity (Q_0) is 35.71 mg g^{-1}, estimated with the Langmuir isotherm model. The kinetic equations were used to assess the rate of adsorption process at different initial dye concentrations and results showed that the pseudo-second-order model best fits the kinetic data. The characteristic studies such as FTIR and SEM also indicated the effective adsorption of crystal violet onto CTC. Future work has to be carried out at higher dye concentrations and for different dyes to demonstrate the efficiency of CTC as an alternate biosorbent. Hence this study shows that *Murraya koenigii* stems has a great potential to be used as a low-cost bio adsorbent in removing toxic dye, crystal violet.

References

[1] P.S. Kumar, A. Saravanan, Chapter 11 – Sustainable Wastewater Treatments in Textile Sector, S.S. Muthu, Sustainable Fibres and Textiles: A Volume in the Textile Institute Book Series, Woodhead Publishing, Chennai, India, 2017,pp. 323–346.

[2] M. Iqbal, J. Abbas, A. Nisar, Nazir, A. Qamar, Bioassays based on higher plants as excellent dosimeters for ecotoxicity monitoring: a review, Chem. Int., 5 (2019) 1–80.

[3] M. Iqbal, *Vicia faba* bioassay for environmental toxicity monitoring: a review, Chemosphere, 144 (2016) 785–802.

[4] M.T. Yagub, T.K. Sen, H.M. Ang, Equilibrium, kinetics, and thermodynamics of methylene blue adsorption by pine tree leaves, Water Air Soil Pollut., 223 (2012) 5267–5282.

[5] V.K. Garg, P. Kaushik, Influence of textile mill wastewater irrigation on the growth of *Sorghum cultivars*, Appl. Ecol. Environ. Res., 6 (2008) 1–12.

[6] V. Gomez, M.S. Larrechi, M.P. Callao, Kinetic and adsorption study of acid dye removal using activated carbon, Chemosphere, 69 (2007) 1151–1158.

[7] R.C. Kuhad, N. Sood, K.K. Tripathi, A. Singh, O.P. Ward, Developments in microbial methods for the treatment of dye effluents, Adv. Appl. Microbiol., 56 (2004) 185.

[8] A. Mittal, L. Kurup (Krishnan), V.K. Gupta, Use of waste materials bottom ash and de-oiled soya, as potential adsorbents for the removal of amaranth from aqueous solutions, J. Hazard. Mater., 117 (2005) 171–178.

[9] P.S. Kumar, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi, S. Sivanesan, Adsorption of dye from aqueous solution by cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions, Desalination, 261 (2010) 52–60.

[10] A. Ajmal, I. Majeed, R.N. Malik, H. Idriss, M.A. Nadeem, Principles and mechanisms of photocatalytic dye degradation on TiO$_2$ based photocatalysts: a comparative overview, RSC Adv., 4 (2014) 37003–37026.

[11] A.A. Vaidya, K.V. Datye, Environmental pollution during chemical processing of synthetic fibres, Colourage, 14 (1982) 3–10.

[12] M.A. Hassaan, A. El Nemr, Advanced oxidation processes for textile wastewater treatment, Int. J. Photochem. Photobiol., 2 (2017) 85–93.

[13] A.E. Ghaly, R. Ananthashankar, M.V.V.R. Alhattab, V.V. Ramakrishnan, Production, characterization and treatment of textile effluents: a critical review, J. Chem. Eng. Process Technol., 5 (2014) 1–19.

[14] Y. Miyah, A. Lahrichi, M. Idrissi, S. Boujraf, H. Taouda, F. Zerrouq, Assessment of adsorption kinetics for removal potential of crystal violet dye from aqueous solutions using Moroccan pyrophyllite, J. Assoc. Arab Univ. Basic Appl. Sci., 23 (2017) 20–28.

[15] A. Mittal, L. Kurup (Krishnan), V.K. Gupta, Use of waste materials bottom ash and de-oiled soya, as potential adsorbents for the removal of amaranth from aqueous solutions, J. Hazard. Mater., 117 (2005) 171–178.

[16] E.D. Morales-Álvarez, C.M. Rivera-Hoyos, S.A. Poveda-Cuevas, E.A. Reyes-Guzmán, A.M. Pedroza-Rodríguez, E.A. Reyes-Montaño, R.A. Poutou-Piñales, Malachite green and crystal violet decolorization by *Ganoderma lucidum* and *Pleurotus ostreatus* supernatant and by rGlLCC1 and rPOXA 1B concentrates: molecular docking analysis, Appl. Biochem. Biotechnol., 184 (2018) 794–805.

[17] A.M. Alkherraz, A.K. Ali, K.M. Elsherif, Removal of Pb(II), Zn(II), Cu(II) and Cd(II)from aqueous solutions by adsorption onto olive branches activated carbon: equilibrium and thermodynamic studies, Chem. Int., 6 (2020) 11–20.

[18] K.B. Daij, S. Bellebia, Z. Bengharez, Comparative experimental study on the COD removal in aqueous solutions of pesticides

by the electrocoagulation process using monopolar iron electrodes, Chem. Int., 3 (2017) 319–27.

[19] N.E. Ibisi, C.A. Asoluka, Use of agro-waste (*Musa paradisiaca* peels) as a sustainable biosorbent for toxic metal ions removal from contaminated water, Chem. Int., 4 (2018) 52–59.

[20] S. Ghezali, A.M.-Benzerdjeb, M. Ameri, A.Z. Bouyakoub, Adsorption of 2, 4, 6-trichlorophenol on bentonite modified with benzyldimethyltetradecylammonium chloride, Chem. Int., 4 (2018) 24–32.

[21] A.A. Ahmad, A. Idris, B.H. Hameed, Organic dye adsorption on activated carbon derived from solid waste, Desal. Water Treat., 51 (2013) 2554–2563.

[22] M. Fazal-ur-Rehman, Methodological trends in preparation of activated carbon from local sources and their impacts on production: a review, Chem. Int., 4 (2018) 109–119.

[23] S.A. Ganiyu, O.O. Ajumobi, S.A. Lateef, K.O. Sulaiman, I.A. Bakare, M. Qamaruddin, K. Alhooshani, Boron-doped activated carbon as efficient and selective adsorbent for ultra-deep desulfurization of 4,6-dimethyldibenzothiophene, Chem. Eng. J., 321 (2017) 651–661.

[24] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of methylene blue on low-cost adsorbents: a review, J. Hazard. Mater., 177 (2010) 70–80.

[25] Y. Song, R. Peng, S. Chen, Y. Xiong, Adsorption of crystal violet onto epichlorohydrin modified corncob, Desal. Water Treat., 154 (2019) 376–384.

[26] K. Legrouri, E. Khouya, H. Hannache, M. El Hartti, M. Ezzine, R. Naslain, Activated carbon from molasses efficiency for Cr(VI), Pb(II) and Cu(II) adsorption: a mechanistic study, Chem. Int., 3 (2017) 301–310.

[27] P.L. Prabha, S.A.F. Rani, B. Jayalakshmi, T. Ramachandramoorthy, Curry tree carbon-a novel adsorbent for the removal of Zn(II) ions in aqueous medium, World J. Pharm. Pharm. Sci., 5 (2016) 1543–1557.

[28] N.E. Ibisi, C.A. Asoluka, Use of agro-waste (*Musa paradisiaca* peels) as a sustainable biosorbent for toxic metal ions removal from contaminated water, Chem. Int., 4 (2018) 52–59.

[29] M. Alshabanat, G. Alsenani, R. Almufarij, Removal of crystal violet dye from aqueous solutions onto date palm fiber by adsorption technique, J. Chem., 2013 (2013) 1–6.

[30] A. Kant, P. Gaijon, U. Nadeem, Adsorption equilibrium and kinetics of crystal violet dye from aqueous media onto waste material, Chem. Sci. Rev. Lett., 3 (2014) 1–13.

[31] C.A.P. Almeida, N.A. Debacher, A.J. Downs, L. Cottet, C.A.D. Mello, Removal of methylene blue from colored effluents by adsorption on montmorillonite clay, J. Colloid Interface Sci., 332 (2009) 46–53.

[32] I. Langmuir, The constitution and fundamental properties of solids and liquids, Part I. Solids, J. Am. Chem. Soc., 38 (1916) 2221–2295.

[33] E. Radaee, M.R. Alavi Moghaddam, M. Arami, The study of the adsorption of reactive blue 19 dye by activated carbon from pomegranate residue, J. Water Wastewater, 25 (2014) 27–34.

[34] I. Chaari, M. Feki, M. Medhioub, J. Bouzid, E. Fakhfakh, F. Jamoussi, Adsorption of a textile dye "Indanthrene Blue RS (C.I. Vat Blue 4)" from aqueous solutions onto smectite-rich clayey rock, J. Hazard. Mater., 172 (2009) 1623–1628.

[35] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem., 57 (1906) 1100–1107.

[36] M.T. Amin, A.A. Alazba, M. Shafiq, Adsorptive removal of reactive black 5 from wastewater using bentonite clay: isotherms, kinetics and thermodynamics, Sustainability, 7 (2015) 15302–15318.

[37] H. El Boujaady, A. El Rhilassi, M. Bennani-Ziatni, R. El Hamri, A. Taitai, J.L. Lacout, Removal of a textile dye by adsorption on synthetic calcium phosphates, Desalination, 275 (2011) 10–16.

[38] S. Savci, M. Yalvac, Z. Karaman, F. Deniz, M.A. Mazmanci, Removal of reactive red 45 using atermit factory solid wastes by adsorption, Fresenius Environ. Bull., 28 (2019) 1724–1732.

[39] V. Chandan, V.K. Singh, Adsorption of safranin dye from aqueous solutions using a low-cost agro-waste material soybean hull, Desal. Water Treat., 57 (2016) 4122–4134.

[40] Y. Song, R. Peng, S. Chen, Y. Xiong, Adsorption of crystal violet onto epichlorohydrin modified corncob, Cell, 1 (2019) 5.

[41] S. Lagergren, About the theory of so called adsorption of soluble substances, Kungliga Sven. Vetenskapsakad. Handlingar, 24 (1898) 1–39.

[42] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, Process Biochem., 34 (1999) 451–465.