COMPARISON ON EQUILIBRIUM AND KINETIC STUDIES ON THE REMOVAL OF DIRECT GREEN 6 FROM AQUEOUS SOLUTIONS USING ACTIVATED CARBONS PREPARED FROM AGRO WASTE

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In the present investigation, activated carbons prepared from Ceiba pentradenta wood waste (CP) and Ipomea Carnea stem waste (IC) were used as an adsorbent for the removal of Direct Green 6 (DG 6) dye. The agro waste product is are of less usage and their availability is waste. The aspire of the present work is to explore the possibility of using these carbonaceous materials as low-cost adsorbents for the removal of DG 6 from wastewater. The effective parameters such as adsorbent dosage, initial dye concentration, pH, kinetics and thermodynamic studies were carried out to evaluate the adsorption capacity of the activated carbons prepared from wood and stem waste.

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1. Introduction

The first synthetic dye was reported in the year 1956, since it the commercially use of dyes has widely increased as the number of textile synthetic dyes used today exceeds $100,000^{[1,2]}$. About 50% of the dye in which 1 million tons of the dyes produced annually are categorized as azo dyes which are characterized by one or more nitrogen to nitrogen double bonds in their (-N=N-) chemical structures ^[3,4]. The effluents that are released from the industries causes serious ill effects to the environment and leads to environment pollution. The discharge of azo dyes to the environment escort to the reduction of azo bond in natural anaerobic condition which can lead to the formation of aromatic amines ^[5,6] which in several cases have been reported to be toxic, mutagenic and carcinogenic ^{[7].}

Many chemical and physical methods of dye-removal, including photocatalytic degradation ^[8], membranes ^[9] and adsorption techniques ^[10, 11] have been used from time to time.

Adsorption process is noted to be superior to other removal techniques because it is economically cost effective, simple and it is capable to efficiently treat dyes in more concentrated form ^{[10].} Direct green 6 has diazo group, it has toxicity and carcinogenic nature. Despite this, very few studies have been conducted on the adsorption of DG 6 from water. Therefore, in this work, two adsorbents CP and IC were used for removal of anionic dye, Direct Green (DR 6), from aqueous solution. The effects of adsorbent dosage, pH and initial dye concentration on dye adsorption by the adsorbents were investigated. The experimental data were analyzed using the Lagergren pseudo-first-order kinetic model, the pseudo-second-order model, the intra-particle

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diffusion model and Boyd model were carried out. Thermodynamics parameters such as ΔH , ΔS and ΔG were calculated .Ea was also deliberate for both the adsorbents.

2. Experimental

2.1. Materials and methods

The wood and stem of Ceiba pentradenta and Ipomea carnea were collected from local areas of Erode and Tirupur (Tamil Nadu). The adsorbate DG 6 was obtained from Sigma–Aldrich (Bangalore, India). The main purpose of using this DG 6 dyes in textile industry to colour various materials like polyester, nylon, cellulose diacetate and triacetate and acrylic fibres and are also used in the dyeing of leather, paints, plastics, papers, wood, oils, cosmetics, pharmaceuticals, metals and also used in food industries, the dye contaminant is discharged as effluents into water. The characteristics and 3 dimensional structure of DG 6 is shown in Table 1 and Fig. 1, respectively. All the other chemicals used were of analytical reagent grade and were purchased from precision scientific company (Coimbatore).

2.2. Preparation of activated adsorbents

The precursors used for the present study were cut into small pieces of 2 to 3 cm in size, dried in the sun light for 10 to 20 days to remove moisture content from the materials. Then the dried materials were used for preparation of activated carbons using phosphoric acid activation methods.

The materials to be carbonized were soaked separately in phosphoric acid in the ratio of 1:1 at 80^oC for 48 hours in a separate beaker. After 48 hours the materials were crushed well using mortar and this crushed materials were kept aside for 12 hours. Then the materials were washed well with hot water until a neutral pH is obtained. The materials were dried at 110° C for 24 hours. The dried masses were subjected to carbonization process at 800 °C for about 10 minutes. The material was followed by thermal activation at 400°C for about 10 minutes in technical nitrogen, N₂ 99.99 purity. The resulting activated carbon materials (CP and IC) were sieved through a 180-250 mesh sieve and separated .The activated adsorbents produced were stored in a separate airtight container for further adsorption studies.

Product Name	CAS Code	MF	MW	λ_{max}	CI
Direct Dark Green BN	4335-05-09	$C_{34}H_{22}N_8Na_2O_{10}S_2$	812.7	635	30295



Fig 1: Three -dimensional structure of DG 6

2.3. Adsorption studies

The adsorption studies parameters such as adsorbent dosage, pH and initial dye concentration for the removal of DG 6 colour from the aqueous solution, batch experiments were carried out in an orbital shaker (Orbitek, Scigenics Biotech, Chennai, India) at a constant speed of 200 rpm at room temperature. The adsorption isotherm experiment was carried out by agitating 50-mL dye solutions of various concentrations was conducted. After agitation, the dye solutions were separated from the adsorbent and were measured using a UV–visible spectrophotometer (ELICO, SL164, India). The effect of initial pH on dye removal was studied over a pH range of 2–11. The initial pH of the dye solution was adjusted by the addition of 0.1N solution of HCl or NaOH. The kinetic experiments were carried out using a known weight of adsorbent and employing DG 6 in the concentration range of 20-60 mg/L. The samples were withdrawn at predetermined time intervals and analysied. The effect of temperature on the adsorption characteristics was studied by determining the adsorption isotherms at 30, 45 and 60°C with a fixed dye concentration and dosage. Same procedure has been adopted for both the precursor CP and IC. The dye removal percentage and amount adsorbed were calculated using the following relationships:

Percentage of dye removal=
$$\frac{(C_0 - Ce)}{C_0} X \, 100$$
 (1)

Amount adsorbed (mg/g) (qe) =
$$(C_0 - C_e) X (V/m)$$
 (2)

where C_0 and C_e are, respectively, the initial and equilibrium concentrations of dye (mg/L), *m* is the mass of the adsorbent (g) and *V* is the volume of the dye solution (L).

3. Theory of biosorption

3.1 Equilibrium isotherms

The biosorbent can be described by sorption isotherm models such as Langmuir, Freundlich and Temkin models at fixed temperature and equilibrium distribution of dye between the aqueous solutions.

3.1.1 The Langmuir model assumes the occurrence of homogeneous biosorption at specific sites on the biosorbent, where by no further biosorption takes place at the same site after it is occupied. This model also assumes no interactions between molecules of neighbouring sites. The linear Langmuir isotherm equation is given by ^[12]

$$\frac{1}{q_e} = \frac{1}{q_{max} k_L} \frac{1}{C_e} + \frac{1}{q_{max}}$$
(3)

where $q_{\text{max}}(\text{mg g}^{-1})$ indicates the maximum biosorption capacity and $K_L(\text{L mg}^{-1})$ refers to the Langmuir constant related to free energy of biosorption. The main feature of the Langmuir model can be represented by the Hall separation factor, R_L (dimensionless). It is defined as ^[13]:

$$R_L = \frac{1}{1 + C_{max} k_L} \tag{4}$$

where C_{max} (mg L⁻¹) is the highest initial dye concentration. The value of R_L indicates the type of isotherm. The condition are as follows (i) $0 < R_L < 1$ indicates favourable isotherm, (ii) $R_L > 1$ unfavourable, (iii) $R_L = 1$ linear and (iv) $R_L = 0$ irreversible.

3.1.2 The Freundlich model assumes the occurrence of biosorption on heterogeneous surface with uneven binding sites. It describes an exponential decrease in the biosorption energy with an increase in the surface coverage. The equation is given by ^[14]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$
(5)

3.1.3 The Temkin model makes the assumption that molecular heat of biosorption decreases linearly with increasing surface occupation on biosorbent, while taking into account the effects of other indirect interactions between the sorbate and biosorbent. The Temkin is given by ^[15]:

$$q_e = \frac{RT}{bT} \ln KT + \frac{RT}{bT} \ln C_e \tag{6}$$

where R (=8.314 J mol⁻¹K⁻¹) is the universal gas constant, T(K) is the temperature, $bT(J mol^{-1})$ is the Temkin constant related to heat of biosorption and $KT(L mg^{-1})$ represents the maximum binding energy.

3.2. Biosorption kinetics

To determine the rate and mechanism of dye biosorption, the experimental data were analysed by several reaction rate and diffusion models, and these included the pseudo-first-order, pseudo-second-order, intra-particle diffusion models and Boyd model.

3.2.1 The pseudo-first order kinetic model predicts the biosorption behaviour based on physisorption process. The equation is represented as ^[16]:

$$\log(q_{\rm e} - q_{\rm t}) = \log q_{\rm e} - \frac{k_1}{2.303}t$$
(7)

where $q_t \text{ (mg g}^{-1)}$ is the biosorption capacity linear equation at time *t* (min)and $k_1 \text{(min}^{-1)}$ is the rate constant for the pseudo-first-order kinetic model.

3.2.2 Pseudo-second-order kinetic model is based on chemisorption process, and it is represented as, ^[17]:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e}$$
(8)

where $k_2(g mg^{-1}min^{-1})$ represents the rate constant for the pseudo-second-order kinetic model.

3.2.3 Intra-particle diffusion model accounts for the mass resistance arising from sorbate diffusion through biosorbent pores. The equation is given by $^{[19]}$:

$$q_t = k_p t^{0.5} + C \tag{10}$$

where k_p (mg g⁻¹min^{-0.5}) represents the intra-particle diffusion rate constant and *C* (mg g⁻¹) provides insight to the boundary layer effect which increases proportionally with the intercept value. The characteristic of t^{0.5} plot indicates the mechanistic step which controls the mass transfer process. If the plot is linear and passes through the origin, in the pores of the biosorbent is the main rate controlling step. If the plot is not linear and does not go through the origin, the sorption dynamic is due to several mechanisms including boundary layer and intra-particle diffusions.

3.2.4 The Boyd diffusion model indicates whether the diffusion of sorbate through the boundary layer controls the biosorption rate ^[20]. The equation is expressed as: where $F (=q_t/q_e, dimensionless)$ is the fraction of solute biosorbed at any time *t* and B_t is the Boyd constant.

$$B_t = -4.977 - \ln(1 - F) \tag{11}$$

3.2.5 Thermodynamic parameters:

To examine the thermodynamic of the biosorption of DG 6 dye by CP and IC prominent parameters such as Gibbs free energy change, ΔG (kJ mol⁻¹), enthalpy change, ΔH (kJ mol⁻¹), and entropy change, ΔS (kJ mol⁻¹K⁻¹), were evaluated by the following equations

$$\ln k_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{12}$$

$$\Delta G = -RT \log K_c \tag{13}$$

where R (=8.314 J mol⁻¹K⁻¹) is the universal gas constant, T (K)is the temperature and K_C is the equilibrium constant defined as ^[9a]:

$$K_C = \frac{q_e}{c_e} \tag{14}$$

From Van't Hoff plot of log K_C against 1/T, the values of ΔH and ΔS can be determined from the slope and intercept, respectively.

3.6 Activation energy determination

The feasibility and spontaneous nature of the adsorption process is reflected by the thermodynamic parameters. Arrhenius equation (15) represents the relationship between rate constant and temperature is given as

$$lnk = \ln A - \left(\frac{E_a}{RT}\right) \tag{15}$$

Where k is the rate constant obtained at different temperature with the best fit kinetic model, E_a (kJ/mol) is the activation energy, A (g/mg min), is the Arrhenius factor, R is the gas constant (8.314 J/mol K) T(K) is the solution temperature.

4. Result and discussion

4.1. Characterization of the adsorbent

BET surface areas, pore volumes and pore size distributions were determined from N_2 isotherm data collected at 77K (Quantachrome, USA) for CP and IP are illustrated in Fig. 2 and Table 2. It is evident from Table 2 that the activated carbons had high surface area and micropore volume. Scanning electron micrographs (SEMs) of CP and IC are shown in Fig. 3.SEM has been a primary tool for characterising the surface morphology and fundamental physical properties of the adsorbent. It is useful for determining the particle shape, porosity and appropriate size distribution of the adsorbent. From Fig 3, it is clear that, both the adsorbents have considerable numbers of pores where, there is a good possibility for dyes to be trapped and adsorbed into these pores. The SEM pictures of CP and IC samples show a very high sign for effective adsorption of dye molecules in the cavities and pores of the adsorbent.

CP 440 0.4641 0.1862 IG 277 0.4204 0.1427)
IC 3// 0.4294 0.143/	

Table 2. Physicochemical properties of various adsorbents



Fig. 2: Pore size distribution and adsorption isotherm of N_2 at 77K for CP and IC.



Fig. 3: SEM images of CP and IC activated carbon using phosphoric acid in presence of N_2 gas at 800 0 C

4.2. Effect of adsorbent dosage

The effect of changing adsorbent dosage on the adsorption rate of DG 6 was studied by varying the concentration of the adsorbent from 0.02 to 1.5 g/L while keeping the other experimental conditions constant. The percentage removal of DG 6 versus adsorbent dosage is shown in Fig 4 by varying the adsorbent dosage and keeping the other parameters are kept constant .An increase in the percentage of adsorption with increasing adsorbent dosage was observed in the two adsorbents. This was due to the availability of more surface functional groups at higher concentrations of adsorbents ^[21]. But the amount of dye adsorbed per unit weight of the adsorbent decreases with increase in dosage, as observed in all the cases. This may be attributed to the aggregation of adsorbent particles at high dosage, which reduces the total surface area of the adsorbent and results in an increase in the diffusion path length ^[22].

4.3 Effect of initial pH:

The effect of initial pH on the adsorption of dye by CP and IC was studied by varying the initial pH of the dye solution from 2 to 11 under constant experimental conditions (as shown in Fig 5). It is evident from Fig. 5 that both the adsorbents showed a better adsorption capacity. DG 6 is polar molecule (R-SO3–) at low pH. The prepared activated carbon is composed of various functional groups, such as amino and carboxyl, which could also be affected by the pH of the solutions. Therefore, the electrostatic attraction, as well as the organic properties of the activated carbon and structure of dye molecules, could play a very important role in the dye adsorption on both the adsorbents. At pH 2, there is high electrostatic attraction existing between the positively

charged surfaces of the adsorbent, due to the ionization of functional groups of adsorbents, and the negatively charged anionic dye molecules. As the pH of the system increases, the number of negatively charged sites is increased. A negatively charged site on the adsorbents does not favour the adsorption of anionic dye molecules due to the electrostatic repulsion. It is known that DG 6, on dissolution, release coloured dye anions into solution. The adsorption of these anionic charged groups onto the adsorbent surface is primarily influenced by the surface functional groups on the adsorbent, which in turn is influenced by the solution pH. Similar results of pH effect were also reported for the adsorption of direct dye ^[23].



Fig 6. Effect of adsorbent dosage on the removal of DG 6 by various adsorbents(t=4h, $C_0 = 20,40 \& 60 \text{ mg/L}$).



Fig. 5. Effect of pH (t=4h, $C_0 = 20 \text{ mg/L}$, m=0.1 g/50 mL)

4.4 Effect of contact time and Initial dye concentration

The adsorption experiments were now carried out for different contact times with a fixed adsorbent dose (0.1g) at room temperatures (Fig.6). The same type of pattern has been observed for both the adsorbents such as CP and IC, the uptake of the dye increases with time. The extent of adsorption is rapid in the initial stage and becomes slow in later stage till saturation is allowed. The final dye concentration did not vary significantly after 3 hours from the initial stage of adsorption process. This shows that equilibrium can be assumed to be achieved at 3 hours of contact time for CP and for IC. It is basically due to saturation of the active site which does not allow further adsorption. The adsorption rate was found to decrease with increase in time. The study of initial dye concentration was studied by varying the dye concentration from 20 to 60 mg/L which leads to a decrease in the percentage of the DG 6 removal as shown in Fig 6. The rapid adsorption takes place in the first 60 Minutes. Then the adsorption rate was decreased gradually and the adsorption reached equilibrium. This is because at low adsorbate/adsorbent ratio, the number of sorption sites in the CP and IC for both the kind of adsorbents was more. The reason was as the ratio increases the adsorption sites are saturated, resulting to decrease in the centre of

particle enhances dye diffusion through the film surrounding the particle and in the porous network of both the adsorbents. At 20ppm, the percentage of dye removed for IC was found to be 96% and at 60ppm it was found to be 80%. Fig. 6 clearly show that as concentration increases the adsorption starts decreasing. But for CP the removal of the dye was found to be slightly high for 20 ppm compared with that of IC, it was 97% and 83% for 60ppm it make be due to more adsorbent sites for CP.



Fig 6. Initial dye concentration (t=4 h, m=0.1 g/50 mL) for the adsorption of DG 6 by CP and IC.

5. Adsorption isotherm

The quantity of dye that could be taken up by an adsorbent is a function of both the concentration of the dye and the temperature. The amount of dye adsorbed is determined as a function of the concentration at a constant temperature, which could be explained by adsorption isotherms. In this study, three isotherms Langmuir , Freundlich and Temkin were tested. The isotherm constants for all the isotherms studied were calculated from the linear form of each model and the correlation coefficients were also reported.

5.1 Langmuir

The Langmuir adsorption model is based on the assumption that adsorbate molecules occur on a homogenous surface with a finite number of adsorption sites, by monolayer adsorption without mutual interactions between the adsorbed molecules.

Fig. 7 shows the comparative fit of Langmuir isotherms model of equilibrium for both the adsorbents CP and IC by plotting C_e/q_e versus C_e . The datas are given in table 3. Moreover, the dimensionless constant R_L lies within the favourable limit. Among the adsorbents studied, CP showed the highest adsorption capacity (124.26 mg/g) when compared with the other adsorbent IC was 63.1 mg/g.

Large surface area is generally a requirement for an optimum adsorbent. However, the total surface area has to possess adequate pore size distribution and surface chemistry to adsorb the targeted species. The adsorbent CP contains large surface area compared to the other adsorbent and it may contain proper pore size distribution to adsorb DG 6.

The low adsorption capacity of IC may be because the pore sizes generated on activation are smaller than the molecular size of DG 6, the resulting microporous structure making it in accessible to the dye molecules ^[24] on the surface so that the adsorption capacity of IC is reduced (as also evidenced by the textural properties and morphology given in BET TABLE). According to Wigmans ^[25], an activated carbon with high percentage of micropores will tend to adsorb low molecular weight compounds; as the percentage of micropores decreases, the carbon can adsorb compounds with a broader range of molecular sizes.



Fig 8. The fit of experimental adsorption data to Langmuir models for the removal of DG 6 by various adsorbents (t=4h,m= 0.1 g/50 mL).

Table 3. Langmuir constants for the removal of DG6 by various adsorbents

ADSORBENT	Q _o mg/g	K _L l/mg	\mathbf{R}^2
СР	124.262883	0.364306725	0.9972
IC	63.096174	0.144920453	0.9971

5.2 Freundlich isotherm

The Freundlich model assumes that the dye molecules are adsorbed on the heterogeneous surfaces of adsorbate, which is characterized based on the adsorption sites at different energies.

Fig.8 shows a straight line with a slope of 1/n and an intercept of $\ln k_F$, when $\ln qe$ is plotted against $\ln C_e$. The values of 1/n were also found to be between 0 and 1, indicating favourable adsorption of DG 6 on both the kind of adsorbents. If the system is of heterogeneity, the values becoming more closer to zero. Freundlich constants (K_F and n) were calculated and recorded, which are listed in Table 4. The low correlation coefficient (R^2) shows poor agreement of Freundlich isotherm with the experimental data for both the adsorbent CP and IC. The result correlated from the table for both the adsorbent concluded that both the adsorbents do not obey Freundlich isotherm model and they do not undergo multilayer of adsorption.



Fig. 8. Freundlich models for the removal of DG 6 by various adsorbents (t=8h, m=0.1 g/50 mL).

Table 4. Freundlich constants for the removal of DG 6 by various adsorbents

ADSORBENT	n	K _f	R^2
СР	1.3993	4.0523	0.9808
IC	2.5579	12.9092	0.9075

The above results showed that the Langmuir isotherm as a better fit with the experimental data than the Freundlich isotherm model. The best fit of experimental data was with the Langmuir model, suggesting that there was monolayer coverage for both the adsorbents CP and IC onto surface.

5.3 Temkin Plot:

The Temkin isotherm assumes that the adsorption free energy is a function of the surface coverage, at the same time; it takes into account interaction between adsorbent and adsorbate. The Temkin isotherm constants were evaluated from the plot of ln C_e versus q_e. Fig 9 and the values of $K_{T, the}$ equilibrium constant, was found to be 0.31296 for CP and for IC was found to be 1.5361. The correlation coefficient was 0.967 for CP and for IC it was found to be 0.9985. Our results showed that the adsorption of DG 6 onto IC was more favourable than CP.



Fig 9. Temkin models for the removal of DG 6 by various adsorbents (t=4h, m=0.1 g/50 mL).

Table 5 : Temkin plot for the removal of DG 6 by various adsorbents

ADSORBENT	K _T	\mathbf{R}^2
СР	0.31296	0.9687
IC	1.53607	0.9985

6.1 Biosorption kinetics

The experimental data were fitted with the pseudo-first-order, pseudo-second-order and Elovich kinetic models in order to determine the rate of biosorption. Table 6 shows the parameters of the models. Assuming pseudo first order kinetic for the adsorption process, $\log (q_e-q_t)$ was and the plotted against t and the linearity of the Pseudo first order plot (Fig. 10) confirmed the same (the correlation coefficient for the plot were in the range of 0.9868 for CP and 0.9991 for IC) .The first order constants evaluated from these plots were between 0.03461 and 0.02413 min⁻¹ for the CP and IC respectively. DG 6 interactions could thus be predicted as reasonably fast. It may be noted that the pseudo first order reaction in two aspects: the expression $k_1(q_e-q_t)$ does not represent the number of available sites and the parameter $\log q_e$ is an adjustable parameter whose value is not equal to the intercept of the plot of $\log ((q_e-q_t) vs t^{1/2})$. The difficulty usually associated with the application of the pseudo first order plot to an adsorption system arising from the uncertainty of finding reliable qe values within a reasonable time was not applicable in the present work as the system was very close to equilibrium.

The pseudo-second-order kinetic plot is shown in Fig 11 from Table 6, it can be seen that the match of the models to the experimental data based on R^2 descended in this order: pseudo-second-order > pseudo-first-order. The results indicated that the pseudo-second-order kinetic

model provided the best fit for the data. The good fit of data to this model also implied that the biosorption of DG 6 dye was predominantly by chemisorption $^{[26]}$



Fig 10.Pseudo-first order sorption kinetics of DG 6 onto CP and IC. Conditions: pH 6, m= 0.1 g/50 mL).



Fig 11.Pseudo-second order sorption kinetics of DG 6 onto CP and IC . Conditions: pH 6, m = 0.1 g/50 mL).

ADSORBENT	Pseudo first o	order kinetics	Pseudo second order kinetics				
	k_L , min ⁻¹	R^2	q _e ,mgg ⁻¹	$K_2 x \ 10^3 mgg^{-1}min^{-1}$	h, mgg ⁻¹ min ⁻¹	R^2	
СР	0.03461	0.9863	10.3591	0.01262	0.7384	0.9988	
IC	0.02413	0.9991	10.3452	0.01823	0.5413	0.9988	

Table 6: Kinetics constants for pseudo-first and pseudo-second order model

6.2 Intra-Particle Diffusion

To determine the rate-controlling step of the biosorption process, the experimental data were analysed by the intra-particle diffusion model (Eq. (10)). The Intra-particle diffusion can be described by three consecutive steps ^[16]:

(i) The transport of adsorbate from bulk solution to outer surface of the adsorbent by molecular diffusion, known as external (or) film diffusion.

(ii) Internal diffusion, the transport of adsorbate from the particles surface into interior sites.

(iii) The adsorption of the solute particles from the active sites into the interior surface of the pores.

The overall rate of the adsorption process will be controlled by the slowest, the rate limiting step. The nature of the rate-limiting step in a batch system can be determined from the properties of the solute and adsorbent. In adsorption systems where there is the possibility of intra-

particle diffusion being the rate-limiting step. Intra –Particle Diffusion pattern for both the adsorbents CP and IC for DG-6 is shown in the fig 12.



Fig 12. Plots of intra-particle diffusion for CP and IC Conditions: pH 6, m = 0.1 g/50 mL).

Table 7 Intra-particle diffusion parameters

Adsorbent	K _{i1}	С	\mathbb{R}^2	K _{i2}	С	\mathbb{R}^2
СР	0.791	1.7439	0.9795	0.0269	9.3255	0.6636
IC	0.8272	0.9528	0.9902	0.0672	8.5014	0.8729

Fig. 10(a) depicts the plot of this model having two different linear segments. The initial steeper segment corresponds to dye diffusion through the boundary layer surrounding the biosorbent and gradual dye diffusion through the internal pores. The second plateau segment describes the equi-librium biosorption of dye on the biosorbent surface. This multilinearity trend suggested that intra-particle diffusion was not the only rate limiting step for the process. Other mechanisms such as the boundary layer diffusion might be involved. The values of intra-particle diffusion parameters, and C, shown in Table 7, were predicted from the slope and intercept of the second linear segment, respectively.

6.3 Boyd model

To investigate whether boundary layer diffusion controls the mass transfer rate, the data were further fitted to the Boyd model .According to this model, a linear plot of Bt versus t which passes through the origin indicates intra-particle diffusion as the main rate determining step; otherwise, the sorption rate is controlled by boundary layer diffusion. As shown in Fig. 13 the plot of this model does not pass through the origin. The deviation from the origin confirmed that boundary layer diffusion has a dominant role in controlling the rate.



Fig 13. Boyd models for CP and IC Conditions: pH 6, m = 0.1 g/50 mL).

6.4. Thermodynamics parameters

The effect of temperature on biosorption of DG 6 dye on *CP* and IC *was* conducted at 303, 318 and 333k. A linear correlation between the biosorption capacity and temperature was obtained (graph is not shown). This indicated that the biosorption of DG 6 was an endothermic process. The thermodynamics properties of the biosorption process were evaluated by using Eqs. (12-14) and Van't Hoff plot is shown in the fig.14. The results of the analysis are displayed in Table 8. The positive value of ΔH confirmed the endothermic nature of the biosorption process. The positive value of ΔS indicated a more disordered behaviour at the solid-liquid interface possibly due to some internal structural changes of the biosorbent arising from interaction with DG 6 dye ^[15]. Both the adsorbent showed similar type of patern. The ΔG values are negative at all temperatures studied (Table 4) which suggested the spontaneous nature of DG 6 dye biosorption.

6.5 Activation energy of adsorption

Arrhenius equation (15) has been used for the determination of activation energy for the adsorption of DG 6 on CP and IC. The rate constant from the best fit model pseudo second order

Kinetic model, k_2 was used to make a plot of lnk_2 vs 1/T. Fig.14 The slope of the best fit line revealed the activation energy (E_a) of the biosorption process to be E_a 4.7161 for CP and for IC it was found to be 3.8492 kJ/mol. This indicates that the biosorption of DG 6 by both the adsorbent CP and IC is chemisorptions in nature.



Fig 14. Determination of activation energy by Arrhenius plot Conditions: pH 6, m = 0.1 g/50 mL).

		CP				Ι	С	
TEMP	ΔH	ΔS	Ea	ΔG	ΔH	ΔS	ΔG	Ea
(K)	J/K/Mole	J/K/Mole	kJ/mol	J/K/Mole	J/K/Mole	J/K/Mole	J/K/Mole	kJ/mol
303				-2525.54			-4865.8998	
318	42.91	28.75	4.7161	-4318.24	3.6933	15.2651	-6325.4137	3.8492
333				-7130.72			-7278.2526	

Table 8: Thermodynamics data of DG 6 dye biosorption onto CP and IC

7. Conclusions

The results of this study show that the activated carbon prepared from the CP and IC have suitable adsorption capacity with regard to the removal of DG6 from its aqueous solution. Activated carbon prepared from CP has better adsorption capacity than the activated carbons prepared from IC. A pH of 6 was found to be optimum for maximum DG 6 removal by both the adsorbents studied. All the two adsorbents are easily available materials and can be inexpensive alternatives for more costly adsorbents for direct dye removal in wastewater treatment. Adsorption followed Langmuir isotherms. Adsorption kinetics was found to follow pseudo-second-order rate expression. The negative values of ΔG indicate spontaneous adsorption of DG 6 on CP and IC. The study confirms that CP and IC can be used as an alternative for more costly adsorbents used for dye removal in wastewater treatment processes.

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