

## A low cost adsorbent prepared from *Curcuma angustifolia* scales for removal of Basic violet 14 from aqueous solution

S Suresh<sup>2</sup>, R Wilfred Sugumar<sup>3</sup> & T Maiyalagan<sup>1\*</sup>

<sup>1</sup>School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 639798, Singapore

<sup>2</sup>Department of Chemistry, Panimalar Institute of Technology Chennai 602 123, India

<sup>3</sup>Department of Chemistry, Madras Christian College, Chennai 600 059, India

E-mail: maiyalagan@gmail.com (T.M).

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The adsorption characteristics of a low cost adsorbent prepared from *Curcuma angustifolia* scales (CA) for the removal of Basic Violet 14 from aqueous solution has been investigated. The experimental data have been analyzed by Langmuir, Freundlich and Temkin isotherm models. The results show that the adsorption isotherm is best defined by the Langmuir isotherm model and the adsorption capacity is found to be 208.33 mg/g for the prepared low cost adsorbent. The adsorption capacity of the prepared low cost adsorbent is superior compared with that of the adsorption capacity of calgon carbon. The kinetic data result at different concentrations have been analysed using pseudo first-order and pseudo-second order model. Boyd plot indicate that the adsorption of dye onto the low cost adsorbent and calgon carbon is controlled by film diffusion. Thermodynamic analysis indicate that the adsorption process is endothermic in nature. The adsorbent is characterized by Fourier transformation infrared spectrometry (FTIR) and scanning electron microscopy (SEM). The material used in this study is an agricultural waste product, economical to use as an alternative to costlier adsorbents and can be an attractive option for dye removal in wastewater treatment processes in industries.

**Keywords:** Low cost adsorbent, Adsorption, Dye removal, Equilibrium, Kinetics

In recent years, the increased industrial activities produce effluents that are highly toxic, and cause environmental problems. More than 100,000 dyes are available commercially, most of which are difficult to decolorize due to their complex structure and synthetic origin<sup>1</sup>. The discharge of dye contaminated wastewater in to the environment is aesthetically undesirable and has serious environmental impact. Without adequate treatment, textile dyes can remain in the environment for an extended period of time<sup>2</sup>. Therefore removal of such colored agents from effluents becomes environmentally important.

Several methods have been tested for color removal from industrial effluents to decrease their impact on the environment. These methods include decolorization by photo-catalysis or photo oxidation processes<sup>3</sup>, electrochemical, membrane filtration, ion exchange<sup>4,5</sup>, chemical oxidation, ozonation and coagulation<sup>6,7</sup>. Most of these processes are costly and cannot effectively be used to treat the wide range of dye wastewater.

Adsorption is one of the most effective processes used for the dye removal from wastewaters. The

advantages of adsorption process are simplicity in operation, inexpensive compared to other separation methods, insensitivity to toxic substances and no sludge formation<sup>8</sup>.

Use of activated carbon as adsorbent has been cited as one of the best available environmental pollution control technologies by the *US Environmental Protection Agency*. Adsorption of dyes and pigments onto granulated activated carbon (GAC) or powdered activated carbon (PAC) is a common practice. The biggest barrier which comes across in the application of these adsorbents widely in the industries is high cost and availability of these adsorbents. This has prompted the use of various materials as adsorbents in order to develop cheaper alternatives by utilizing agricultural and other wastes. Such low-cost adsorbents have been investigated at the laboratory scale for treatment of colored effluents with different degrees of success<sup>9</sup>. Some low cost materials studied for dye(s) removal are bamboo dust, coconut shell, rice husk<sup>10</sup>, silk cotton hull, sago waste, maize cob<sup>11</sup>, coir pith<sup>12</sup>, curry tree stem<sup>13</sup>, curry tree seed<sup>14</sup>, agricultural wastes<sup>15</sup>

etc. In India, more than 200 million tons of agricultural residues are generated annually and this solid waste is not used for any purpose and is disposed into roadside pits. Hence any process using solid waste will be economical<sup>16</sup>.

In the present study the scale used is a waste material obtained from *Curcuma angustifolia* (East Indian arrowroot), which is an attractive ginger with stout underground rhizomes. The objective of this study is to explore the feasibility of using a low cost adsorbent prepared from the scales of *Curcuma angustifolia* (commonly known as East Indian Arrowroot) for the removal of Basic Violet 14 from aqueous solution and compare the adsorption capacity with calgon carbon.

## Experimental Section

### Materials

Basic Violet 14 is a triaminotriphenylmethane dye (CI - 42510; Molecular weight: 337.85 g mol<sup>-1</sup>; Molecular Formula: C<sub>20</sub>H<sub>19</sub>N<sub>3</sub>HCl; Maximum Wavelength: 540 nm) and is a mixture of three dyes namely *p*-Rosaniline, Rosaniline, and Magenta II. It is inflammable in nature. The dye is used as coloring agent for textile and leather materials. The dye on ingestion may cause gastrointestinal irritation with nausea, vomiting, diarrhea and inhalation of dye causes irritation to respiratory tract. In humans and animals, its toxicity includes carcinogenic and mutagenic effects<sup>17</sup>. The molecular structure of Basic Violet 14 is shown in Fig. 1.

### Preparation of adsorbent

The raw material (*Curcuma angustifolia* scale) was collected and it is washed several times with water to remove dirt, dust and other surface impurities. The washed scales are dried for 24 h. The dried scales are then soaked in 18 mol/L H<sub>2</sub>SO<sub>4</sub> (1:2 ratio) and kept in a muffle furnace for 12 h at 120°C. The product is washed several times with distilled water and soaked in 1% sodium bicarbonate solution for 12 h to remove any residual acid and kept in oven at 110°C for 12 h. The carbonized material thus obtained is crushed and sieved to uniform particle size using ASTM standard sieve (Mesh No.100). The material thus obtained from *Curcuma angustifolia* scales (CA) is stored in airtight plastic container for further use<sup>18,19</sup>. Commercial calgon carbon (CC) was purchased and used for the comparative study.

### Characterization of adsorbent

Infrared spectra of CA and CC samples were obtained using a Fourier transform infrared spectrometer (FTIR 1725 X, Perkin-Elmer) and the chemical characterization of functional groups are studied. The measurements were carried out over the range 4500-450 cm<sup>-1</sup>. Adsorbent samples (0.33 wt%) were stirred with dry KBr (Merck, spectroscopy grade) and then pressed to form appropriate tablets<sup>20</sup>. The surface morphologies of adsorbents (CA and CC) were analyzed by scanning electron microscopy using a SEM (Hitachi S3000N).

### Batch adsorption experiments

The equilibrium adsorption experiments were carried out to study the efficiency to remove Basic Violet 14 from aqueous solution and to find the isotherm constants. For each experimental run, 50 mL of various concentrations of dye solutions in conical flask with fixed adsorbent dosage was

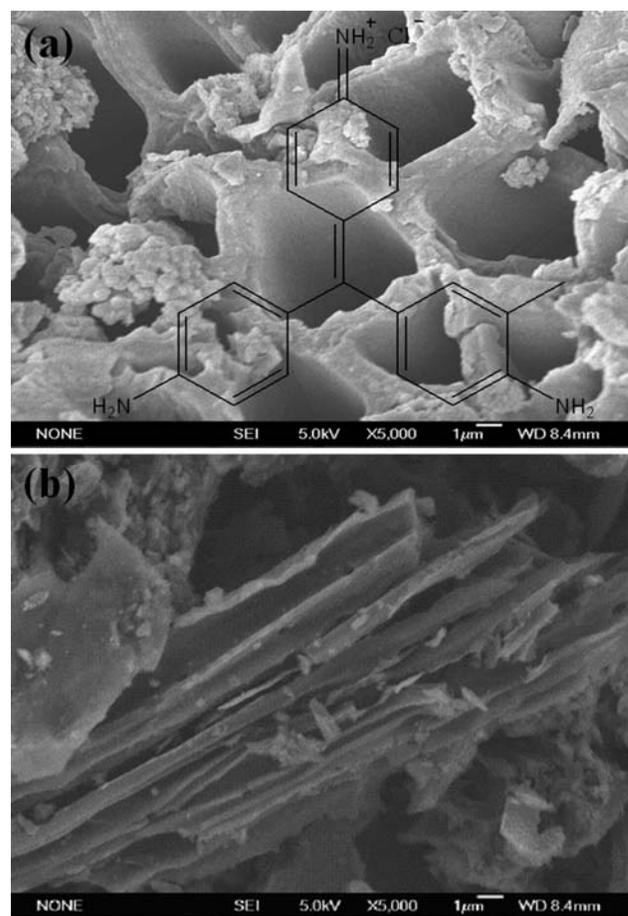


Fig. 1—SEM micrograph of (a) *Curcuma angustifolia* adsorbent (inset is molecular of Basic Violet 14) and (b) Commercial calgon carbon

taken. All experiments were carried out with optimum solution pH at room temperature. This mixture was agitated on a mechanical shaker at a constant speed for about 1 h. The dye removal was determined spectrophotometrically by measuring the absorbance changes at the wavelength of maximum absorbance (540 nm). The effect of adsorbent dosage was studied with varying adsorbent dosage and 50 mL of 160 mg/L dye solution at equilibrium time. The percentage dye removal was calculated using the equation

$$\text{Percentage dye removal} = \frac{C_i - C_f}{C_i} \times 100 \quad \dots (1)$$

The amount adsorbed at equilibrium  $q_e$  (mg/g) was calculated by

$$\text{Amount adsorbed } (q_e) = \frac{(C_i - C_f)V}{M} \quad \dots (2)$$

where  $C_i$  and  $C_f$  are the liquid phase concentrations of the dye at initial and final concentrations (mg/L) respectively.  $M$  the mass (g) of adsorbent and  $V$  is the volume of dye solution (L).

## Results and Discussion

### Characterization with SEM and FTIR

SEM is used as a tool for characterization. It reveals the surface morphology of the adsorbents. The morphological study by SEM of CA and CC is shown in Fig.1. From the examination of SEM micrographs of CA and CC, it is observed that the pores of different size and shape were clearly found on the surface of CA. From the high magnification SEM photograph Fig. 1(a), it is observed that a micro porous material with narrow pore size distribution has been prepared from CA. The presence of more micro pores on the surface of CA creates high affinity for adsorbate adsorption. The adsorbent CC appears to have a rough surface on the adsorbent. The well developed pore on CA has led to good adsorption capacity of the dye when compared to CC<sup>21</sup>.

The FTIR spectrum of the low cost adsorbent prepared from scales of *Curcuma angustifolia* and calgon carbon is shown in the Fig. 2. The FTIR spectra of the adsorbent display the number of absorption peaks, indicating the complex nature of adsorbent. The peaks due to the presence of various functional groups can be identified from the spectrum. The fundamental peaks of the adsorbent CA are due to O—H, C=O, C—H stretching. The peaks at 3415

and 2918  $\text{cm}^{-1}$  are due to O—H bond stretching and the peaks at 1617  $\text{cm}^{-1}$  is due to C=O stretching of carboxylic acid<sup>22</sup>. The peak at 1384  $\text{cm}^{-1}$  is assigned to the formation of or to an increase in the already available oxygen functionalities<sup>19</sup>. The band at 1128  $\text{cm}^{-1}$  is due to C—O stretching in alcohol or ether or hydroxyl group<sup>23</sup>. The peak at 616  $\text{cm}^{-1}$  can be assigned to the bending modes of the C—H group. In CC the band at 3415  $\text{cm}^{-1}$  is due to —OH stretch vibration. The band at 1617 and 1384  $\text{cm}^{-1}$  is similar to CA. The peak at 1161  $\text{cm}^{-1}$  is attributable to the stretching vibration of C—O in acids, alcohols and phenol. The peak at 616  $\text{cm}^{-1}$  can be assigned to the bending modes of the C—H group. The absorption peak observed at 1617, 1384 and 1128  $\text{cm}^{-1}$  are shifted to 1587, 1364 and 1153  $\text{cm}^{-1}$  in CA. In CC the peaks

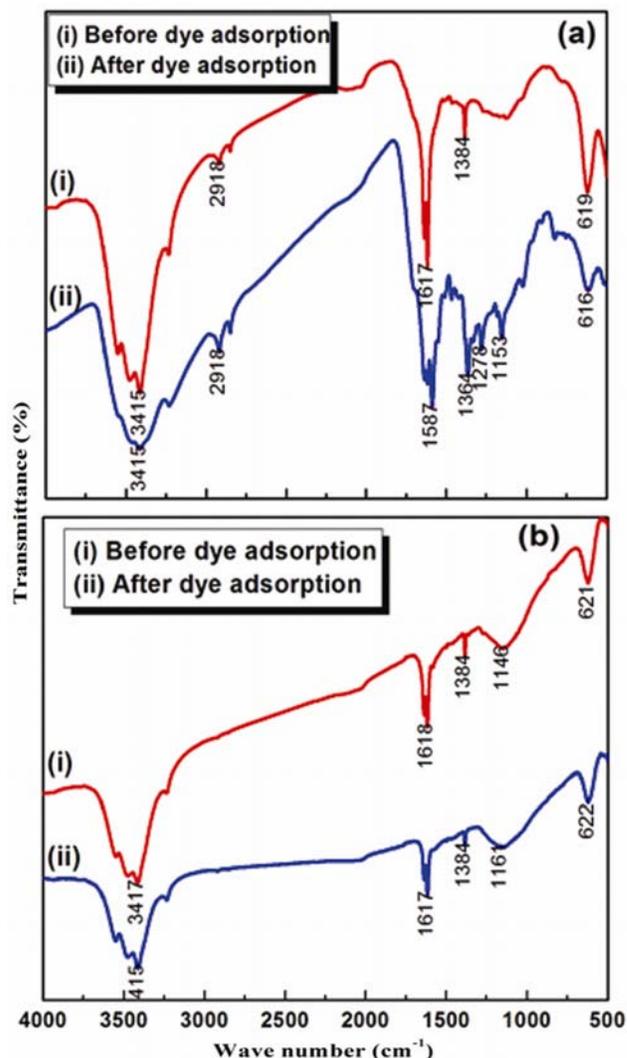


Fig. 2—FT- IR spectra of (a) *Curcuma angustifolia* adsorbent and (b) commercial calgon carbon.

at 3415 and 1161  $\text{cm}^{-1}$  are observed to be shifted to 3417 and 1146  $\text{cm}^{-1}$  when CC is loaded with dye. It seems that the functional groups in this region participate in dye binding. The above observation agrees to the fact that carbons with more surface properties create a high affinity for adsorbate adsorption.

#### Effect of adsorbent dosage

The percent adsorption of Basic Violet14 on CA and CC were studied at different adsorbent doses varied in a range of 5-40 mg for CA and 25-150 mg for CC and a fixed adsorbate concentration of 160 mg/L at a constant volume (50 mL) keeping all other experimental conditions constant.

From Fig. 3(a), it is evident that dye adsorption increases with the increase in adsorbent doses and after a particular limit it becomes almost constant for CA and CC. It is observed that dye removal by CA is effective at low adsorbent dosage whereas CC utilizes high adsorbent dosage for dye removal. In CC, the initial percentage dye removal is low but when the

adsorbent dosage is increased, there is a gradual increase in dye removal and maximum dye removal is observed at a dosage greater than 100 mg. whereas, it is observed that percentage dye removal in CA is almost 100 % at an adsorbent dosage of 35 mg. The increase in percentage colour removal in CA and CC with adsorbent dosage can be attributed to the availability of adsorption sites for dye adsorption<sup>24</sup>.

#### Effect of pH

The percentage dye removal was observed to increase in the pH range of 2 to 11 from 30.01 to 88.05 for CA and 27.30 to 77.25% for CC [Fig.3(b)]. Based on the highest removal of dyes by CA and CC subsequent studies were carried out at pH 8 for CA and CC. The  $pH_{ZPC}$  was found to be 4.6 for CA and 6.4 for CC. The surface of the adsorbent will react as negatively charged when the solution pH is above  $pH_{ZPC}$  and as positively charged when the solution pH is below  $pH_{ZPC}$ . In CA and CC when the pH is greater than  $pH_{ZPC}$  the surface gets negatively

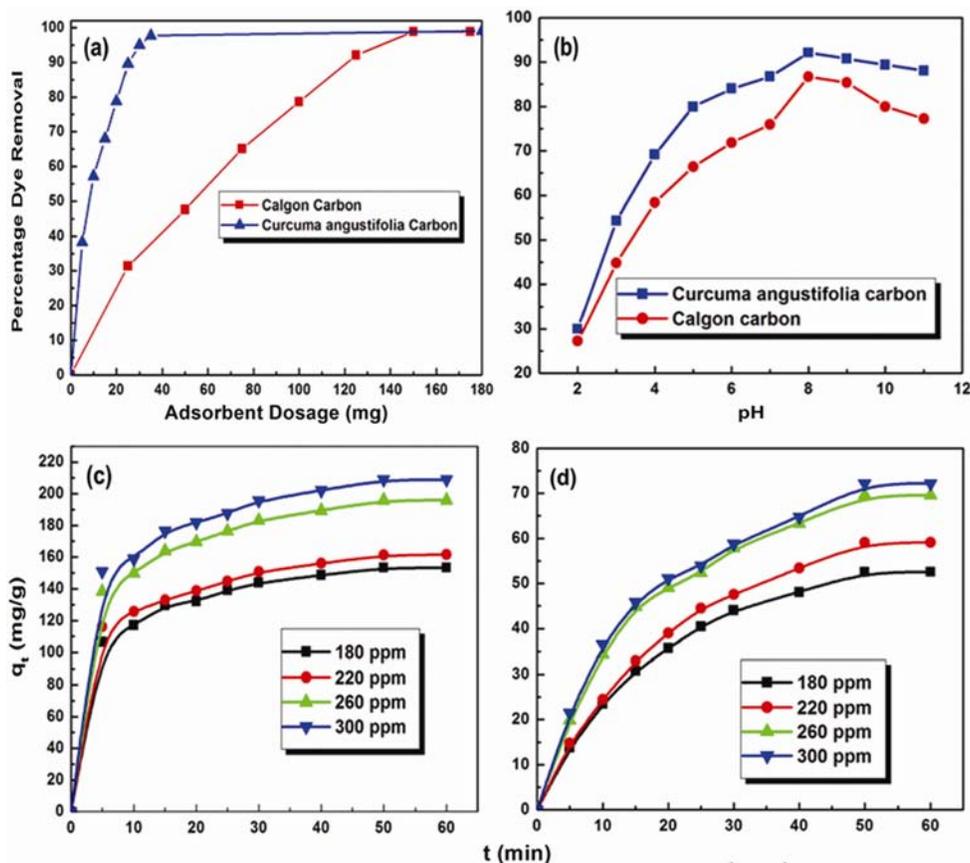


Fig. 3—(a) Effect of adsorbent dosage *Curcuma angustifolia* adsorbent and Calgon carbon ( $C_0 = 160$  mg/L;  $V=0.05$  L;  $pH= 8$ ) (b) Effect of pH for *Curcuma angustifolia* adsorbent ( $C_0 = 160$  mg/L;  $V=0.05$  L;  $m=0.02$ g) and Calgon carbon ( $C_0 = 160$  mg/L;  $V=0.05$  L;  $m= 0.075$ g) (c) Effect of contact time for *Curcuma angustifolia* adsorbent ( $m=0.02$ g/50 mL;  $pH=8$ ) and (d) Effect of contact time for Calgon carbon ( $m= 0.075$ g/50 mL;  $pH=8$ )

charged, which attracts the positively charged dye cations through electrostatic force of attraction. When the pH is lower than  $pH_{ZPC}$ , the  $H^+$  ions compete effectively with the dye cations resulting in a decreased percentage dye removal<sup>25</sup>.

#### Effect of agitation time

Figures 3(c,d). show the agitation time necessary for adsorption of dye onto CA and CC to reach equilibrium. From the results it is observed that the amount of dye adsorbed increases for CA and CC and reached saturation in 50 min. The amount of dye adsorbed for CC increased from 13.80 to 72.18 mg/g and for CA it increased from 106.64 to 208.95mg/g respectively, as the concentration increase from 180 to 300 ppm. In CC adsorption increased and follows a smooth and saturation curve suggesting the possibility of the formation of monolayer coverage of dye on carbon surface. In CA the adsorption of dye is rapid in the beginning due to adsorption on the external surface of the adsorbent. When it is near saturation the dye ions entered into the pores of CA that takes time for saturation. Similar phenomenon was observed in literature<sup>26</sup>.

#### Adsorption Isotherms

The equilibrium nature of adsorption of the adsorbents was studied by three well known isotherms namely Langmuir and Freundlich and Tempkin. An adsorption isotherm describes the relationship between the mass of the adsorbate that is adsorbed per unit weight on the adsorbent and the concentration of dissolved adsorbate in the liquid phase at equilibrium. The adsorption isotherm is important from theoretical and practical point of view. In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlations of the equilibrium data of each system<sup>27</sup>.

#### Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm is based on the assumption that the adsorption process takes place on a homogeneous surface, so a monolayer of adsorbate is formed at saturation on the adsorbent surface. The linear form of Langmuir equation is represented as:

$$C_e/q_e = 1/Q_m K_L + C_e/Q_m \quad \dots (3)$$

Where  $C_e$  is the concentration of the dye solution (mg/L) at equilibrium,  $q_e$  the amount of dye adsorbed

per unit weight of adsorbent (mg/g) and  $K_L$  is the constant related to the free energy of adsorption (L/mg).  $Q_m$  is the maximum adsorption capacity. The values of  $Q_m$  and  $K_L$  were calculated from the slope and intercept of the linear plot. The equilibrium concentration and hence the amount of dye adsorbed are calculated by varying the dye concentration with a fixed adsorbent dose (for CA and CC) and all other experimental conditions kept constant.

The isotherm constants for the Langmuir adsorption isotherm of CA and CC were studied from the linear plot obtained. The applicability of the Langmuir isotherm for both CA and CC suggests the monolayer coverage of adsorbate on the surface of adsorbents<sup>28</sup>. The essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless constant called equilibrium parameter,  $R_L$ :

$$R_L = 1/(1+K_L C_0) \quad \dots (4)$$

The value of  $R_L$  indicates the type of isotherm to be favourable ( $0 < R_L < 1$ ), linear ( $R_L=1$ ), unfavourable ( $R_L > 1$ ) or irreversible  $R_L =0$ , where  $K_L$  is the Langmuir constant and  $C_0$  is the highest initial dye concentration (mg/L). The value of  $R_L$  is found to be in the range of 0.1479 to 0.1004 for CA and 0.0810 to 0.0536 for CC, which proves that the value of  $R_L$  is between 0 and 1 indicating favorable adsorption of Basic Violet14 on to CA and CC.

From Table 1  $Q_m$ , the maximum monolayer adsorption capacity of CA is found to be 208.33 mg/g and for CC it is found to be 95.23 mg/g. This study shows that the adsorption capacity of CA is better than CC. The enhanced adsorption in CA may be due to difference in surface properties and pore size of the adsorbent when compared to CC. The applicability of the linear form of Langmuir model to CA and CC,

Table 1—Langmuir, Freundlich and Temkin constants for CA and CC.

Langmuir constants	CA	CC
$Q_m$ (mg/g)	208.33	95.23
$K_L$ (L/mg)	0.032	0.063
$R^2$	0.9992	0.9994
$R_L$	0.1479-0.1004	0.0810-0.0536
Freundlich constants	CA	CC
$K_F$ (mg/g)	66.19	44.74
$n$	5.2029	7.7339
$R^2$	0.9967	0.9938
Tempkin constants	CA	CC
$K_T$ (L/mg)	1.389	20.863
$B_1$	32.51	10.622
$R^2$	0.9948	0.9923

was proved by the high correlation coefficients  $R^2 > 0.99$ . This suggests that the Langmuir isotherm provides a good model of the sorption system.

#### **Freundlich Adsorption Isotherm**

Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. A linear form of the Freundlich expression can be written as,

$$\log q_e = 1/n \log C_e + \log K_F \quad \dots (5)$$

The Freundlich constants  $K_F$  and  $n$  can be calculated from the slope and intercept of the linear plot with  $\log q_e$  versus  $\log C_e$ . The magnitude of the component 'n' gives an indication of the favourability of adsorption process and  $K_F$  is the constant related to the adsorption capacity.

The experimental result on the adsorption of the dye with a fixed adsorbent dosage and variable dye concentration of CA and CC with all other experimental parameters kept constant is studied.

The Freundlich model assumes that the adsorption of the dye occurs on a heterogeneous surface by multilayer adsorption and the amount of the adsorbate adsorbed increases rapidly with an increase in concentration.

According to Treybal<sup>29</sup>, it has been shown that  $n > 1$ , represents favorable adsorption. The  $n$  value was found to be 5.2 for CA and 7.7 for CC which indicates favourable adsorption.  $1/n$  indicates the adsorption intensity of dye onto the adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to 0. A value of  $1/n$  below 1 indicates a normal Freundlich isotherm while  $1/n$  above 1 indicates co-operative adsorption<sup>30</sup>. The isotherm constants  $K_f$  and  $n$  were calculated from the linear form of the model and the value of  $K_f$ ,  $n$  and the Correlation Coefficients are given in the Table 1. The correlation coefficients  $R^2 > 0.99$  for CA and CC shows that the Freundlich model is comparable to the Langmuir model.  $K_f$  is related to the bonding energy. It give the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration for CA and CC.  $K_f$  value for CA is higher than that for CC. This evidence shows that adsorption capacity is higher for CA compared to CC.

#### **Temkin Adsorption Isotherm**

The effect of indirect sorbate/adsorbent interactions on adsorption isotherms is considered by Temkin and Pyzher and it is suggested that the heat of adsorption

and the interactions of the molecules will decrease linearly with coverage<sup>31</sup>. The adsorption is characterized by a uniform distribution of binding energy. The linear form of Temkin model is given by the equation:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad \dots (6)$$

where  $B = RT/b$  and  $K_T$  is the Temkin isotherm constant (L/g), where these constants can be calculated from a plot of  $q_e$  versus  $\ln C_e$  and are presented in the Table 1. The constant  $b$  is related to the heat of adsorption.  $R$  is the universal gas constant, 8.314 J /mol/K.  $T$  is the absolute temperature in Kelvin.

The linear form of the Temkin equation is used to analyze the adsorption data and it is observed that the Temkin isotherm fitted well when compared with the Langmuir isotherm. The correlation coefficients  $R^2 > 0.99$  for CA and CC shows that Temkin model is comparable to Freundlich and Langmuir equations. The  $R^2$  values were found to be high ( $>0.99$ ) for all the three isotherms studied for CA and CC hence, it can be concluded that both monolayer and heterogenous surface conditions exists in the present study.

#### **Kinetics**

In order to test the suitability of the prepared adsorbent for the removal of Basic Violet 14, the data were analyzed using both the pseudo first-order and second-order rate equations. A detailed discussion is presented as follows. The rate of the adsorption process is explained by adsorption kinetics. The kinetic parameters give important information for designing and modeling the adsorption process. It is observed that the adsorption of dye on the adsorbent surface takes place by an initial rapid binding of the dye molecule on the adsorbent.

#### **Pseudo-first order kinetics**

A simple kinetic analysis of adsorption is the pseudo first order kinetics<sup>32</sup> and its integrated form is given by

$$\log(q_e - q_i) = \log q_e - k_1/2.303t \quad \dots (7)$$

The slope and intercept of the plot of  $\log(q_e - q_i)$  vs time [Fig.4(a,b)] for CA and CC enables to determine the rate constant  $k_1$  and the results are given in Table 2. The adsorption kinetics of Basic Violet 14 from aqueous solution by CA and CC is studied and the influence of various operating parameters on the adsorption process is evaluated. It is observed that the

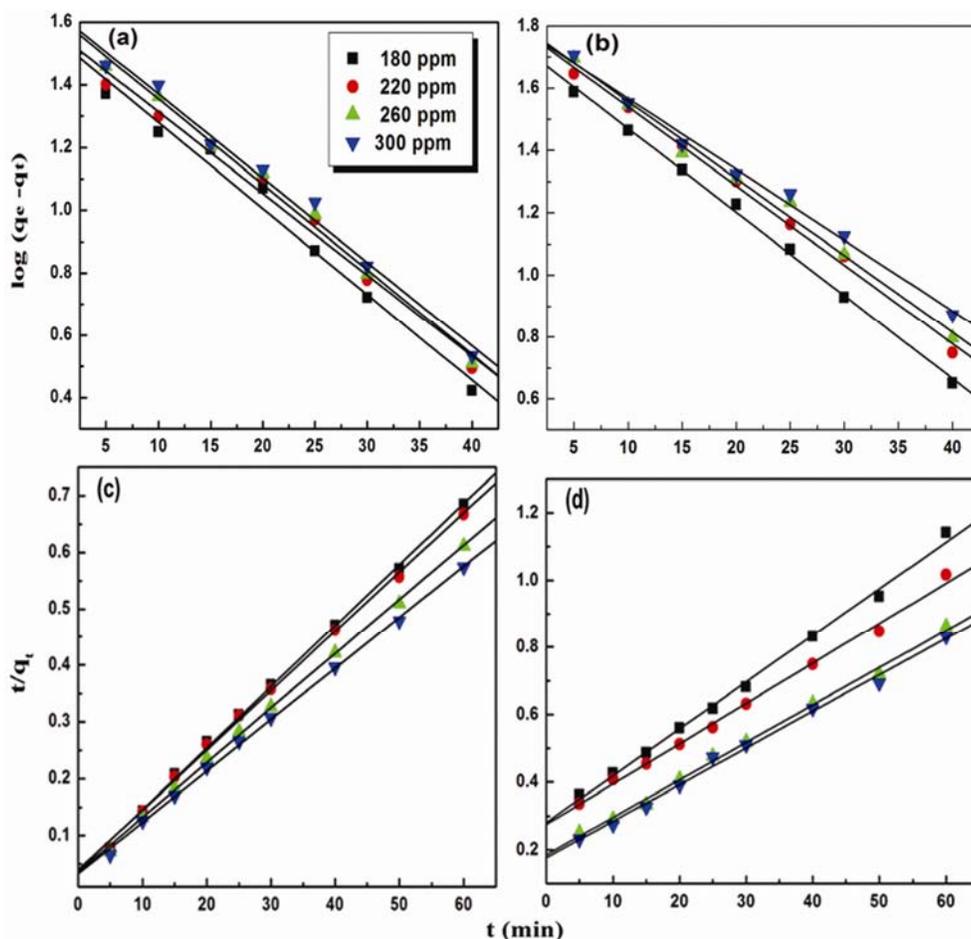


Fig. 4—Pseudo first order kinetics plot for the adsorption of Basic violet 14 onto (a) *Curcuma angustifolia* adsorbent and (b) Calgon carbon. Pseudo second order kinetics plot for the adsorption of Basic violet 14 onto (c) *Curcuma angustifolia* adsorbent and (d) Calgon carbon

Table 2—Kinetic model values for the adsorption of Basic violet 14 on to CA and CC.

Adsorbent	Concentration (mg/L)	$q_{e(\text{exp})}$ (mg/g)	Pseudo first order values			Pseudo second order values			
			$q_{e(\text{Calcd})}$ (mg/g)	$K_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_{e(\text{Calcd})}$ ( $\text{mg g}^{-1}$ )	$K_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$h$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )	$R^2$
CA	180	87.56	35.82	$6.31 \times 10^{-2}$	0.9916	92.59	$3.1 \times 10^{-3}$	26.57	0.9993
	220	89.77	37.50	$6.01 \times 10^{-2}$	0.9925	95.23	$2.7 \times 10^{-3}$	24.85	0.9991
	260	98.14	42.31	$6.24 \times 10^{-2}$	0.9960	104.06	$2.5 \times 10^{-3}$	27.07	0.9994
	300	104.47	43.45	$6.14 \times 10^{-2}$	0.9932	110.62	$2.5 \times 10^{-3}$	30.59	0.9994
CC	180	52.54	48.13	$5.73 \times 10^{-2}$	0.9941	66.26	$9.9 \times 10^{-4}$	4.37	0.9957
	220	59.05	62.09	$5.83 \times 10^{-2}$	0.9978	83.96	$5.1 \times 10^{-4}$	3.63	0.9980
	260	69.57	63.79	$5.69 \times 10^{-2}$	0.9956	90.25	$6.6 \times 10^{-4}$	5.40	0.9982
	300	61.61	53.69	$5.47 \times 10^{-2}$	0.9972	78.17	$8.5 \times 10^{-4}$	5.21	0.9978

dye uptake was very rapid and the saturation time was found to be 60 min irrespective of the initial dye concentration used in both CA and CC. The  $R^2$  value is found to be in the range of 0.9916-0.9960 for CA and 0.9941-0.9978 for CC. Also it is observed that the predicted  $q_e$  value and the experimental  $q_e$  values does

not coincide for pseudo-first order model in CA. Whereas, it is in close agreement with pseudo first order model for CC.

#### Pseudo- second order kinetics

The Pseudo second order model is given by the equation:

$$t/q_t = 1/k_2 q_e^2 + t/q_t \quad \dots (8)$$

A plot of  $t/q_t$  vs  $t$  enables to calculate the rate constant  $k_2$  that is used to calculate the initial sorption rate  $h$  as follows:

$$h = k_2 q_e^2 \quad \dots (9)$$

Now, the initial sorption rate  $h$ , rate constant  $k_2$  and  $q_{e(\text{calc})}$  for CA and CC can be obtained from the plot of  $t/q_t$  vs  $t$  [Fig. 4(c,d)]. The  $q_e$  values calculated from the pseudo-second order model system is in good agreement with the experimental  $q_e$  values for CA. Whereas in CC it deviates and is not in agreement with the calculated values. The second order rate constant  $k_2$  was found to decrease with increase in Basic Violet 14 concentration on to CA. Literature survey also reveals a similar trend of decrease in  $k_2$  with increase in solute concentration<sup>33</sup>. In CC there is a fall and rise in  $k_2$  value for an increase in initial dye concentration. A similar trend was observed in the sorption of Basic Red 18 by activated clay<sup>34</sup>. The correlation coefficient ( $R^2$ ) of the linear plot is very high (>0.99) for all the concentrations studied. This indicates that the adsorption follows second order model and the adsorption process is a chemisorption process. The values of kinetic constants and  $q_e$  of Basic Violet 14 adsorption onto CA and CC are given in Table 2.

The Table 3 gives the adsorption capacity of some low cost adsorbents used for the adsorption of dyes along with CA and CC. From the table it is observed that the adsorption of CA is comparatively good when compared with some of the low cost adsorbents already reported for the adsorption of basic dyes from aqueous solution. The adsorption capacity of the adsorbent ( $Q_m$ ) prepared suggests that Basic Violet 14 is comparatively adsorbed easily by the low cost adsorbent used in the present study.

#### Adsorption mechanism

The diffusion mechanism involved in the adsorption process of CA and CC can be understood by analyzing the kinetic data using intraparticle diffusion model<sup>41</sup>:

$$q_t = k_{id} t^{1/2} + C$$

where  $k_{id}$  is the intraparticle diffusion rate constant and  $C$  is the intercept that is obtained from the slope of the plot of  $q_t$  vs  $t^{1/2}$  [Fig. 5(a,b)]. It was observed that the adsorption follows two stages in both CA and CC. The slope of the second linear portion of the plot for CA and CC is used to find the parameter  $k_{id}$  and the results are shown in Table 4. The initial curved portion in the plot of CA and CC shows the boundary layer effect, while the next portion in the plot may be due to intraparticle or pore diffusion. Since the plots do not pass through the origin for CA and CC, it is obvious that intraparticle diffusion was not the rate controlling step. A similar result was reported for the adsorption of methylene blue onto mango seed kernel particles<sup>42</sup>. The intraparticle diffusion plot for CA and CC shows the presence of both film and pore diffusion and hence the actual slow step in the adsorption process was identified by using the Boyd kinetic model<sup>43</sup>:

$$Bt = -0.4977 - \ln(1 - F)$$

where  $F$  is the fraction of solute adsorbed at any time  $t$  and  $Bt$  is a mathematical function of  $F$ .

$$F = \frac{q_t}{q_e}$$

A plot of  $Bt$  vs time [Fig. 5(c,d)] can be employed to test the linearity of the experimental values. From the graph it is observed that the linear lines in the plot for both CA and CC, does not pass through the origin for all the dye concentrations, suggesting that the

Table 3—Adsorption capacities of different low cost adsorbents for dye removal from aqueous solution.

Adsorbent	Dyes	Adsorption capacity (mg/g)	Reference
Neem sawdust	Basic Violet 10	2.35	[35]
Sugarcane dust	Basic Violet 10	13.90	[36]
Coir pith	Basic Violet 10	2.56	[37]
Neem sawdust	Basic Violet 3	3.79	[35]
Activated sludge biomass	Basic Violet 3	113.6	[38]
Sugarcane dust	Basic Violet 3	3.79	[39]
Deoiled Soya	Basic Violet 14	12.03	[40]
Bottom ash	Basic Violet 14	6.39	[40]
Calgon Carbon(CC)	Basic Violet 14	95.23	This work
Curcuma angustifolia scales (CA)	Basic Violet 14	208.33	This work

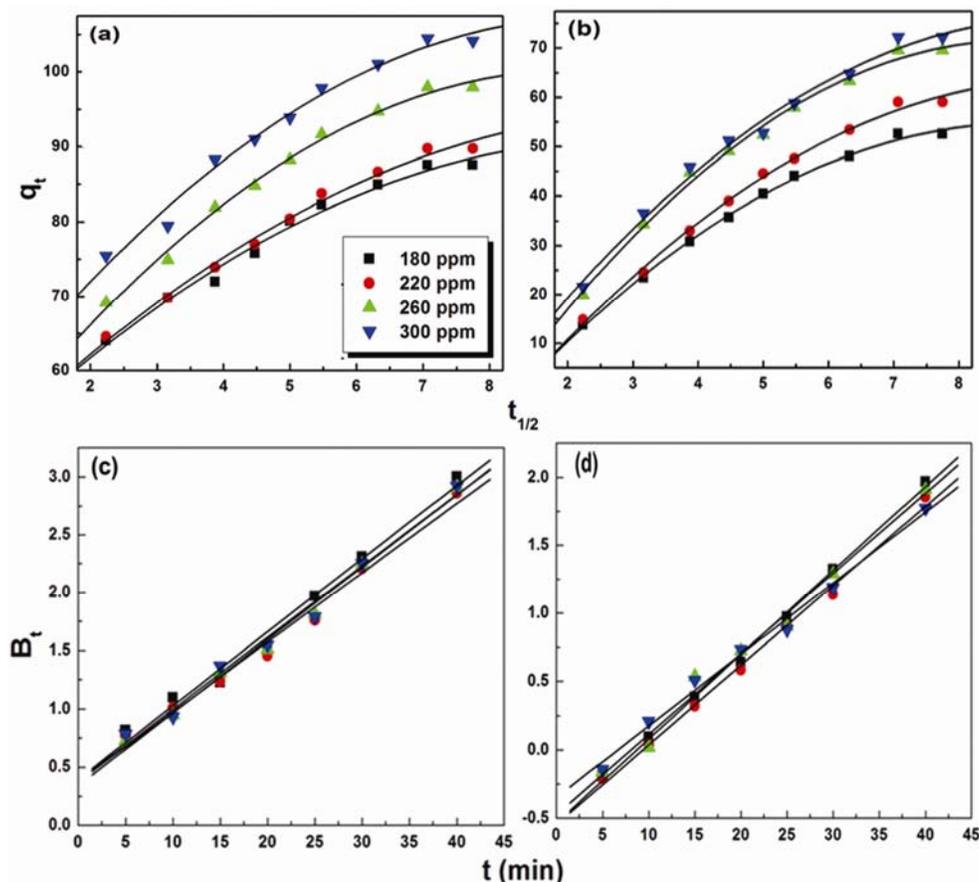


Fig. 5—Intraparticle diffusion plot for the adsorption of Basic violet 14 onto (a) *Curcuma angustifolia* adsorbent and (b) Calgon carbon. Boyd plot for the adsorption of Basic violet 14 onto (c) *Curcuma angustifolia* adsorbent and (d) Calgon carbon

adsorption of Basic Violet 14 on to the adsorbents is mainly controlled by film diffusion. The  $D_i$  values were obtained by using the calculated B values for CA and CC using the equation

$$B = \frac{\pi^2 D_i}{r^2}$$

where  $D_i$  is the effective diffusion coefficient, and  $r$  is the radius of the adsorbent. The calculated  $D_i$  values for CA and CC are shown in Table 4.

#### Thermodynamic studies

Thermodynamic parameters evaluates the feasibility and spontaneous nature of the adsorption process. The three thermodynamic parameters such as gibbs free energy ( $\Delta G$ ), enthalpy change ( $\Delta H$ ) and the entropy change ( $\Delta S$ ) were determined using the following equations:

$$\Delta G = -RT \ln K_c \quad \dots (10)$$

Table 4—Intraparticle diffusion coefficient and Diffusion coefficient ( $D_i$ ) for CA and CC.

Adsorbent	Concentration (mg/L)	$K_{ip}$ (mg/g min <sup>0.5</sup> )	$D_i$ (cm <sup>2</sup> /s)
CA	180	2.47	$7.41 \times 10^{-11}$
	220	2.83	$7.02 \times 10^{-11}$
	260	2.96	$7.34 \times 10^{-11}$
	300	3.02	$7.22 \times 10^{-11}$
CC	180	4.01	$7.23 \times 10^{-11}$
	220	5.39	$6.83 \times 10^{-11}$
	260	5.52	$6.91 \times 10^{-11}$
	300	6.37	$6.12 \times 10^{-11}$

$$\log K_c = \frac{\Delta S}{2.303 R} - \frac{\Delta H}{2.303 RT} \quad \dots (11)$$

The value of  $K_c$  is evaluated as  $K_c = C_{Ae}/C_c$ .  $K_c$  is the equilibrium constant. T is the temperature in Kelvin. The value of  $\Delta H$  and  $\Delta S$  were determined from the slope and intercept of vant hoffs plot and the various thermodynamic parameter values are given in

Table 5—Thermodynamic parameters calculated for the adsorption of Basic Violet 14 on to CA and CC.

Adsorbent	$\Delta G$ (kJ/mol)			$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol)
	303K	318K	333K		
CA	-5.1382	-6.9832	-9.1235	29.8886	0.1160
CC	-1.1346	-2.3649	-3.5905	4.6048	0.0521

Table 5. The negative value of  $\Delta G$  for both CA and CC indicates that the process is feasible and the nature of adsorption is spontaneous, also the  $\Delta G$  value becomes more negative with increase in temperature, indicates that the adsorption process is more favorable. The positive value of  $\Delta H$  for the adsorption of Basic Violet 14 onto CA and CC indicates that the adsorption process is endothermic in nature. The increased adsorption at high temperature may be due the diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent, resulting in a decrease in the viscosity of the solution<sup>44</sup>. The positive value of  $\Delta S$  for both CA and CC suggests increase in the randomness at the solid/solution interface during the adsorption and good affinity of the dye towards both the adsorbents<sup>38</sup>.

### Conclusion

The removal of Basic Violet 14 from aqueous solution using activated carbon prepared from scales of *Curcuma angustifolia* and commercial carbon (Calgon) has been investigated under different experimental conditions in batch mode adsorption studies. The adsorption of Basic Violet 14 is dependent on adsorbent surface characteristics, adsorbent dose and dye concentration in aqueous solution. The experimental data correlates well with the Langmuir, Freundlich and Temkin adsorption isotherms. The adsorption isotherm is best defined by the Langmuir isotherm model and the adsorption capacity is found to be 208.33 mg/g for CA and 95.23 mg/g for CC. The  $R_L$  value (from Langmuir Isotherm) between 0 and 1 shows favorable adsorption. The comparative studies of prepared activated carbon (CA) and commercial carbon (CC) on Basic Violet 14 show a better percentage of dye removal for CA. The adsorbent dosage studies shows that comparatively more adsorbent dosage is utilized by CC to obtain the percentage of dye removal acquired by CA. The double nature of the intraparticle diffusion plot suggests that the adsorption proceeds by boundary layer effect in the initial stages and intraparticle diffusion in the later stage. Boyd plot

confirms film diffusion as the slowest step involved in the adsorption of Basic Violet 14 onto CA and CC. Thermodynamic analysis shows that the adsorption of both the process is endothermic in nature. This work shows that the adsorbent (CA) can be used as an effective material in wastewater treatment process.

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