



## Sequestration of crystal violet from aqueous solution using ash of black turmeric rhizome

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### ABSTRACT

Activated carbon obtained from rhizomes of black turmeric is used for the removal of industrial pollutant crystal violet dye from aqueous solution. The ash was characterized by Fourier transform infrared, X-ray diffraction (XRD), and scanning electron microscopy. Powder XRD pattern of the adsorbent reveals the peaks at  $2\theta$  angles  $26.7^\circ$ ,  $28.6^\circ$ ,  $30.5^\circ$ ,  $32.8^\circ$ ,  $34.1^\circ$ ,  $40.64^\circ$ ,  $43.4^\circ$ , and  $45.1^\circ$  and pattern was found to remain unchanged after every cycle (after desorption) till eighth cycles. The calculated column adsorption capacity lower than the batch adsorption capacity. IR peaks of black turmeric ash before adsorption were observed at  $1,397.33$  and  $1,007.13$   $\text{cm}^{-1}$  and after adsorption it shifted to  $1,012.62$   $\text{cm}^{-1}$ . Studies on effect of various parameters viz. dye concentration, dose of adsorbent, contact time, pH, and temperature were carried out. The dye adsorption increases with increasing pH and temperature. In higher pH ranges the adsorbent surface carries negative charge which benefits the adsorption of cationic crystal violet dye through electrostatic interaction. 100% dye removal was achieved at  $40^\circ\text{C}$  and above. Mechanism and kinetics of the adsorption process have also been investigated. Temkin adsorption isotherm was found best fit for adsorption process indicating the presence the energetically non-equivalent adsorption sites present on the surface of adsorbent and the adsorption of CV takes place on the more energetic adsorption site at first. Pseudo-second-order kinetics with rate constant  $1.85 \times 10^{-4}$   $\text{g/mg min}$  is best fit for the adsorption process. Adsorption was found to be endothermic and processed via chemisorption.

*Keywords:* Crystal violet; Adsorption isotherms; Adsorption kinetics; Dye removal; Black turmeric

### 1. Introduction

Water is crucial for life. It is essential to save water to safeguard the earth as well as future of mankind. With development of science and technology and rapid industrialization, our world is touching new horizons but we are paying a high cost of it in form of widespread problem of environmental pollution. About 80% of world's wastewater is dumped to water bodies mostly without proper treatment. One of the important classes of water pollutants is organic dyes, being used in paper, textile, leather, plastic, food, cosmetics, and pharmaceutical industries. High concentration of dyes in water bodies stop the oxygenation capacity of

the receiving water and cut of sun light thus upsetting the biological activity of aquatic life and photosynthesis process of aquatic plants such as algae. Polluting effects of these dyes is also due to their non-biodegradability, they keep on accumulating in aquatic animals and plants as well as in the sediments. Decomposition of dyes into pollutants in carcinogenic or mutagenic compounds causing allergies, skin irritation, or different tissue changes [1]. It is desired to eliminate the organic dyes from industrial effluents prior to throwing it to water bodies. It is difficult to treat dye containing wastewater due to diverse chemical nature of dyes. Treatments like chlorination cannot be used as it release mutagenic products even from less harmful dyes [2].

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Adsorption has been revealed to be one of the most effective and established treatment of wastewater in textile industry as it is an economically achievable process for dyes removal and decolorization of textile effluents. The process involves the transfer of soluble organic dyes from wastewater to the surface of the adsorbent which is solid and highly porous material. The adsorbent adsorbs each compound to be removed to its capacity and when it is “spent” should be replaced by fresh material. The spent adsorbent may be either regenerated or incinerated. The main factors which influence dye adsorption are: interaction between dye and adsorbent, surface area, and particle size of adsorbent, pH, temperature, and time duration of contact. The most commonly used adsorbent is activated carbon. The cationic mordant and acid dyes are removed with high removal rates [3], whereas dispersed, vat, direct, pigment, and reactive dyes are removed with moderate removal rates [4]. Besides adsorption, several methods viz. photochemical degradation, chemical oxidation, advanced oxidation process (AOP), biological degradation, coagulation, reverse osmosis, flotation, electrochemical treatment, etc., are also used for dye removal study [5–11]. However, adsorption is most advantageous due to its cost-effectiveness, efficiency, and reusability. Various adsorbents viz. agricultural waste, coal, wood, fly ash, activated carbon, clay, and other porous materials have been used for the adsorptive removal of dye from its aqueous solutions [12–26]. It is also well-known that during the combustion of biomass or biomass/coal blends, the large amounts of alkali metals and alkaline earth metals in biomass or coal can also result in severe ash-related problems [27–29].

Black turmeric (*Curcuma caesia*) belonging to family *Zingiberaceae*, is a perennial herb with bluish black rhizomes. *C. caesia* has been used by tribal communities for medicinal purpose viz. hemorrhoids, leprosy, asthma, epilepsy, fever, wound, vomiting, menstrual disorder, tumor, piles, aphrodisiac, inflammation, gonorrhoeal discharges, since ancient times [30]. Some plant species belonging to family *Zingiberaceae* are reported to act as adsorbent for adsorptive removal of dyes [31]. However, still there arises a great need to explore new low cost adsorbent materials with high adsorption capacity. In the present study, we have undertaken to explore the potential role of *C. caesia* ash for removal of crystal violet from wastewater. Crystal violet (molecular formula  $C_{25}H_{30}N_3Cl$ , molecular weight 407.98 g/mol) is a cationic dye used in several industries such as dyeing and textile, paper, ball point pen, leather, additives, cosmetics, and analytical chemistry/biochemistry. Structure of dye is shown in Fig. 1. It has carcinogenic and mutagenic effects in rodents. It is known to cause eye irritation, skin irritation, digestive tract irritation, permanent injury to cornea, and conjunctiva. The dye reduces to leuco moiety, leucocrystal violet in effluent, leading to environmental deterioration [32–35]. In our previous and latest research, for the first time, *C. caesia* ash was used for the efficient removal of malachite green dye from aqueous solution where batch and column adsorption studies of malachite green onto *C. caesia* ash were carried out. Adsorption capacity for column process is found to be 38.16 mg/g which is less than that of batch process. Value for change in Gibbs free energy is negative over

the entire temperature range, indicating the process to be spontaneous. The adsorption process is endothermic. [47].

In the present investigation, *C. caesia* ash is prepared from rhizome and explored for adsorptive removal of crystal violet dye from aqueous solution. The aim of the present study is to find the optimum conditions for the removal of crystal violet. For this purpose effect of parameters viz. pH, initial dye concentration, dose, temperature, and contact time has been investigated. Two techniques batch [36–38] and column processes [39,40] have been applied to study dye removal by *C. caesia* ash.

## 2. Experimental section

### 2.1. Materials and characterization techniques

All chemicals and reagents used in the present work are commercially available and used without any further purification. Concentration of crystal violet (CV) dye solution during adsorption was estimated spectrophotometrically using Shimadzu (Kyoto, Japan) UV 1800 spectrophotometer with a 10 mm quartz cuvette by recording absorbance at 589 nm ( $\lambda_{max}$ ). Stock solution of the dye (100 mg/L) was prepared in distilled water. All working solutions with desired dye concentration were prepared from the stock solution by successive dilution. Scanning electron microscopy (SEM) micrographs of the adsorbent before and after adsorption were recorded using Merlin VP compact (Carl ZEISS Germany make) having air lock chamber [41]. The IR spectrum of the adsorbent was carried out using Nicolet iS10, Thermo Fisher Scientific Instrument, Madison, USA, OMNIC 9, and TQ analysis software packages Fourier transform infrared (FTIR) spectrometer. Zeta potential of the adsorbent suspended in aqueous solution was determined using a zeta-sizer nano-ZS (Malvern) at room temperature. The characterization of the adsorbent was done by adopting strategies similar to earlier studies [42,43].

### 2.2. Preparation of the adsorbent ash

In the dye removal study, ash of *C. caesia* was used as adsorbent. Fresh Bluish black rhizome of *C. caesia* was procured from Kandhamal, Odisha, India. The collected rhizomes were sun-dried and powdered. The powdered rhizomes were converted into ash by heating in a muffle furnace at 550°C for 5 h. After cooling, the ash is collected and used without any chemical treatment.

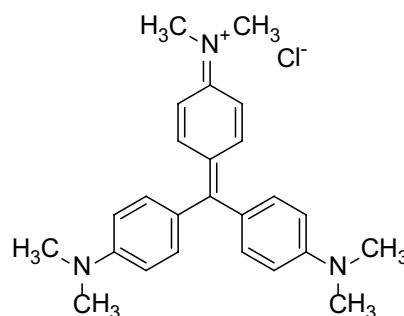


Fig. 1. Chemical structure of crystal violet dye.

### 2.3. Dye adsorption study via batch technique

Batch adsorption experiments were carried out with 10 mL CV dye solution for 3–8 mg/L initial dye concentrations, 5–30 mg of adsorbent, 4–9 pH, 1–24 h contact time, and 25°C–45°C temperature. pH of dye solution was adjusted by adding dilute solutions of HCl and NaOH. Dye concentration was analyzed spectrophotometrically by UV-vis spectrophotometer at maximum wavelength ( $\lambda_{\max}$ ) 589 nm in absorbance mode. The removal efficiency ( $R$ , %), amount of dye adsorbed at time  $t$  ( $Q_t$ , mg/g), and amount of dye adsorbed at equilibrium ( $Q_e$ , mg/g) were calculated using the reported formulas [44].

### 2.4. Adsorption equilibrium

Equilibrium experiments were performed in 10 mL dye solutions of different initial concentrations (3–8 mg/L) mixed with 0.01 g of adsorbent. 24 h is considered as an equilibrium time. After 24 h samples were analyzed as mentioned earlier.

### 2.5. Adsorption kinetics

Experiments for adsorption kinetic study were carried out by adding 0.01 g of adsorbent with 10 mL aqueous solution of CV dye having 8 mg/L initial dye concentrations. The remaining dye concentrations in the samples were recorded at different time intervals as described earlier.

### 2.6. Dye adsorption study via column run technique

For column adsorption, 0.5 g ash of *C. caesia* adsorbent was filled in a glass column to make a fixed bed of 1.3 cm height and 0.2 cm<sup>2</sup> cross-sectional area. The glass column has 0.5 cm internal diameter and 19 cm length. Through this fixed bed aqueous solution of CV dye having 5 mg/L initial dye concentration was allowed to run in a down flow motion with a flow rate of 1.3 mL/min and after each 5 min time interval, 6.5 mL aqueous effluent samples were collected and dye concentration was determined by measuring characteristic absorbance of the dye. The dynamic behavior of column is explained by breakthrough curve [19,35] which is obtained by plotting a graph of normalized concentration, ratio of effluent dye concentration at time  $t$  to initial dye concentration ( $C_t/C_0$ ), vs. time. Breakthrough parameters, that is, total amount of dye ( $m_{\text{total}}$ ) passed through the column at time  $t$ , percentage removal of dye  $R$ (%), and column adsorption capacity of the adsorbent  $q_t$  (mg/g) at time  $t$  were calculated using the reported formulas [19,35].

Column studies differ to the batch studies in a way that in column operations adsorbent remains continuously in contact with the solution of the adsorbate as a result of which the concentration of the adsorbate solution remains constant throughout its contact with the adsorbent. However, in case of batch operations the concentration of the adsorbate, which is in contact with the adsorbent, decreases gradually during adsorption. Therefore, due to gradual adsorption of the adsorbate over the surface of adsorbent effectiveness of the adsorbent drops off with time. Thus, in the batch adsorption the time required for the

adsorbent and adsorbate to attain substantial equilibrium is large and additional time is required for the filtration process. Because of these limitations batch reactors do not give precise data and the practical applicability of the use of the adsorbent materials is ascertained through column operations [45–48]. It is also observed that the exhaustion capacity in the fixed bed operations is relatively higher, indicating thereby better efficiency of column operations than the batch removal [49,50]. This is due to formation of continuous larger concentration gradient at the interface zone as the influent dye solution passes through the column. Moreover, fixed bed column operations are simple to operate, can be scaled-up from a laboratory process and effects of adsorbent recycling ability can be judged through this method [51]. Because of these reasons continuous adsorption in fixed-bed column is often desired from industrial point of view. In the present studies, continuous flow system in which the adsorbent is continuously in contact with fresh solution of adsorbate is used and column is prepared as described in several other studies [52,53].

## 3. Result and discussion

### 3.1. Characterization of adsorbent

Scanning electron micrographs of *C. caesia* ash before and after CV dye adsorption are shown in Figs. 2a and 2b, respectively. Fig. 2a reveals the presence of porous texture in the surface of the adsorbent and adsorption of CV dye at the ash surface is confirmed by the coverage of ash surface depicted in Fig. 2b. Change in IR peaks of the ash adsorbent before and after adsorption (Figs. S1 and S2) also confirms the adsorption process. IR peaks of *C. caesia* ash were observed at 1,397.33 and 1,007.13 cm<sup>-1</sup> before adsorption of dye which was shifted to 1,012.62 cm<sup>-1</sup> after adsorption of crystal violet. The observation indicates formation of chemical bond in the course of adsorption. X-ray diffraction (XRD) pattern of the adsorbent is shown in Fig. S3 which reveals the peaks at  $2\theta$  angles 26.7°, 28.6°, 30.5°, 32.8°, 34.1°, 40.64°, 43.4°, and 45.1°. XRD pattern was found to remain unchanged (after desorption) after every cycle till eighth cycles.

### 3.2. Effect of initial dye concentration and contact time

On increasing initial dye concentration, an increase in removal efficiency of CV dye is found as shown in Fig. 3 which may be probably due to increase in the mass gradient between the dye solution and adsorbent ash as the initial dye concentration increases [54]. Further, Fig. 3 also reveals increase in the removal of CV dye with increasing contact time.

### 3.3. Effect of adsorbent dose

Fig. 4 shows the effect of amount of adsorbent ash of *C. caesia* on CV dye removal and it is observed that the removal of CV dye removal increases as the amount of the adsorbent is increased from 5 to 30 mg. This can be attributed with the increase in the surface area and adsorption sites on increasing amount of adsorbent [55]. 99.95% dye removal has been observed at 30 mg dose of adsorbent.

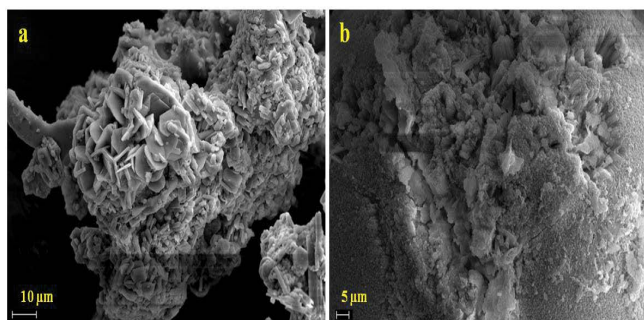


Fig. 2. SEM micrographs of *Curcuma caesia* ash (a) before and (b) after adsorption of CV dye.

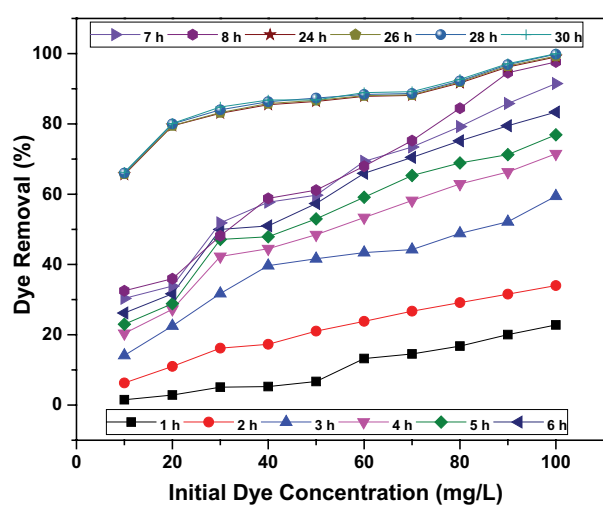


Fig. 3. Effect of initial dye concentration and contact time.

### 3.4. Effect of temperature

Effect of temperature on removal of CV dye was studied at different temperatures viz., 25°C, 30°C, 35°C, 40°C, and 45°C and the results obtained are presented in Fig. 5. Here, amount of adsorbent (*C. caesia ash*) was taken 15 mg at all temperatures. The removal of dye from its aqueous solution increases with increasing temperature, revealing the endothermic nature of adsorption process, and increase in mobility of dye molecules with increase in temperature [54,56].

### 3.5. Effect of pH of dye solution

pH of the CV dye solution was adjusted in the range between pH 4 and 9 to study the effect of pH of dye solution on dye removal and here, the amount of adsorbent (*C. caesia ash*) was taken 15 mg at all pH 4–9. The obtained experimental data indicated that the CV dye removal was more effective at higher pH as shown in Fig. 6a. This behavior of adsorbent on different pH can be explained on the basis of protonation and deprotonation of CV dye in acidic and basic mediums, respectively. At lower pH, presence of excess  $H^+$  ions makes dye molecules highly positive charged, suggesting the existence of repulsion between

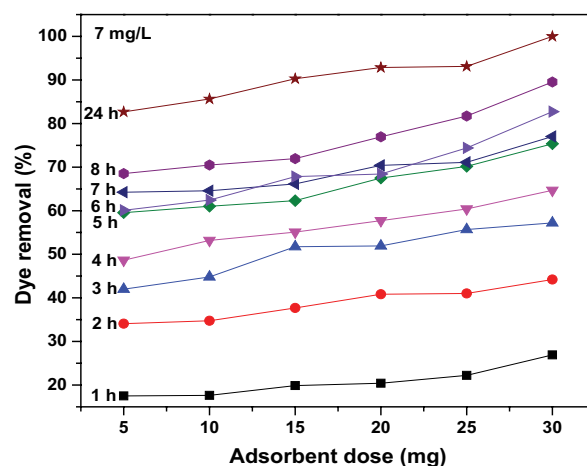


Fig. 4. Effect of adsorbent dose on removal of crystal violet dye.

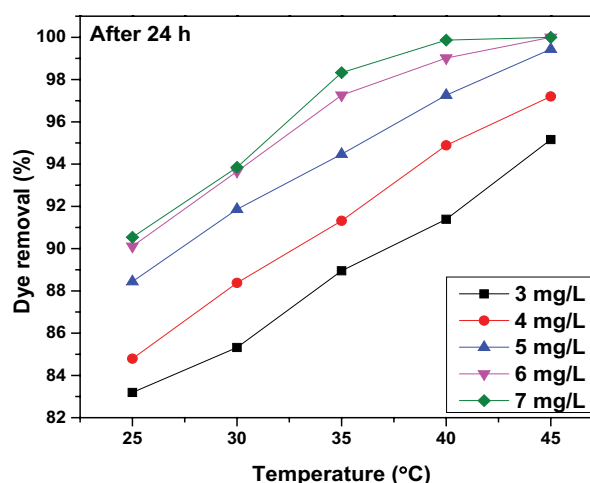


Fig. 5. Effect of temperature on removal of crystal violet dye.

positively charged surface and the positively charged dye molecules. Therefore, lower adsorption of dye molecules. On the other hand, in the basic medium the formation of electric double layer changes its polarity and consequently the dye uptake increases [21,57].

On the other hand, effect of initial pH of dye solution can be explained by surface charge of the adsorbent which was determined by zeta potential. As shown in Fig. 6b, the adsorbent has positive zeta potential at lower pH indicating the positive surface charge which turns negative as the pH increases. In higher pH ranges the adsorbent surface carries negative charge which benefits the adsorption of cationic CV dye through electrostatic interaction. Therefore, adsorption rate were improved with increasing pH values [58,59].

### 3.6. Adsorption isotherm study

To explain the interaction behavior of CV dye molecules with the adsorbent and distribution of dye molecules between the two phases, that is, solid phase and liquid

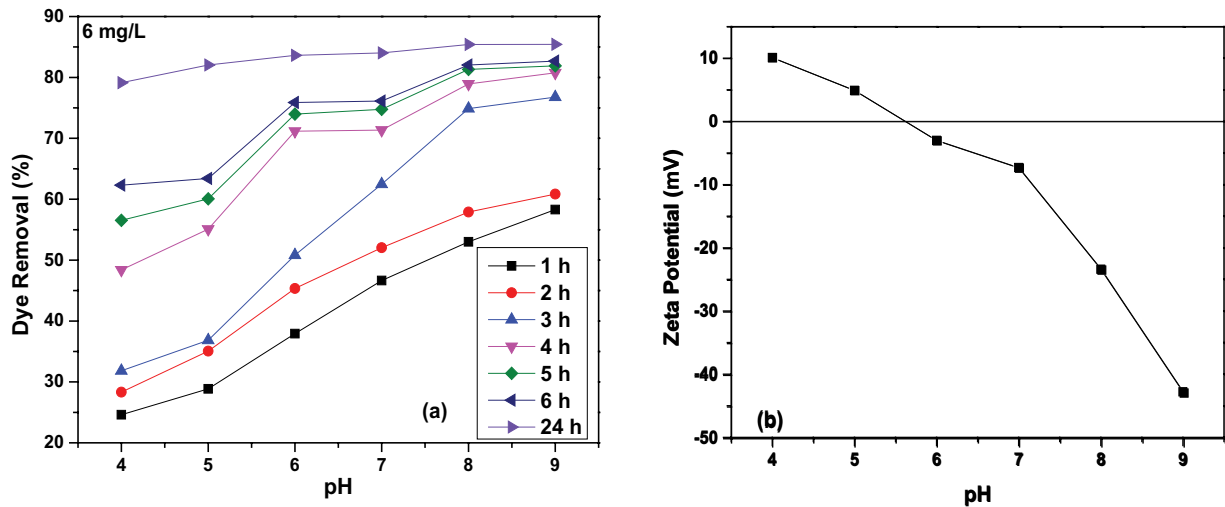


Fig. 6. (a) Effect of pH on removal of crystal violet dye and (b) zeta potential of ash of *Curcuma caesia* ash.

phase, three adsorption isotherm models viz., Freundlich, Langmuir, and Temkin isotherm model were applied and linear equations of these three isotherm models are given as following Eqs. (1)–(3), respectively.

*Freundlich adsorption isotherm:*

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (1)$$

*Langmuir adsorption isotherm:*

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_L} + \frac{1}{K_L Q_L} \quad (2)$$

*Temkin adsorption isotherm:*

$$Q_e = \frac{RT}{b_T} \ln C_e + \frac{RT}{b_T} \ln K_T \quad (3)$$

Here,  $C_e$  is the equilibrium concentration (mg/L) of CV dye solution,  $Q_e$  is the adsorption capacity (mg/g). Freundlich model explains adsorption on the heterogeneous surface with non-uniform distribution of heat of adsorption. It assumes that there is an interaction between adsorbed molecules [55,58]. Freundlich constants  $K_f$  and  $n$  are related to the adsorption capacity and adsorption intensity, respectively. Value of constant  $n$  provides the information about how favorable is the adsorption process. If the value of  $1/n$  is closer to 0, adsorption becomes more heterogeneous [59].

Langmuir isotherm takes into account the monolayer adsorption of dye molecules onto homogeneous surface of adsorbent without any interaction between the adsorbed dye molecules.  $K_L$  and  $Q_L$  are the Langmuir constant related to rate of adsorption and adsorption capacity, respectively [56,60,61].

According to Temkin isotherm, there is a linear increase in the heat of adsorption of all the molecules with coverage

of adsorbate over adsorbent surface. The Temkin isotherm constants ( $b_T$  and  $K_T$ ) can be calculated from slope and intercept of the plot of  $\ln C_e$  vs.  $Q_e$ .  $K_T$  is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy and constant  $b_T$  is related to the heat of adsorption [32].

Plots for the above three adsorption isotherm models were drawn using the experimental data (Figs. 7–9) and their corresponding constants are listed in Table 1. From Table 1, the Temkin isotherm model revealed the best fit with highest  $R^2$  value (0.96933) compared to the other two models. This indicates the presence of the energetically non-equivalent adsorption sites on the surface of adsorbent and the adsorption of CV takes place on the more energetic adsorption site at first [61].

### 3.7. Kinetic study

In order to interpret the experimental data of adsorption process, three kinetic models Lagergren's pseudo-first-order model, Ho's pseudo-second-order model, and Weber and Morris' intraparticle diffusion model were applied whose linear forms can be expressed as given in Eqs. (4)–(6) [62,63].

*Pseudo-first-order kinetics:*

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (4)$$

*Pseudo-second-order kinetics:*

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2} \quad (5)$$

*Intraparticle diffusion:*

$$Q_t = k_t t^{1/2} + C \quad (6)$$

Here,  $Q_e$  (mg/g) and  $Q_t$  (mg/g) are the amount of dye adsorbed at equilibrium and at time  $t$  (min), respectively,

and  $k_1$  ( $\text{min}^{-1}$ ),  $k_2$  ( $\text{g/mg min}$ ),  $k_i$  ( $\text{mg/g min}^{1/2}$ ) are rate constant of adsorption for pseudo-first-order, pseudo-second-order, and intraparticle diffusion respectively. In intraparticle diffusion constant  $C$  reflects the boundary layer effect [62].

Three linear plots for the kinetic models are presented in Figs. 10–12 and their corresponding parameters

are listed in Table 2. The value of  $R^2$  (0.989) for pseudo-second-order kinetics is closer to unity and is greater than that of the two other kinetic models. This suggests that the pseudo-second-order kinetic model with rate constant  $1.85 \times 10^{-4}$   $\text{g/mg min}$  is best fit for the present study which indicates the CV dye was removed from its aqueous solution via chemisorptions process [19]. Further, the calculated uptake capacity ( $Q_e^{\text{cal}} = 23.753$   $\text{mg/g}$ ) is in good agreement with the experimental uptake capacity ( $Q_e^{\text{exp}} = 20.809$   $\text{mg/g}$ ).

### 3.8. Determination of thermodynamic parameters

To determine the thermodynamic parameters, that is, enthalpy ( $H$ ), entropy ( $S$ ), and free energy ( $G$ ) for the present study following Eqs. (7) and (8) were used:

$$\ln \frac{Q_e m}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{7}$$

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

where,  $\Delta S$ ,  $\Delta H$ , and  $\Delta G$  are the change in entropy ( $\text{kJ/mol/K}$ ), enthalpy ( $\text{kJ/mol}$ ), and Gibb's free energy ( $\text{kJ/mol}$ ), respectively.  $m$  is the adsorbent dose ( $\text{g/L}$ ),  $C_e$  is the equilibrium concentration ( $\text{mg/L}$ ) of dye solution,  $Q_e$  is the

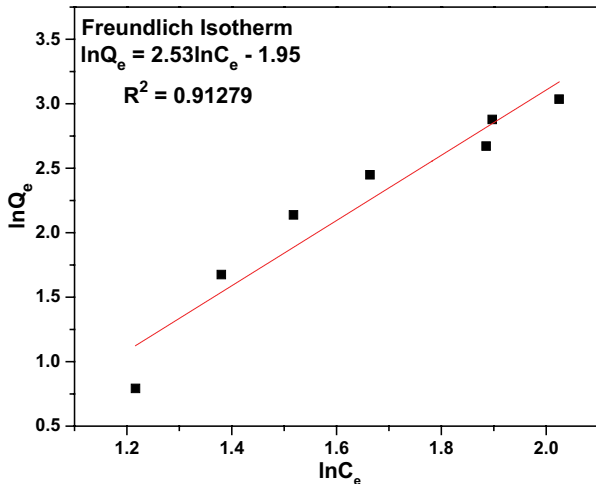


Fig. 7. Linear plot for Freundlich adsorption isotherm.

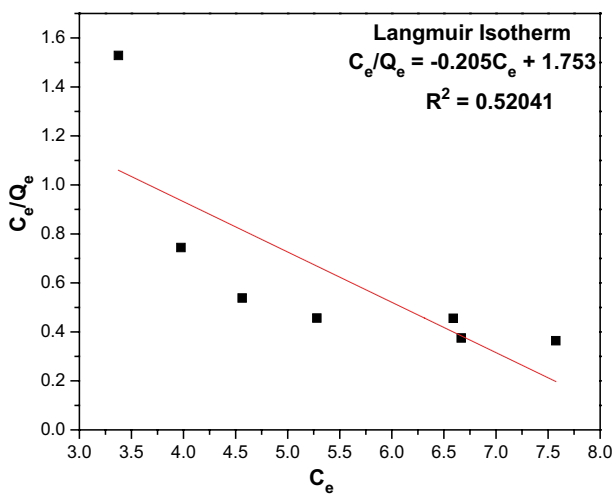


Fig. 8. Linear plot for Langmuir adsorption isotherm.

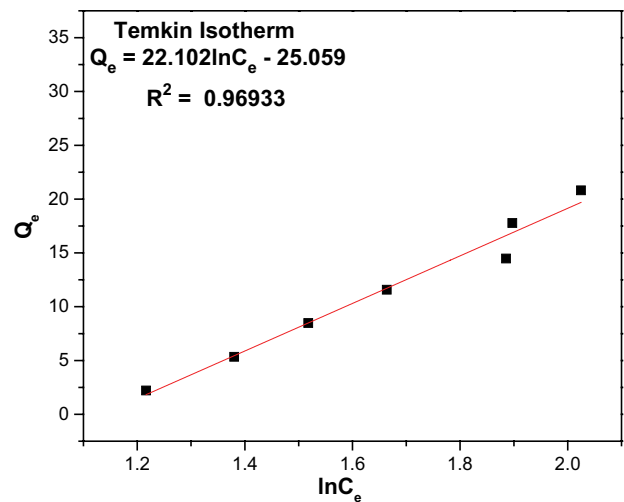


Fig. 9. Linear plot for Temkin adsorption isotherm.

Table 1  
Adsorption isotherm parameters for adsorption of crystal violet dye on *Curcuma caesia* ash

S. No.	Adsorption isotherms	Parameters	$R^2$
1	Freundlich adsorption isotherm	$n = 0.395$ ( $1/n = 2.532$ ) $K_f = 0.142$ $\text{mg/g}$	0.91279
2	Langmuir adsorption isotherm	$K_L = -0.117$ $\text{mg/g}$ $Q_L = -4.878$ $\text{mg/g}$	0.52041
3	Temkin adsorption isotherm	$b_T = 113.978$ $\text{J/mol}$ $K_T = 0.322$ $\text{L/mol}$	0.96933

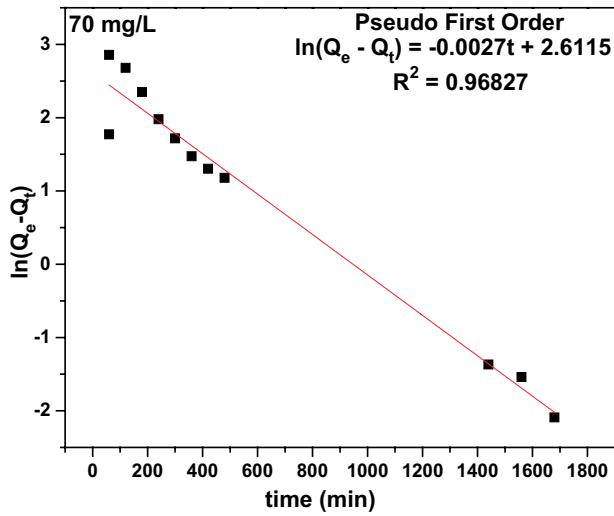


Fig. 10. Linear plot for pseudo-first-order kinetic model.

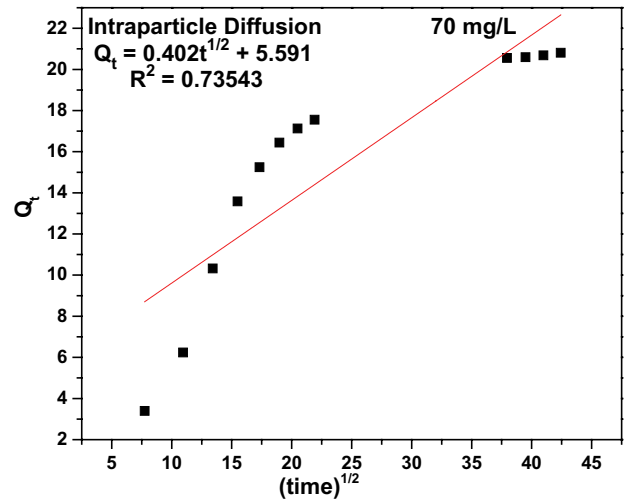


Fig. 12. Linear plot for intraparticle diffusion kinetic model.

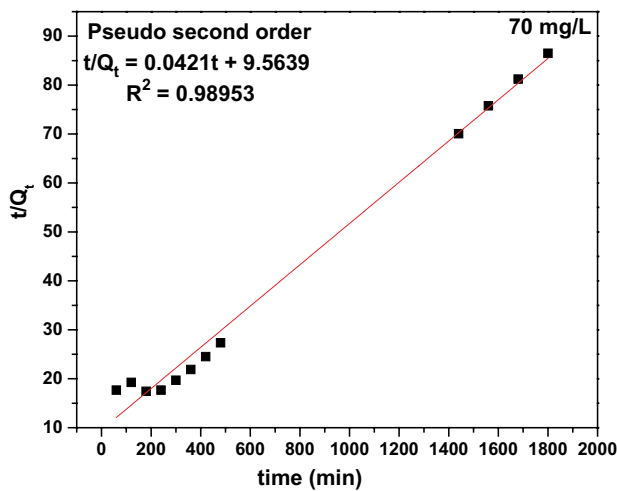


Fig. 11. Linear plot for pseudo-second-order kinetic model.

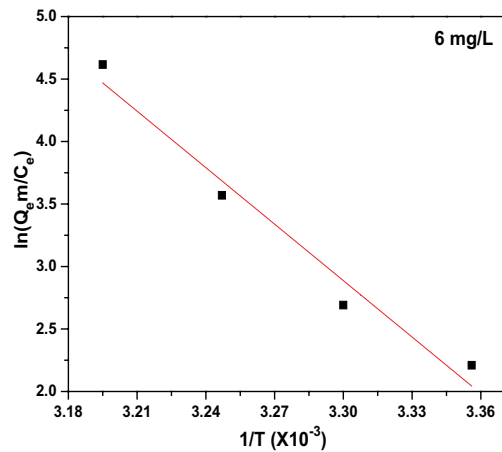


Fig. 13. Plot of  $\ln(Q_e m/C_e)$  vs.  $1/T$  to give thermodynamic parameters.

amount of dye adsorbed at equilibrium (mg/g),  $R$  is the gas constant (8.314 J/mol/K), and  $T$  is temperature (K).

The values of  $\Delta H$  and  $\Delta S$  were calculated using the slope ( $\Delta H/R$ ) and intercept ( $\Delta S/R$ ) of a linear plot which is drawn between  $\ln(Q_e m/C_e)$  and  $1/T$  as shown in Fig. 13 and the values of  $\Delta G$  at different temperatures were calculated using Eq. (8). The values of thermodynamic parameters obtained are presented in Table 3. The feasibility of the adsorption process and its spontaneous nature is confirmed by the negative values of free energy [64]. Further,

the increase in absolute value of free energy  $\Delta G$  with temperature indicates that the adsorption is favorable at higher temperature [65]. The positive  $\Delta H$  value confirms the endothermic nature of the adsorption. Positive value of  $\Delta S$  indicates an increase in randomness at the solid-solution interface during the adsorption process [65].

### 3.9. Column adsorption study of CV dye removal on black turmeric ash

Column operation was carried out to check the practical usability of the adsorbent. To analyze the column efficiency

Table 2  
Kinetic parameters for adsorption of crystal violet dye on *Curcuma caesia* ash

$Q_e^{exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
	$Q_e^{cal}$	$k_1$	$R^2$	$Q_e^{cal}$	$k_2$	$R^2$	$k_i$	$C$	$R^2$
20.809	13.619	0.003	0.968	23.753	0.0001853	0.989	0.402	5.591	0.735

Table 3  
Thermodynamic parameters for CV adsorption on *Curcuma caesia* ash

$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol/K)	$\Delta G$ (kJ/mol) at temperatures				
		298 K	303 K	308 K	313 K	318 K
125.26	0.44	-5.07	-7.26	-9.44	-11.63	-13.82

Table 4  
Breakthrough parameters for column adsorption study of CV dye using *Curcuma caesia* ash

Flow rate (mL/min)	Time (min)	Peak area (mg min/L)	Column adsorption capacity (mg/g)	Amount of dye passed through the column (mg)	Amount of dye adsorbed by the column (mg)	Percentage removal of dye (%)
1.3	355	1,370.58	3.56	2.31	1.78	77.06

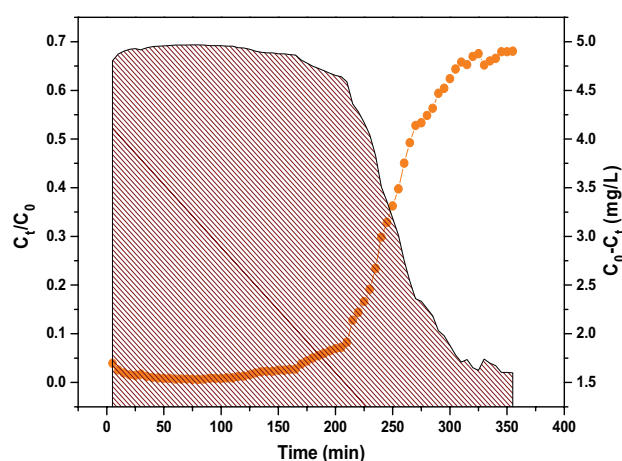


Fig. 14. Breakthrough curve (line, left vertical axis) and integral area (oblique line, right vertical axis) of crystal violet dye on ash of *Curcuma caesia* fixed bed column.

of an adsorbent breakthrough curve is used which is plotted between  $C_t/C_0$  and time. The breakthrough curve and its integral area (drawn by software OriginPro 8) are shown in Fig. 14. The calculated breakthrough parameters are shown in Table 4. According to integral area, the calculated column adsorption capacity was found to be 3.56 mg/g which is relatively lower than the batch adsorption capacity.

#### 4. Conclusion

Crystal violet dye was successfully removed from its aqueous solutions by using natural adsorbent black turmeric and the influences of several factors affecting the adsorption process were studied. The adsorption was found to be endothermic in nature and favored in basic medium (pH 9). Complete removal of dye was achieved at 40°C and above. 99.95% dye removal was observed at 30 h at adsorbent dose of 30 mg. The adsorption process for dye removal was controlled by pseudo-second-order kinetics with rate constant  $1.85 \times 10^{-4}$  g/mg min and Temkin adsorption isotherm. The endothermic nature of the process was also confirmed

by the thermodynamic parameters. Thermodynamic parameters also revealed the feasibility and spontaneous nature along with the favorability at higher temperatures. For the present study, the column adsorption capacity was lower than the batch adsorption capacity. The calculated uptake capacity ( $Q_c^{cal} = 23.753$  mg/g) was found in good agreement with the experimental uptake capacity ( $Q_c^{exp} = 20.809$  mg/g).

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### Supplementary information

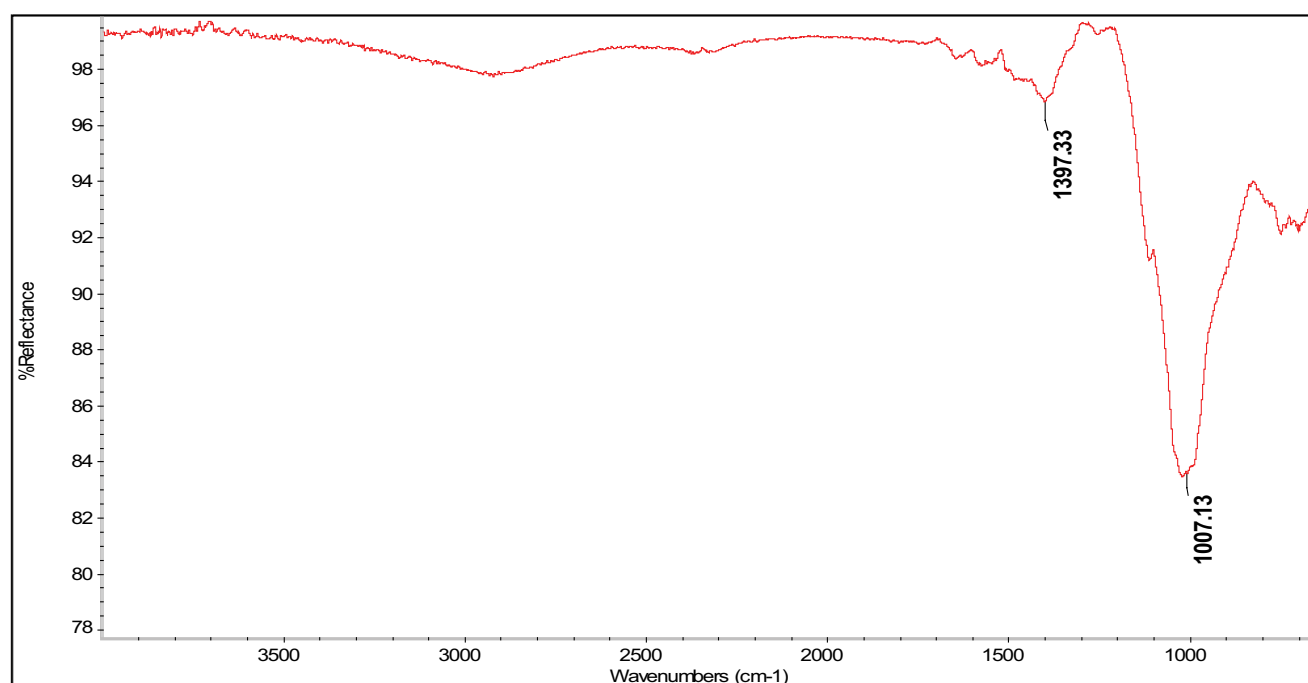


Fig. S1. IR spectra of *Curcuma caesia* ash before adsorption.

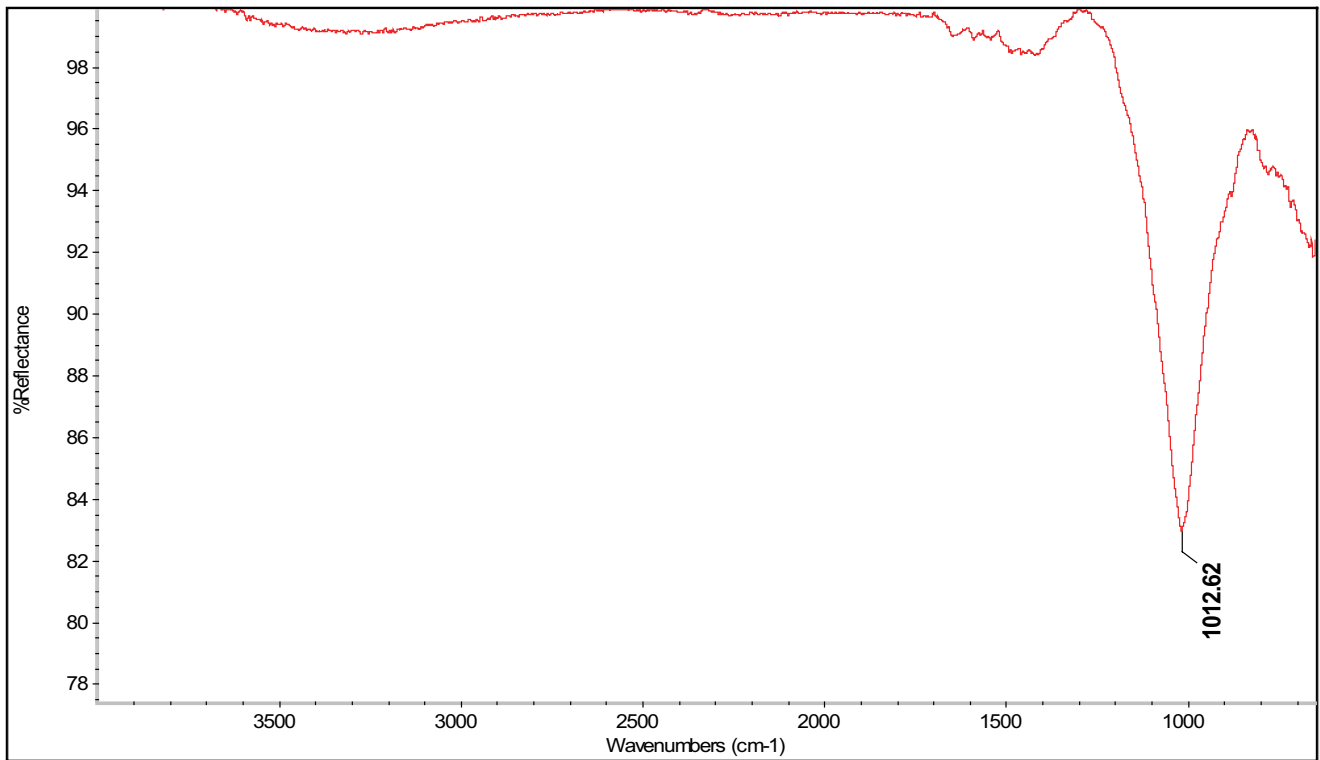


Fig. S2. IR spectra of *Curcuma caesia* ash after adsorption of CV dye.

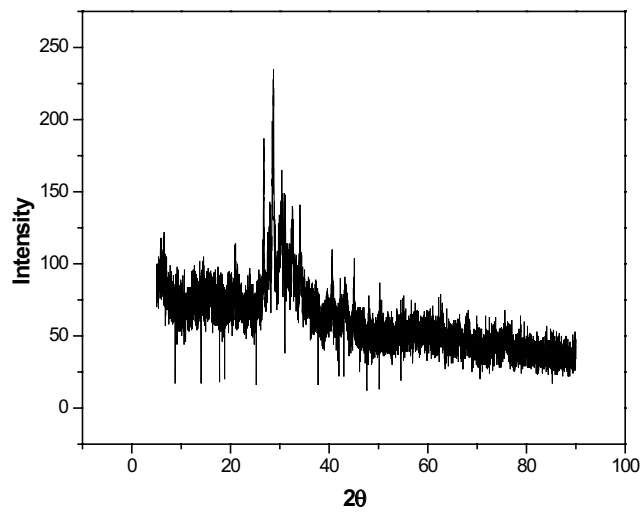


Fig. S3. PXRD pattern of ash of *Curcuma caesia*.