Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1066272

57 (2016) 14728–14738
July

Taylor & Francis
Taylor & Francis Group

Tea dust as a potential low-cost adsorbent for the removal of crystal violet from aqueous solution

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Received 13 January 2015; Accepted 17 June 2015

ABSTRACT

The present work demonstrates tea dust (TD) as a potential low-cost adsorbent for the removal of crystal violet (CV) from aqueous solution by batch adsorption technique. Reaction kinetics and isotherm studies were carried out under various conditions of initial dye concentration, contact time, adsorbent dosage, and pH. The adsorbent was characterized by scanning electron microscopy, Fourier transform infrared spectroscopy (FTIR) and Brunauer–Emmett–Teller. FTIR results showed complexation and ion exchange appeared to be the principle mechanism for CV adsorption. The adsorption isotherm data were fitted to Langmuir and Freundlich equations; and the maximum adsorption capacity was found to be 175.4 mg/g. The removal of CV by TD followed the unified approach model. Therefore, TD can be employed as an efficient and cost-effective adsorbent in industrial wastewater treatment for the removal of basic dyes.

Keywords: Adsorption; Tea Dust; Crystal Violet; Isotherm; Kinetics; Unified Approach Model

1. Introduction

At the beginning of the twenty-first century, the earth, with its diverse and abundant life forms, including over six billion humans, is facing a serious water crisis. All the signs suggest that the demand for water entitled “Water for People Water for Life” (United Nations World Water Development Report UNESCO) is increasing tremendously with agricultural, industrial, and domestic sectors consuming 70, 22, and 8% of the available fresh water, respectively, and this has resulted in the generation of large amounts of wastewater containing a number of pollutants [1,2]. One of the important classes of the pollutants is dyes. Their discharge into hydrosphere possesses a significant source of pollution due to their recalcitrance nature. This offers undesirable color to the water body that reduces sunlight penetration as well as resists photochemical and biological attacks to aquatic life [3]. On the basis of up-to-date data, more than 100,000 commercial dyes are known with an annual production of over 7×10^5 tonnes/year [4]. The total dye consumption in the textile industry worldwide is more than 10,000 tonnes/year and approximately 100 tonnes/year of dyes is discharged into water streams [5].

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In fact, the chemical structures of dyes are complicated aromatic structures that hardly degrade in conventional wastewater treatment processes due to their stability to sunlight, oxidizing agent, and microorganisms [6]. The effluent coloration by dyes even in low concentration can affect photosynthesis process as well as aquatic ecosystem. Incomplete degradation of dyes by bacteria in the sediment may produce toxic amines [7] under anaerobic conditions known as carcinogenic that is harmful to human and aquatic system [8,9].

Crystal violet (CV) is a monovalent cationic dye [10], widely used in textiles and printing industries for dyeing of cotton, wool, silk, nylon, leather, etc. [7,11]. Moreover, CV is applied as biological stain, dermatological agent, veterinary medicine, and additive to poultry feed to inhibit propagation of mold. This type of dye is a mutagen and mitotic poison [12]. CV becomes hazardous in case of eye contact or irritation, ingestion, inhalation, and skin contact. Therefore, removal of CV is an essential issue of wastewater treatment before discharge.

There are numerous methods to treat dye-bearing effluents. Despite the availability of many techniques to remove dye contaminants from wastewaters, such as coagulation, chemical oxidation, membrane separation process, adsorption, electrochemical, and aerobic and anaerobic microbial degradation; each of these methods has inherent limitations [13,14]. However, adsorption has been found to be superior to other techniques in terms of flexibility and simplicity of design, initial cost, insensitivity to toxic pollutants, and ease of operation [12]. Adsorption also does not produce harmful substances [15]. Factors that influence the adsorption efficiency include adsorbate–adsorbent interaction, adsorbent surface area, adsorbent to adsorbate ratio, adsorbent particle size, temperature, pH, and contact time. [15,16]. Commonly, the widely used adsorbent in the industry is activated carbon which has extensive surface area, high surface reactivity, microporous structure, and high adsorption capacity [12,17,18]. However, the performance of activated carbon is dependent on the type of carbon used and the characteristic of wastewater. The disadvantages using activated carbon are high operating and regenerating cost make its use limited [10,12,17–19]. Because of these drawbacks, other nonconventional adsorbents have been used to remove CV from wastewater such as natural low-cost adsorbents whereby represent higher potentiality and simplicity. Peat [20], rice husk [21], neem leaf [22], clay [23], and fly ash [23] were used for color removal from wastewater and effectiveness of dye adsorption was comparable to activated carbon [18]. Mohanty et al. [12] investigated the adsorption process for the removal of CV from industrial wastewater by available natural product rice husk-based activated carbon.

Tea waste is a common household waste, rich in tannin and polyphenolic compounds. Therefore, biodegradation of tea waste, an oxygen-demanding pollutant, is complicated [24]. Recently, a number of researchers paid attention to explore tea waste [25,26] or rejected tea [27,28] as cost-effective potential adsorbents for aqueous dye separation through liquid–solid adsorption technique. Heavy metals and dyes are removed from wastewater by tea-based adsorbents such as tea leaves for methylene blue [29], waste tea leaves carbon for chromium [30], tea waste leaves for lead, cadmium, and zinc [31]. However, to the best of our knowledge, none yet studied the potentiality of tea dust (TD) on CV dye removal from industrial wastewater.

Tea dust which is a waste material obtained from tea plantation is proposed as adsorbent for the removal of CV from the aqueous solution. In Malaysia, tea plants are commonly grown in the highland area located at Cameron Highland and the present sample collected from Sungai Palas Tea Centre, Pahang. Tea refers to the agricultural products of the leaves, leaf buds, and internodes of *Camellia Sinensis*, which has been prepared and cured by various methods, i.e. wilting, bruising, oxidation, fixation, yellowing, shaping, drying, curing, and packaging. During the transformation of the leaves into the dried leaves for brewing tea; there is a possibility to form dust as a waste material, known as tea dust (TD) considered for the study. Cay et al. [32] reported that nearly 30,000 tonnes/year TD is produced in Turkey alone and this value is approximately 5.5% of the total production. An estimation of more than 10,000 tonnes of rejected tea is generated annually in Malaysia [28]. TD accumulates in the agro-industrial yards where it has no significant industrial value and is not marketable. It has long been used as fuel in the tea-manufacturing processes (4,410 kcal/kg) or as fertilizer in local tea cultivation after composting. However, TD becomes an issue of health hazard and environmental concerns. Therefore, any attempt to utilize this waste will open a new economic window and will be beneficial.

In this study, tea dust was used as a low-cost adsorbent to remove CV dye from aqueous solution. Effective parameters such as adsorbent dosage, initial dye concentration, contact time, and pH were investigated. The Langmuir and Freundlich isotherms were used to fit the equilibrium data. The kinetic data were verified with pseudo-first-order, second-order, and unified approach models.

2. Materials and Methods

2.1. Materials

Tea dust was collected from Sungai Palas Tea Centre, Pahang, Malaysia. TD was boiled with distilled water for 90 min followed by further boiling with 0.1 M HCl for 60 min. Then, it was washed with boiled water and finally with distilled water for at least 10 times until the original color was completely removed confirmed apparently. After filtration, the adsorbent was dried in the oven at 60˚C for 24 h. The dried TD was ground and sieved using sieve shaker (Model: RETSCH, AS 200 Basic). Particle size used for the experiment was in the range of 315–500 µm. Finally, the resulting material was stored in airtight container for about three months in order to further use.

Crystal violet dye was purchased from Merck, Germany. A 500 ppm of stock solution was prepared by dissolving 0.2 g of the solid CV into the distilled water. pH of the solution was adjusted with 0.1 M HCl and 0.1 M NaOH. All working solutions were prepared by diluting the stock solution with deionized water.

2.2. Characterization method

Fourier transform infrared (FTIR) analysis was applied to determine the surface functional groups, using FTIR spectroscope (model: Spectrum 100, Perkin Elmer), where the spectra were recorded from 4,000 to 400 cm^{-1}. Surface morphology was studied using scanning electron microscopy (SEM) (model: Zeiss Evo 50). About 0.2 g of TD was used before and after the adsorption of CV during the experiments. Specific surface area based on N_2 physisorption was measured using Brunauer–Emmett–Teller (BET) (model: ASAP 2010, Micromeritics). The samples were degassed at 100 ˚C for 2 h prior to the sorption measurement.

2.3. Adsorption procedure

The effect of adsorbent dosages was studied by adding different amounts of TD in the range of 0.1–1 g in the 100 mL of solution. In the equilibrium study, 0.2 g of TD was added into 200-mL adsorbate with different concentrations in the range of 50–200 mL at room temperature and pH 7. Initial pH adjustments were carried out by adding either 0.01 M HCl or 0.01 M NaOH solution. This experiment was conducted in batch mode for 7 h. After the equilibrium was reached, the samples were centrifuged to separate solid particles before analyzed the equilibrium concentration. The concentration of CV was determined by UV–vis spectrophotometer (model: Hitachi U 1,800) at $\lambda_{\max} = 664$ nm. Adsorption kinetics experiments were performed by contacting 200 mL of CV solution of various initial concentrations ranging (50–200 mg/L) with 0.2 g of TD in a 500-mL stopper conical flask at room temperature. At fixed time intervals, ~5 mL of the samples were withdrawn and centrifuge. The concentration of the dye in the supernatant was determined. All experiments were carried out in triplicate and the mean values are reported. Standard deviation for the experimental points is obtained through one-way analysis of variance (ANOVA) using Microcal Origin 8 statistical software.

2.4. Isotherm studies

2.4.1. Langmuir isotherm

The Langmuir isotherm originally derived for the adsorption of gas molecules on solid surfaces. The isotherm was modified to fit the adsorption of solutes onto solid surfaces in solution systems [33]. This model adapted to liquid system by replacing the partial pressure with equivalent concentration [34]. This is important to establish the most befitting to the correlation of equilibrium curves. Langmuir isotherm is for single adsorption layer and homogeneous system [35]. Langmuir model for liquid–solid system expressed as in Eq. (1):

$$\frac{1}{q} = \frac{1}{Kq_\infty} . \frac{1}{q} + \frac{1}{q_\infty} \tag{1}$$

where K is the Langmuir constant ($\mathrm{m}^3\,\mathrm{kg}^{-1}$), q_∞ is the maximum adsorption capacity ($\mathrm{mg\,g}^{-1}$), and q is the amount of adsorbed at equilibrium (kg adsorbate/kg adsorbent).

2.4.2. Freundlich isotherm

The Freundlich isotherm was derived by assuming a heterogeneous surface with a nonuniform distribution of heat adsorption over the surface. The isotherm is shown as in Eq. (2):

$$\log q_\mathrm{e} = \left(\frac{1}{n}\right) \log C_\mathrm{e} + \log k_\mathrm{f} \tag{2}$$

where q_e is the amount of dye adsorbed (kg/kg), C_e is the equilibrium dye concentration, $1/n$ is the adsorption intensity, and k_f is the adsorption coefficient that represents the quantity of adsorbed species for a unit equilibrium concentration. n and k_f are Freundlich constants.

2.5. Kinetics studies

2.5.1. Legergren pseudo-first-order

Lagergren pseudo-first-order has been applied to determine the specific rate constant for adsorption. The Lagergren pseudo-first-order equation generally represented as in Eq. (3):

$$\log(q_\mathrm{e} - q_t) = \log q_\mathrm{e} - k_\mathrm{ad} t \tag{3}$$

where q_e is the amount of dye adsorbed at equilibrium (mg g^{-1}), q_t is the amount of dye adsorbed at time t (mg g^{-1}), and k_ad is the rate constant of pseudo-first-order kinetics (min^{-1}).

2.5.2 Pseudo-second-order

Pseudo-second-order model has been developed to analyze the kinetic data. Adsorption capacity of dye on the adsorbent particles was assumed proportional to the active site of the surface. For pseudo-second-order kinetic rate, the equation is as in Eq. (4):

$$\frac{t}{q_t} = \frac{1}{kq_\mathrm{e}^2} + \frac{1}{q_\mathrm{e}} t \tag{4}$$

where, all parameters are already defined.

2.5.3. Unified approach model

The removal rate decreases because of the formation of monolayer coverage of dye molecules on the outer surface of the adsorbent and pore diffusion onto the inner surface of the adsorbent particles through the film due to continuous agitation. The equilibrium data fitted well with the Langmuir model; however, unified approach model was used to explain the kinetic data. In the unified model, the adsorption process is considered as physicochemical interaction as in Eq. (5) in the simplified form:

$$q = (\alpha - \beta)\frac{\left(\frac{\beta}{\alpha}\right)e^{(\beta-\alpha)ak_1 t}}{\left(\frac{\beta}{\alpha}\right)e^{(\beta-\alpha)ak_1 t}} + \beta \tag{5}$$

$$\alpha = \frac{b + \sqrt{b^2 - 4ac}}{2a}, \beta = \frac{b - \sqrt{b^2 - 4ac}}{2a}$$

where $a = w_a$, $b = C_0 + w_a q_\infty + \frac{1}{K}$ and $c = q_\infty C_0$.

k_1 is determined from the slope and k_2 is determined from the relation $k_2 = \frac{k_1}{K}$. k_1 and k_2 are independent of different initial concentrations and adsorbent dosages.

2.6. Studies on point of zero charge

Zero point charge of adsorbent surface was determined by titration method. 0.1 M HCl and NaOH were used to analyze surface charge (Q) of the adsorbent in the aqueous phase. Q was calculated using Eq. (6) and graph of Q vs. pH system was plotted to determine the zero point charge.

$$Q = \frac{1}{w}(C_\mathrm{A} - C_\mathrm{B} - [\mathrm{H}^+] - [\mathrm{OH}^-]) \tag{6}$$

where w is the dry weight of adsorbent in aqueous system (g L^{-1}), C_A is the concentration of acid added into the aqueous system (mol L^{-1}), C_B is the concentration of base added into the aqueous system (mol L^{-1}), [H$^+$] is the concentration of H$^+$ (mol L^{-1}), and [OH$^-$] is the concentration of OH$^-$ (mol L^{-1}).

2.7. Statistical analysis

Best-fit mathematical model was selected on the basis of error analysis. For this purpose, Chi-square (χ^2) test has been used. The Chi-square can be calculated as Eq. (7):

$$\chi^2 = \sum \frac{(q_\mathrm{e} - q_\mathrm{cal})^2}{q_\mathrm{cal}} \tag{7}$$

where q_e, q_cal (mg/g) are the experimental and calculated amounts of dye adsorbed at equilibrium obtained from experiment and mathematical model, respectively.

3. Results and discussion

3.1. Adsorbent characterizations

3.1.1. FTIR study of the adsorbent

The FTIR spectra of TD before and after the adsorption of CV dye are shown in Fig. 1. As shown in Fig. 1, the FTIR spectroscopic analysis indicated broad bands at 3,416.29 cm^{-1}, representing the stretching frequency of bonded –OH groups. The absorption frequency observed at 2,942.89 cm^{-1} could be assigned due to the stretching frequency of C–H bond of methyl and

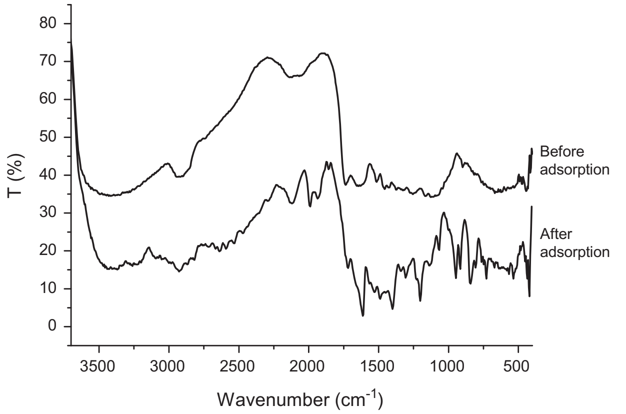

Fig. 1. FTIR spectra of TD before adsorption and after adsorption of CV dye.

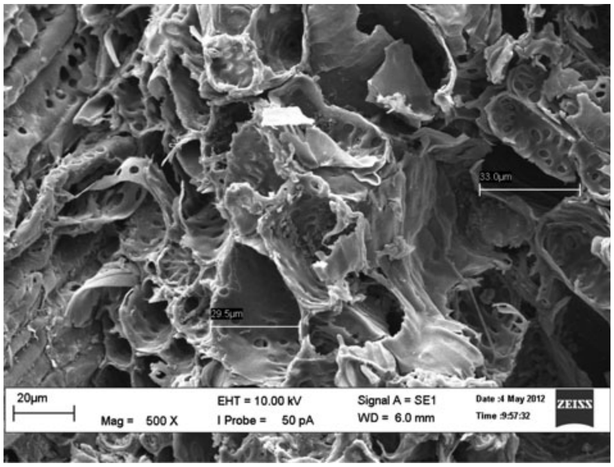

Fig. 2. SEM micrograph of TD at 500× magnification.

methylene groups. The absorption frequency observed at 1,734.23 cm^{-1} was assigned due to the carbonyl group (C=O) of unionized carboxylate stretching of carboxylic acid or pectin ester, while the peak at 1,646.20 cm^{-1} was attributed due to the C=O stretching of carboxylic acid with intermolecular hydrogen bonding form. The peak observed at 1,543.43 cm^{-1} corresponds to secondary amine group. The bending deformation observed at 1,456 cm^{-1} could be assigned due to the $–CH_3$ groups. The absorption frequencies observed at 1,252 and 1,128 cm^{-1} could be assigned due to the $–SO_3$ stretching and C–O stretching vibrations of ether groups, respectively.

After adsorption, the peaks of C=O of unionized carboxylate group of carboxylic acid and that of C=O of carboxylic acid with intermolecular hydrogen bonding forms are shifted from 1,734.23 to 1,715.99 cm^{-1}and 1,646.20 cm^{-1} to 1,608.81 cm^{-1}, respectively. Therefore, there are some red shifts observed through the C=O groups and the calculated units are 18.24 and 37.39, respectively. This indicates that COOH of TD could be the potential adsorption sites for interaction with the cationic CV dye.

3.1.2. SEM and BET analysis

SEM micrograph of TD with 500 times magnifications is shown in Fig. 2. The result revealed that TD consisted of fibers with significant pore and uneven surface structure. This surface characteristic will substantiate the higher adsorption capacity. The specific surface area of TD has been observed by BET method (figure not inserted due to simplicity) and the results are inserted in Table 1. In addition, the surface properties of TD such as BET surface area, pore diameter, and pore volume were obtained from BET experiment and compared with carbonaceous samples. From the data presented in Table 1, it is very clear that while TD does not have a very high surface area (59.9 m^2/g) as compared to the more expensive alternatives of activated carbon (AC) and carbon nanotubes (CNT) or even rattan sawdust (RS); it is still reasonably higher than the more expensive graphene oxide (GO)-based adsorbent. Furthermore, TD is still a better alternative in comparison to sawdust as well as carbonaceous adsorbents due to its worldwide availability, in contrast to the very location-based availability and rather costly. The average pore diameter of TD obtained

Table 1
Surface properties of tea dust (TD) obtained from BET experiment and compared with carbonaceous samples (RS, AC, GO, and CNT)

Sample name	BET surface area (m^2/g)	Average pore diameter (nm)	Pore volume (cm^3/g)	References
TD	59.9	5.33	0.031	Present study
Rattan sawdust (RS)	1,083	2.77	0.64	Hameed et al. [36]
Activated carbon (AC)	1,688	2.5	1.04	Li et al. [37]
Graphene oxide (GO)	32	17.3	0.11	Li et al. [37]
Carbon nanotubes (CNT)	177	12.1	0.54	Li et al. [37]

from BET is 5.33 nm verified by SEM analysis (3–6 nm). The pore size is classified as a mesopore, and mesoporous adsorbents are greatly sought for in adsorption processes due to the faster rate of adsorption and high maximum amount of solute-adsorbed quantities.

3.2. *Effect of initial concentration and contact time on CV adsorption*

The effect of the initial dye concentration (50–200 mg/L) on the adsorption of CV is shown in Fig. 3. It was observed that the amount of CV adsorbed was rapid for the first 20 min and thereafter it proceeded at a slower rate (20–100 min) and finally reached saturation. The equilibrium adsorption increases from 15.2 to 62.2 mg/g, with an increase in the initial CV concentration from 50 to 200 mg/L. As the initial concentration increases, the mass transfer driving force becomes predominant, hence resulting in higher CV adsorption [28]. It is also shown in figure that the contact time needed for CV solutions with initial concentrations of 50–200 mg/L to reach equilibrium was ~100 min. The initial concentration provides an important driving force to overcome all mass transfer resistances of the CV between the aqueous and solid phases. However, the experimental data were measured at 180 min to be sure that full equilibrium was attained.

3.3. *Surface charge (pH_{pzc}) and effect of pH on CV adsorption*

The point of zero charge (pH_{pzc}) is an important factor that determines the linear range of pH sensitivity and then indicates the type of surface active centers and the adsorption ability of the surface [38]. Many researchers studied the point of zero charge of adsorbents that prepared from agricultural solid wastes in order to better understand the adsorption mechanism. Cationic dye adsorption is favored at $pH > pH_{pzc}$, due to the presence of functional groups such as OH–, COO– groups. Anionic dye adsorption is favored at $pH < pH_{pzc}$ where the surface becomes positively charged [39,40]. The intersections of the curves with the straight line are known as the end points of the pH_{pzc}, and the value for TD is 4.2 as shown in Fig. 4. The effect of pH on the adsorption of CV is shown in Fig. 5. The experiments were conducted at 250 mL of 100-mg/L initial CV concentration and 0.20-g TD dose. It was observed that pH gives a significant influence to the adsorption process. CV is a cationic dye, which exists in aqueous solution in the form of positively charged ions. As a charged species, the degree of its adsorption onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the solution pH. As shown in the figure, the removal was minimum (112 mg/g) at pH 2, this increased up to pH 7.5 and then decreased (128 mg/g) at pH 9. This phenomenon occurred due to the presence of excess H^+ ions in the adsorbate and the negatively charged surface adsorbent. Lower adsorption of CV at acidic pH ($pH < pH_{pzc}$) is due to the presence of excess H^+ ions competing with the cation groups on the dye for adsorption sites. At higher solution pH ($pH > pH_{pzc}$), the TD possibly negatively charged and enhanced the positively charged dye cations through electrostatic forces of attraction. Therefore, pH 7 was considered for adsorption and kinetic experiments (Fig. (5)).

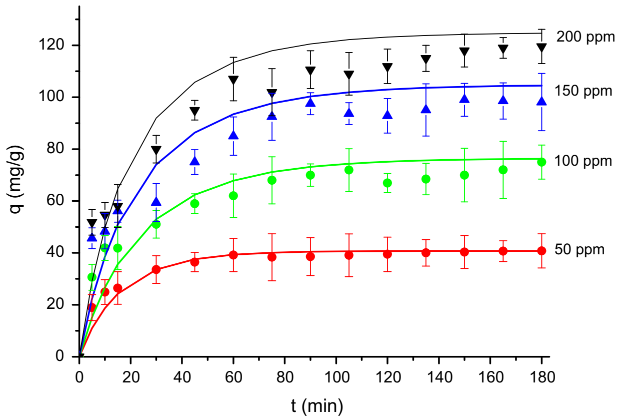

Fig. 3. Effect of contact time and initial concentrations of CV adsorption on TD.

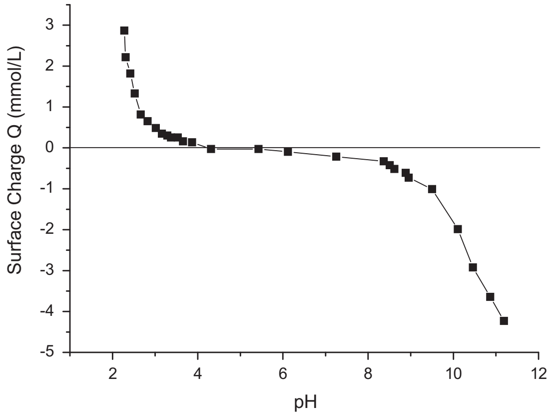

Fig. 4. Plot of determination of point of zero charge of tea dust presenting surface charge vs. system pH.

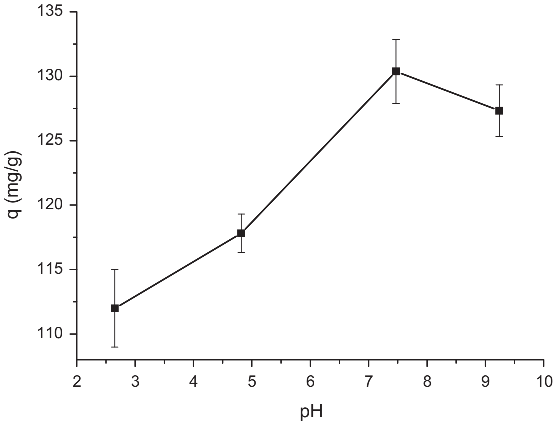

Fig. 5. Effect of pH on the adsorption of CV on TD.

3.4. Effect of adsorbent dosage on CV adsorption

Adsorbent dose has significant effect on the removal of CV. The different amounts of adsorbent doses used in the range 0.1–1 g. Based on the Fig. 6, it shows that as the adsorbent dosage increased, the percent of dye removal also increased might be due to the increased number of active sites and conglomeration of the adsorbent on the surface during adsorption. Similar results obtained by Bajpai and Jain [7], Mohanty et al. [12].

3.5. Isotherm studies

Analysis of the isotherm data is important to develop equations that correctly represent the results and could be used for design purposes. Fig. 7 and Table 2 show the fitting parameters for the measured isotherm data for CV adsorption onto TD on the nonlinear forms of Langmuir and Freundlich models. The values of nonlinear correlation coefficients (R^2) for the isotherm models indicate good fittings. The applicability of the isotherms showed that there were effectively monolayer sorption and a homogeneous distribution of active sites on the surface of biosorbent. The maximum CV adsorption capacity (mg/g) belongs to TD as shown in Table 2. The monolayer capacity ($q_{\max}$) is 175.4 mg/g as calculated from Langmuir at 313 K. The Freundlich model assumes that the uptake of CV occurs on a heterogeneous adsorbent surface. The magnitude of the Freundlich constant n gives a measure of favorability of adsorption. Values of $n > 1$ represent a favorable adsorption process [41].

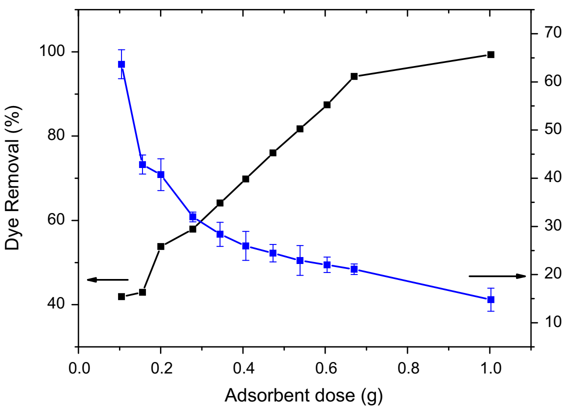

Fig. 6. Effect of adsorbent dosage on CV adsorption.

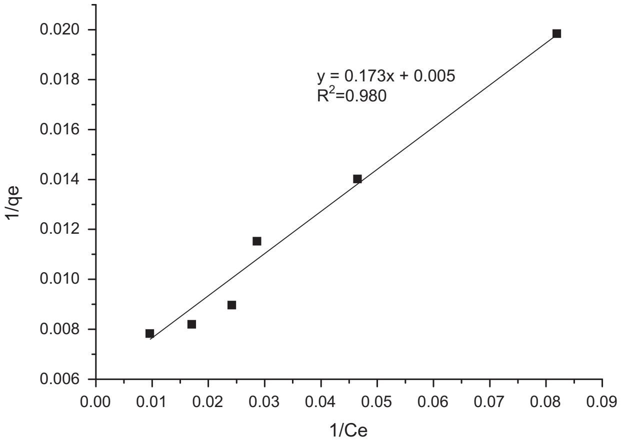

Fig. 7. Langmuir isotherm plot of CV adsorption onto TD.

3.5.1. Langmuir isotherm

The plot of $1/q_e$ vs. $1/C_e$ is linear with correlation R^2 is 0.98 as shown in Fig. 7. The χ^2 value for this model was calculated as 0.467. The higher value of R^2 and the low value of χ^2 indicate a close agreement between the experimental and calculated q_e. Maximum adsorption capacity $q_{\max}$ and equilibrium constant K were calculated from the slope and intercept of the plot, respectively, and found to be $q_{\max}$ and K were, respectively, 175.5 mg/g and 0.033 L/mg. The removal of CV through rice husk reported by Mohanty et al. [12] found the corresponding values as 11.175 mg/g and 0.0015 L/mg. This shows that TD is a potential adsorbent to remove CV from wastewater.

3.5.2. Freundlich isotherm

For Freundlich isotherm, the plot of log q_e vs. log C_e is linear with correlation R^2 was 0.915 as shown in Fig. 8. The χ^2 value obtained for Freundlich model (1.249) was higher than that of the Langmuir

Table 2
Isothermal and kinetic parameters for adsorption of CV onto TD at various initial concentrations

C_0 (ppm)	q_e (exp.)	Langmuir parameter		Pseudo-first-order				Pseudo-second-order				Unified approach model		
		$q_\alpha(\frac{\text{mg}}{\text{g}})$	$K(\frac{\text{L}}{\text{mg}})$	k_{ad} (1/min)	R^2	q_e (Calc.)	χ^2	k (g/mg min)	R^2	q_e (Calc.)	χ^2	$k_1 \times 10^4$ (L/mg min)	$k_2 \times 10^3$ (1/min)	χ^2
50	40.8			0.032	0.898	26.50	1.854	0.0020	0.999	45.46	0.107			0.242
100	74.9	175.40	0.032	0.016	0.861	43.34	1.808	0.0003	0.973	100.00	1.023	2.5 ± 0.05	6.0 ± 0.15	0.887
150	104.2			0.014	0.879	60.16	4.818	0.0005	0.998	111.11	0.662			1.210
200	124.1			0.015	0.950	77.40	1.123	0.0030	0.995	142.86	4.398			1.17

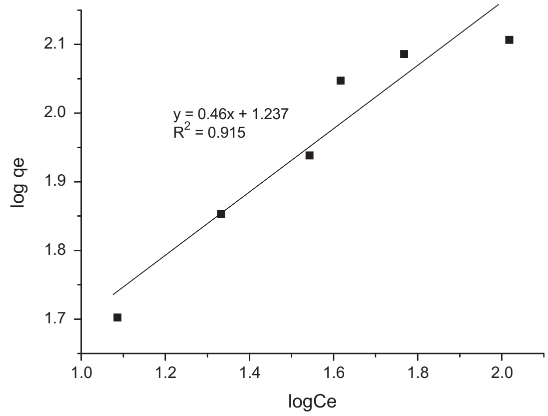

Fig. 8. Freundlich isotherm of CV adsorption onto TD.

model. The k_f and n constants were found to be 17.26 ((mg/g) $(\text{L/g})^{1/n}$) and 2.1,739, respectively. The value for 1/n is 0.46 indicating a normal Langmuir isotherm [42].

3.6. Adsorption kinetics studies

The adsorption rate is an important factor for kinetic study of the process as well as a better choice of material to be used as an adsorbent. Kinetics data were evaluated using pseudo-first-order, pseudo-second-order, and unified approach model for different initial concentrations and the fitness of models was ascertained by comparing the R^2 and χ^2 values and also by judging the closeness of experimental and calculated q_e values.

For the Lagergren pseudo-first-order model, the adsorption rate was expected to be proportional to the first power of concentration, where the adsorption was characterized by diffusion through the boundary. The pseudo-first-order model sometimes does not fit well for the whole range of contact time when it failed theoretically to predict the amount of dye adsorbed and thus deviated from the theory. In that case, the pseudo-second-order equation was employed based on the sorption capacity of the solid phase, where the pseudo-second-order model assumes that chemisorptions may be the rate-controlling step in the adsorption processes.

3.6.1. Lagergren pseudo-first-order

The kinetic data were fitted with Eq. (3) and the rate constant value was evaluated and the data are presented in Table 2. The correlation coefficient, R^2 values for all initial concentrations were found to be much lower than 1 ($R^2 << 1$) and the χ^2 values were in the range of 1.123–4.818. The values of calculated q_e do not match with the experimental values indicating that the kinetic data are not in good agreement with the pseudo-first-order model (figure not inserted due to simplicity).

3.6.2. Pseudo-second-order

Considering pseudo-second-order equation, the linear plot of t/q vs. t gives the values of q_e and k for different initial concentrations (Fig. 9). Values of q_e and k were deduced from the slope and intercept of the plot and they are presented in Table 2. The application of pseudo-second-order model provides better correlation coefficient, R^2 and the χ^2 values were in the range of 0.107–4.398. Low χ^2 values and the closeness of the calculated q_e values with the experimental values indicate that the adsorption of CV onto TD follows the pseudo-second-order kinetic model. Although the kinetic data fit well with this model, the rate constants still depend on the initial concentrations which make them difficult for application in adsorption process modeling.

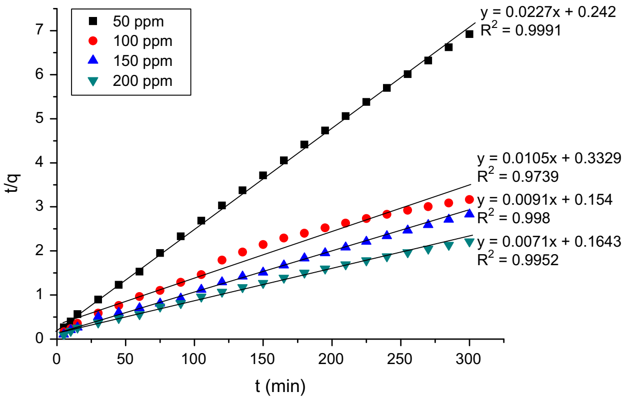

Fig. 9. Kinetic model for adsorption of CV onto TD based on pseudo-second-order rate equations.

3.6.3. Unified approach model

The kinetics data were fitted in Eq. (5) and the rate constants k_1 and k_2 were determined from the relation and presented in Table 2. Theoretical q values at different times for different initial concentrations were calculated from Eq. (5) using the parameters of rate constant and q_∞ as presented in Fig. 3. It is clearly predicted that adsorption data were in good agreement with experiment data and the rate constant parameters were independent of the initial concentrations. The χ^2 values for all concentrations were in the range of 0.242–1.210. Table 2 shows the summary of kinetic parameters for Langmuir, pseudo-first-order, pseudo-second-order, and unified approach model. The results showed that the unified approach model described the equilibrium and kinetics effectively well and useful for modeling the adsorption of CV onto TD.

3.7. Adsorption capacity of various adsorbents for dyes

Table 3 represents adsorption capacity of various adsorbents for removal of dyes from wastewater. It is obvious from the table that TD has higher adsorption capacity which is 175.4 mg/g than the other adsorbents as considered. Hence, TD was regarded as a viable adsorbent for the removal of CV from aqueous solution. Recently, researchers are more interested in naturally available low-cost activated systems than as-obtained deactivated adsorbents due to the significant improvement in adsorption capacity using small amount of chemicals. Pirbazari et al. [25] obtained q_{max} as 461 mg/g for alkali-treated Foumanat tea waste, whereas that for untreated sample reported as 213 mg/g, not much higher than our present finding.

Table 3
Comparison of maximum adsorption capacity based on Langmuir isotherm of dyes on various adsorbents.

Adsorbent	Adsorption capacity (mg/g)	References
Activated carbon	85.84	Senthilkumaar et al. [43]
Neem sawdust	4.02	Khattri and Singh [44]
Rice husk	11.175	Mohanty et al. [12]
Coniferous pink bark powder (CPBP)	32.78	Ahmad [45]
Water hyacinth	24	Alam et al. [46]
Tea waste	85.5	Uddin et al. [26]
Rejected tea	156	Nasuha et al. [28]
Tea dust	175.4	Present study

4. Conclusion

The removal of CV from aqueous solution using tea dust has been investigated quite effectively under different experimental conditions in batch mode. Maximum adsorption capacity of CV onto TD was observed as high as 175.4 mg/g. The percentage of dye removal increased with increasing adsorbent dosage as well as pH of the solution. The adsorption data were fitted to Langmuir and Freundlich isotherms. The kinetics of adsorption followed pseudo-second-order reaction kinetics based on Lagergren equations. The proposed TD adsorbent not only demonstrated higher adsorption efficiency and fast kinetics, but also showed cost-effectiveness and eco-friendliness.

Acknowledgment

The project was funded by Universiti Malaysia Pahang, Malaysia (RDU 100395), which the authors are very grateful.

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