



Removal of 2, 4 dichlorophenol from aqueous medium using chemically modified low-cost adsorbent: kinetics, isotherm, thermodynamics and regeneration studies

G. Ramya Devi, D. Vidhya Lakshmi, N. Nagendra Gandhi*

Department of Chemical Engineering, AC Tech campus, Anna University, Chennai – 25, Tamil Nadu, India,
email: gramyabiotech@gmail.com (G.R. Devi), vidhyapurushoth@gmail.com (D.V. Lakshmi), nagendragandhi.n@gmail.com (N.N. Gandhi)

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ABSTRACT

Elimination of 2,4 D from water bodies is very much essential and possible using adsorption. Using commercial adsorbents, removal of 2,4 D can be efficient but requires high operating cost and hence this study focuses on feasibility of producing Activated Carbon (AC) from agricultural residue for removing the 2,4 D from aqueous solutions was analyzed. The adsorbent prepared using the chemical method with phosphoric acid at 1:2 ratio and activated at 500°C, washed and dried AC was characterized for understanding its properties. Batch adsorption analysis of 2, 4 D adsorption on AC was conducted to study the effects of initial 2, 4 D concentration (200 mg/L to 1000 mg/L), pH (2–12), contact time (0–360 min) and temperature (30–50°C). The adsorption efficacy of prepared AC on 2, 4 D was determined with the optimized adsorbing conditions. The equilibrium data were analyzed using different isotherm models (Langmuir, Freundlich, Temkin, and Dubinin Radushkevich) and kinetics models (Pseudo-first order, Pseudo-second order). Also, the adsorption mechanism was found using the intra-particle diffusion model. The activated carbon from the selected agricultural residue was shown to be an efficient adsorbent by removing 87.59% of 2, 4 D. The thermodynamic and regeneration studies were carried out to find the feasibility and reusability of adsorbent. From the results, it was confirmed that the system follows Langmuir isotherm, Pseudo-second order and the reaction is spontaneous and endothermic in nature. The maximum regeneration of adsorbent was obtained using NaOH among the other eluents.

Keywords: 2,4 dichlorophenol; Batch adsorption; Low-cost adsorbent; Agricultural residues; Chemical activation; Isotherm; Regeneration

1. Introduction

The phenolic compounds are very harmful to the ecosystem even at a lower concentration due to its carcinogenicity, low biodegradability and severe toxicity properties [1]. It can permeate through human skin and gets readily absorbed by the gastrointestinal tract on the human system and most of such exposure takes place in work places [2,3]. And also the phenol and its derivatives in the water sources create severe threats to the water quality by affecting the taste and odour which directly affects human health, peril

to the environment and more toxic to aquatic life and hence its removal from aqueous system is very much essential.

There are number of ways have been developed to remove phenol from wastewater, including chemical techniques such as electrochemical oxidation, solvent extraction, coagulation, photocatalytic degradation and physical techniques like membrane separation, ion exchange and biological methods. These methods have some limitations such as sludge production, the formation of secondary wastes and high operational cost [4]. Thus, the alternative method which can overcome all these problems was adsorption using activated carbon. It will be the most desirable method because of its efficiency, simple operation design, sludge-

*Corresponding author.

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free operation, high adsorption capacity and low operational cost. The activated carbon can eliminate different types of pollutants such as phenols, metal ions, dyes, detergents, pesticides, humic substances, chlorinated hydrocarbons and organisms.

But, the significant disadvantage is the high cost of activated carbon due to its ample of applications; so many researchers were focused on developing low-cost adsorbent from a variety of sources such as agricultural wastes, and industrial sludge. The activated carbon (AC) is made by process of raw material dehydration followed by carbonization and activation. Selection AC precursor material are based on availability, cost, low organic content and high inorganic content. The product generally has a porous structure with high surface area ranging from 600 to 2000 m²/g [5]. The features of activated carbon are determined by its pore structure, pore volume and surface chemistry [6].

Many researchers reported the adsorption on phenol and its derivatives with different activated carbons using a various activating agents like coconut husk [7], Husks of black gram, green gram and rice husk [8], coconut shell [9], *Tectona grandis* sawdust [10], Powdered activated carbon charcoal of bamboo, coconut shell and coal [11], Rice Husk [12], Tea waste derived activated carbon [13], Agricultural residue of *Phragmites australis* [14], and Waste Eggshell [15]. Hence, this study focuses on utilising ample agricultural waste as precursor material for activated carbon preparation and is to enhance the reduction of the carcinogenic pollutant like 2, 4 D from the environment using low-cost agricultural residue as an adsorbent.

2. Materials and methods

All the chemicals were of analytical-reagent grade. The 2, 4 D used at the adsorption studies, were diluted with a 1000 mg/L using distilled water to prepare a stock solution. Then, the adsorption studies were carried out with the prepared low-cost adsorbent, and the final concentration of the liquid phase was determined at the maximum light absorbance using a UV-visible spectrometer (Elico). The relationship between concentration and absorbance was calculated by a calibration curve up to the concentration of 200–1000 mg/L. The accuracy of absorbance method depends upon the optimized condition and handling. The pH of the solution was calculated using the pH meter.

2.1. Preparation of activated carbon

2.1.1. Collection and preparation of *Casuarina equisetifolia* residues

The activated carbon was prepared using *Casuarina equisetifolia* residues; collected from Villupuram Dist. *Casuarina* residues were washed thoroughly with distilled water to remove all the dust particles. The washed residues were dried in sunlight for two days and oven dried at 110°C for overnight. The oven dried sample was then carbonized at 400°C for 30 min; carbonized product was ground in a mechanical grinder until powdered. For chemical activation, Phosphoric acid (H₃PO₄) was used at 1:2 ratio (Char: Acid) for 2 h. Impregnated solution decanted off, the

impregnated char was air dried and activated at 500°C for 30 min. The prepared activated carbon was washed with distilled water sufficiently, and 1 M NaOH was used until the neutral pH obtained, dried and powdered. The particle size of prepared activated carbon was 64.34 μm (0.064 mm).

2.1.2. Characterization of activated carbon

The visual validation of surface morphology of the adsorbent was analysed using scanning electron microscopy (SEM - Superscan SS-550, Shimadzu) with 2000 magnification. The active groups and active sites present on the surface were examined using Fourier transform infrared spectroscopy (FTIR) for adsorbent before adsorption and after the adsorption process. The surface area for activated carbon was calculated using the BET technique. The activated carbon was degassed under vacuum condition at 300°C for 2 h before analysis. The sample was cooled in liquid nitrogen at 77 K to find the nitrogen adsorption-desorption isotherm by permitting the optimum volume of nitrogen in and out of the sample and calculating the pressure at equilibrium. Methylene blue number, iodine number, point of zero charge (pH_{pzc}), moisture content, volatile matter, fixed carbon and ash content was determined using the standard method [16].

2.1.3. Adsorption experiments

The batch adsorption experiments were carried out by adding a particular amount of prepared low-cost activated carbon into 50 mL of 2,4 dichlorophenol (2,4 D) solution. The various initial concentration of the 2, 4 dichlorophenol (200–1000 mg/L) were used in this study, and concentration was calculated using a UV-visible spectrophotometer. The amount of 2, 4 D adsorbed by low-cost activated carbon (adsorption capacity) was calculated using Eq. (1).

$$q_e = \frac{(C_0 - C_1)V}{W} \quad (1)$$

where q_e = adsorption capacity (mg g⁻¹), C_0 and C_1 are the initial and final concentration of the adsorbent in the solution (mg L⁻¹) respectively, V_d is the volume of the solution (L), W is the weight of the adsorbent (g).

3. Results and discussion

The activated *Casuarina equisetifolia* carbon (ACEC) was prepared from residues by chemical activation. The bulk density of the adsorbent depends on the concentration of the activating agent [17]. The characteristics of prepared AC were given in Table 1. The surface area of prepared activated carbon is 599.78 m²/g, it increases with increase in adsorption capacity. The surface area of adsorbent increases directly when the number of pores increases, and hence the adsorption capacity also increases [18,19]. The methylene blue number (MB) and iodine number are used to calculate the ability of the adsorbent to adsorb high and low molecular weight pollutant respectively. The above table shows that the prepared activated carbon is more porous with both meso and micropores.

The activated carbon will be more porous at optimized condition. In this case, impregnation ratio, impregnation time and activation temperature were fixed based on the preliminary study. Hence, the carbon preparation condition is optimized for optimum results. From that it was concluded that for selected case the activated carbon has more pores at optimum preparing conditions. The surface area of the activated carbon particularly depends on the type of raw material, preparation and activation conditions [20,21]. The moisture content for prepared activated carbon was inscribed in Table 1 as 18.94%. The moisture content has no effect on the carbon activity, but it dilutes the carbon. As per SNI standards, the ash content is low (3.93%) attributes the mechanical strength, adsorptive capacity and higher fixed carbon of adsorbent [22]. The prepared activated carbon was highly porous; this property directly increases the adsorptive power of activated carbon.

3.1. Surface morphology of ACL

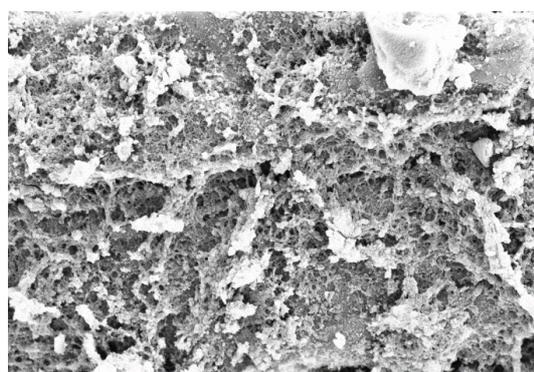
SEM micrograph's of ACL before and after adsorption of 2, 4 D are depicted in Figs. 1a, b, c. It is clearly shown that the prepared activated carbon shows rough areas with highly porous and a number of edges on the adsorbent, it may be due to the interconnectivity of pores. The increased concentration of H_3PO_4 and activation process will create the pits and cracks on the surface of the activated carbon because of the evaporation of phosphoric acid during carbonization [23].

The pore size was calculated from 3–10 μm and the size of the pore shows the adsorbate has high molecular weight from the image. White particles scattered on the image are the particles of H_3PO_4 used as activated agent. Washing of activated carbon was done until the wash water pH becomes neutral and hence traces of H_3PO_4 were observed in the SEM image [24].

3.2. Surface chemistry of ACL

The prepared ACL consists of the hetero-atoms like hydroxyl groups, alkane groups, carboxylate groups, alco-

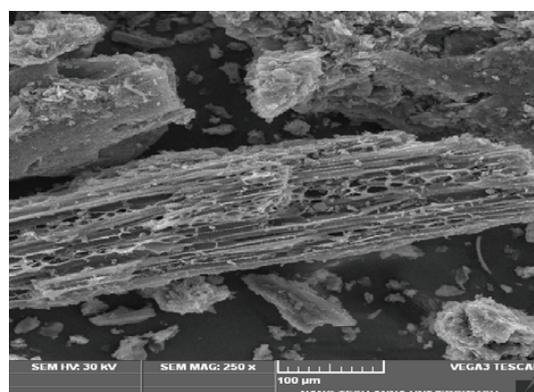
hol groups and sulphur groups. The FT-IR spectroscopy is a useful method to find out the functional groups and active sites present on the surface of the activated carbon. The absorption of infrared radiation spectrum in the range of 4500 to 500 cm^{-1} . The functional groups of activated carbon before and after adsorption of 2, 4 D is depicted in Figs. 2 and 3. The wide band around 3410 and 3433.29 cm^{-1} in CL char and ACL were attributed to the surface hydroxyl groups. The bands between 2924 and 2854 cm^{-1} were recognized +- as stretching vibration of C–H alkane group and small peaks observed in CL char at 1442–1300 cm^{-1} can be assigned to COO- carboxylate groups respectively. The



(a)



(b)



(c)

Table 1
Characteristics of ACL

Properties	ACL
Yield (%)	46
Bulk density (g/cc)	0.366
pH_{PZC}	6.48
Surface area (m^2/g)	599.78
Pore volume (cm^3/g)	0.2894
Iodine number (mg/g)	1079.5
Methylene blue number(mg/g)	137.78
Particle size (μm)	64.34
Moisture content (%)	18.94
Volatile matter (%)	50.67
Fixed carbon (%)	26.46
Ash content (%)	3.93

Fig. 1. SEM image of (a) ACL before adsorption; (b and c) ACL after adsorption.

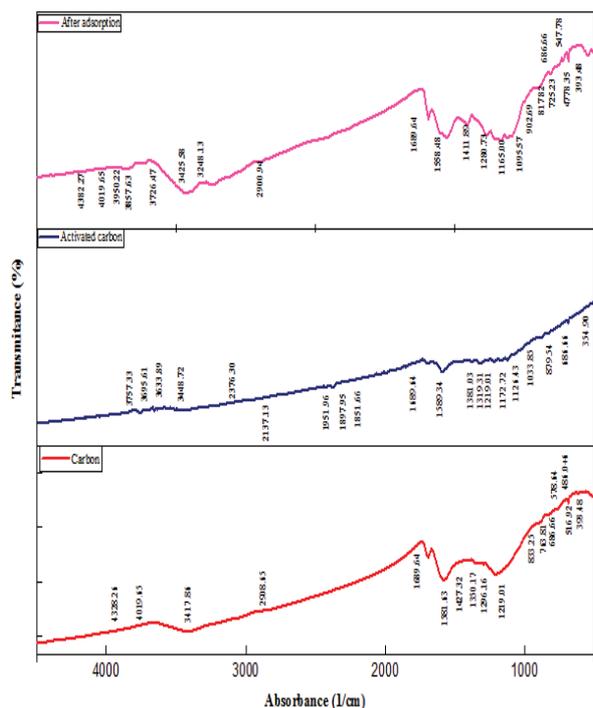


Fig. 2. FT-IR spectra of (a) Char (b) ACL before adsorption (c) ACL after adsorption.

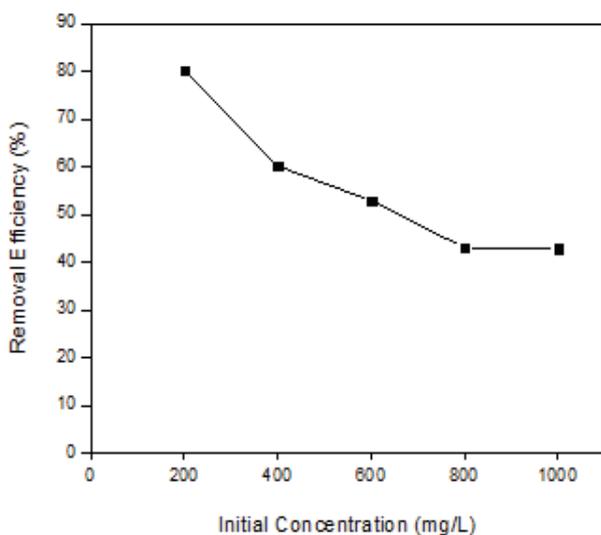


Fig. 3. Equilibrium removal percentage of 2, 4 D on prepared AC at 30°C.

stretch in CL char from 1300–1000 cm^{-1} represents C-O alcohol group. The peak at 1689 cm^{-1} represents C=O stretch, and 1165 cm^{-1} indicates C-O alcohol group in ACL. The sharp band at about 1581 cm^{-1} in ACL is assigned to C-C vibration in aromatic rings. Peaks between 600–800 cm^{-1} suggests the presence of Alkyl halides.

Fig. 2 of ACL with adsorbate contains more functional group peaks than char and before adsorption sample. Those compounds are adsorbed from the liquid phase as adsor-

bate are halides and bands between 4382.27 and 3726.47 in ACL with adsorbate has O-H stretch. The peak ranges from 3425.58 and 3248.13 has intermolecular H bonds and NH stretching vibrations. The peak at 1689.64 has amide groups, 902.69 has cyclic alcohols. The peaks at the finger print region have C-C, C-N and C-O groups.

3.3. Effect of adsorption on initial concentration

The removal percentage of 2, 4 D from the aqueous solution by adsorption on ACL at different initial concentrations from 200 mg/L to 1000 mg/L was analysed. The adsorbate removal through activated carbon was found to decrease with increasing concentration. The movement of molecule from solution to adsorbent was increasing with increase in concentration. The 2, 4 D adsorption capacity varies with respect to the initial concentration of adsorbate from 40.1 mg g^{-1} , 60.14 mg g^{-1} , 79.36 mg g^{-1} , 86.03 mg g^{-1} , 124.03 mg g^{-1} respectively. The increment of the uptake was due to the high mass driving force effect which allows more adsorbate to move from bulk phase boundary to the carbon surface. Fig. 4 shows the equilibrium adsorption capacity of 2, 4 D on ACL. It demonstrates a sudden increase in adsorption while increasing the concentration of the adsorbate; this indicates high affinity of adsorbate towards prepared low-cost adsorbent.

Fig. 5 shows the effect of removal of 2, 4 D at various temperature from 30 (303 K) to 50°C (323 K). Here temperature increases with increase in adsorption capacity and then decreases. It shows high removal of 2, 4 D at 40°C (313K). It shows an endothermic reaction to specified temperature.

3.4. Effect of adsorption on pH

Fig. 6 shows the effect of removal of 2, 4 D at different pH from 2 to 12. The pH plays a significant role because the adsorption capacity highly dependent on the surface charges, while the pH varies the charges also varies. The pH increases with decreasing removal percentage of 2, 4 D.

In this study the maximum adsorbate removal was calculated at pH 2 with high 2, 4 D as 97.44% at initial concentration of 200 mg/L. When pH is greater than pH_{PZC} , cations will be adsorbed and the pH is lesser than pH_{PZC} anions will be adsorbed. The removal percentage of 2, 4 D greater at lower pH, so it might removes all the anions from the solution. This was may be due to the characteristics of activated carbon and pH_{PZC} and also the acidic pH contains more protons which increase the electrostatic attraction. The mechanism behind this removal capacity as a function of pH was the increase in pH increasing the dissociation of 2, 4 D which produces the chlorophenolate anions. If the surface charge of activated carbon is neutral or negative, this repels the identical charged particles. This directly reduces the adsorption capacity [31].

3.5. Adsorption isotherms

The adsorption isotherm indicates about the molecular distribution occurs between two different phases at equilibrium condition and also explain the interaction between the adsorbate and adsorbent. The adsorption isotherm can

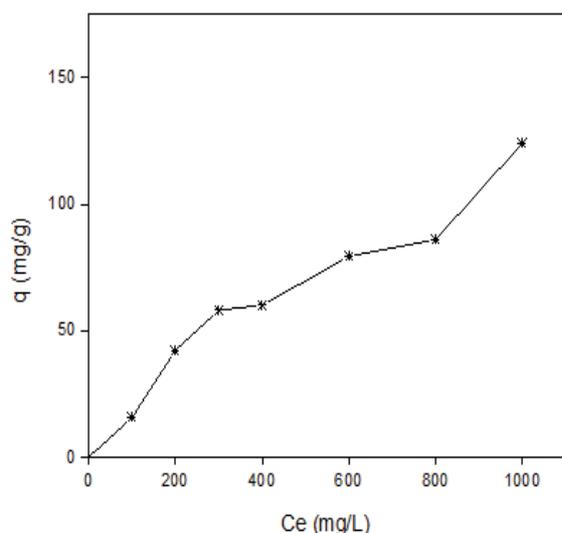


Fig. 4. Equilibrium adsorption capacity of 2, 4 D on prepared AC at 30°C.

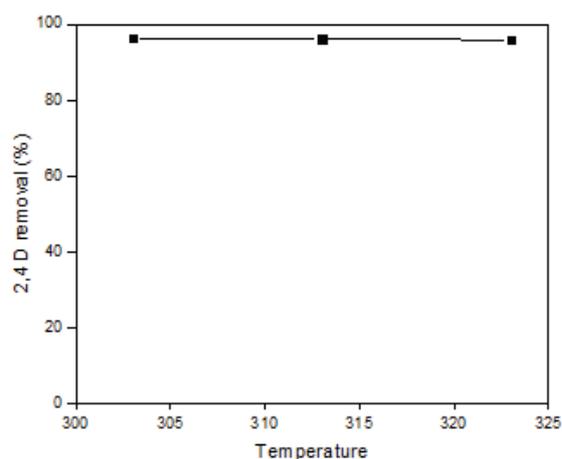


Fig. 5. Removal percentage of 2, 4 D at various temperatures.

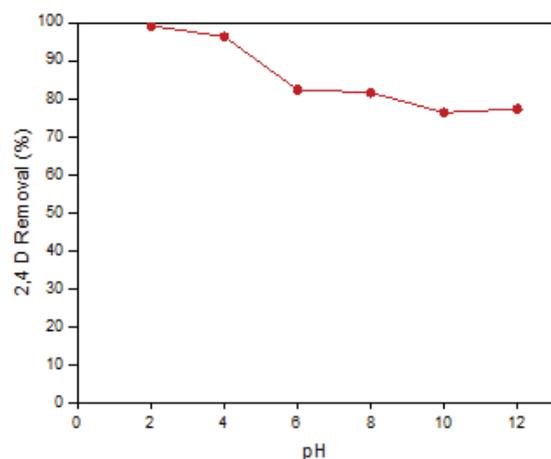


Fig. 6. Effect of pH on removal percentage of 2, 4 D at 30°C, initial concentration 200 mg/L.

be calculated quantitatively using the mathematical models like Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The Langmuir isotherm can be calculated, when C_e/q_e was plotted against C_e , this gives a straight line with the slope of $1/Q_0$. The Langmuir constants Q_0 and b were calculated using the equation and depicted in Fig. 8a. The Freundlich isotherm was calculated by plot $\log q_e$ against $\log C_e$, a linear line with the slope of $1/n$ as 0.44, as depicted in Fig. 8b.

From the graph, the Freundlich constants K_F and $1/n$ were calculated. These are the indicators of the adsorption capacity and adsorption intensity, respectively, and are listed in Table 2. For the Temkin adsorption isotherm, plot of q_e versus $\ln C_e$ as shown in Fig. 8c was plotted to find the constants A and B and results were presented in Table 2. Dubinin–Radushkevich isotherm plot ($\ln q_e$ versus ϵ^2) depicted in Fig. 8d and the constants q_s and E were calculated and provided in Table 2.

From Table 3, the R^2 value is a statistical measure of how close the data are to the fitted regression line and also known as the coefficient of determination. The regression value of Langmuir isotherm was well fitted while compared to other isotherm models for adsorption of 2, 4 D on prepared low-cost activated carbon. From this study, the Langmuir shows a high adsorption capacity is 125.75 mg/g indicates that amount of adsorbate adsorbed per unit weight of adsorbent to form complete monolayer on the surface. The high adsorption capacity of prepared activated carbon was due to its high surface area and micro porous surface. The possibility of adsorption of adsorbate on the adsorbent forms a monolayer and forms a homogenous surface. In Freundlich isotherm, the slope ($1/n$) value is 0.3488, so it attains the normal adsorption process. The result of present study was compared with adsorption capacity using various adsorbents in Table 3.

3.6 Adsorption kinetics

Adsorption kinetic's of the present study provides the detailed description about the mechanism of adsorption of 2, 4 dichlorophenol on prepared ACL. In this study, the well-known kinetic models like pseudo first order kinetic model, pseudo second order kinetic model and intra particle diffusion were employed to determine the system kinetics [36].

Table 3 presents the results of the kinetic models at various concentrations, from which it can be concluded that Pseudo second order model fits best for adsorption of 2, 4 dichlorophenol on the prepared low cost adsorbent. The $q_{e(\text{exp})}$ and calculated values are agreed satisfactorily with the pseudo second order and also the R^2 values obtained from the kinetic model were maximum greater than 0.9 for 2, 4 D concentrations.

The intraparticle diffusion model was studied to analyse the rate controlling step for the adsorption system. The process was diffusion controlled when the rate is dependent upon the rate at which the components diffuse each other. For intra particle diffusion, the constants k_p and C was calculated from the plot of q_t vs. $t^{1/2}$.

Here K_p is the rate constant and C is the thickness of the boundary layer. The effect boundary layer effect increases with the boundary layer thickness [37]. In the plot, the

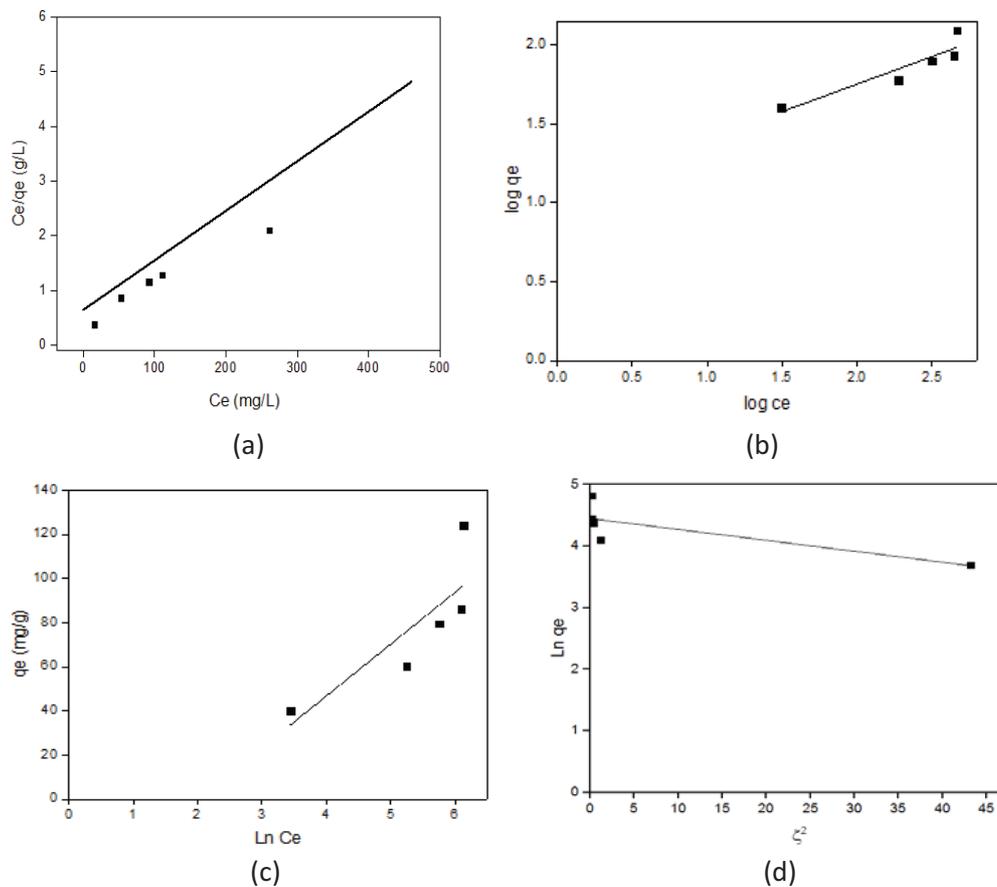


Fig. 7. Mathematical analysis of 2, 4 D adsorption on prepared AC at 30°C (a) Langmuir isotherm (b) Freundlich isotherm (c) Temkin isotherm and (d) Dubinin–Radushkevich isotherm.

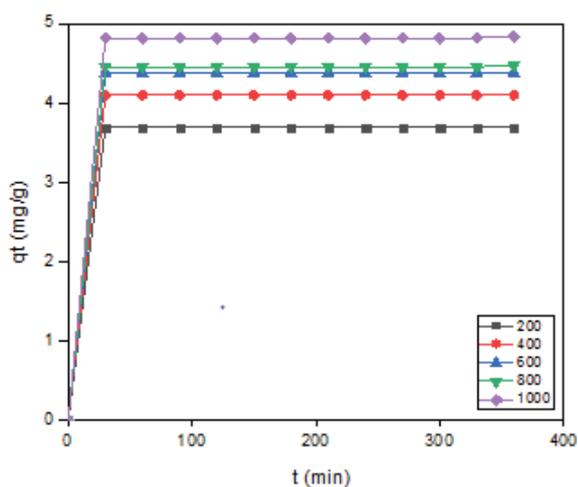


Fig. 8. Pseudo first order kinetic model for 2, 4 D on prepared AC.

lines are not passing through the origin because of the wide distribution of pores [38]. The R^2 value is lower when compared to pseudo second order but higher than pseudo first order.

Table 2

FTIR spectra of Char, activated char and AC after adsorption

S. No	Peak range (cm ⁻¹)	Functional group	Reference
Char			
1	3433	Surface hydroxyl groups	25
2	1689	C=O stretch	26
3	1581	C-C vibration	26
4	1165	Alcohol group, carboxyl acids	27
After activation			
5	3410	Surface hydroxyl groups	27
6	2924 and 2854	Alkane group	27
7	1604	Carbonyl stretching	28
8	1442	C-C stretching	27
9	600–800	C-OH stretching	27
After adsorption			
11	3726.47	Amide	29
12	3425.58 and 3248.13	H and NH stretching	30
13	1689.64	C-O Stretching	30

The intra particle diffusion has three stages during the first stage adsorption is faster because the concentration of adsorbent will be more or less equal to adsorbate. The second stage is the rate limiting stage due to the low adsorbate compared to the first stage and also it shows slower adsorption. In some cases, third stage occurs in which the particle adsorption starts to slow down because of extremely low adsorbate [39].

In the intraparticle diffusion, the adsorption capacity was decreased after it reaches the equilibrium. Here the linear portion of the curve didn't pass through the origin; it explains that the pore diffusion was not the rate controlling step, so majorly film diffusion controls the mass transfer [40].

3.7 Thermodynamics

In order to understand the adsorption affecting parameters, thermodynamic properties (Gibb's free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°)) were analyzed. The Van't Hoff equation.

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H^\circ}{RT} \quad (2)$$

ΔH° and ΔS° were calculated using the above formula; Gibb's free energy was calculated using the equation.

$$\Delta G = -RT \ln K_d \quad (3)$$

where K is the distribution coefficient, which can be calculated using the equation:

$$K_d = Q / C_e \quad (4)$$

The negative values of ΔG° for prepared low cost activated carbon in the adsorption of 2, 4 D illustrates that the nature of the process was spontaneous. The increase in temperature increases the negative value of Gibb's free energy; this indicates that the adsorption rate was more in higher temperature. The ΔH value explains that the reaction was endothermic. The positive value of ΔS clarified the affinity of activated carbon towards adsorbate and increased in randomness at the solid solute interface.

Table 3

Mathematical model of isotherm

Model	Isotherm parameter		
Langmuir	Q_o (mg g ⁻¹)	b (L mg ⁻¹)	R^2
	125.75	0.00039	0.9674
Freundlich	k_f (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	$1/n$	R^2
	11.398	0.3488	0.8503
Temkin	A (L g ⁻¹)	b (J mol ⁻¹)	R^2
	0.1338	2.40E+01	0.6971
Dubinin-Radushkevich	q_{max} (mg g ⁻¹)	E (kJ mol ⁻¹)	R^2
	85.4268	12.3624	0.6425

Table 4

Comparison of maximum monolayer adsorption capacity of different adsorbents

Adsorbent	Adsorbate	Max. Monolayer adsorption capacity (mg/g)	References
Oil palm empty fruit bunches	2,4 Dichlorophenol	22.2	32
Coir pith carbon	2,4 Dichlorophenol	19.12	33
Palm pith carbon	2,4 Dichlorophenol	19.16	34
Commercial grade coconut shell-based activated carbon	2,4,6-Trichlorophenol	112.35	35

Table 5

Kinetic models for adsorption of 2, 4 D

C_0 mg/L	$q_{e,exp}$	Pseudo first order kinetic model			Pseudo second order kinetic model		
		q_e (cal) mg/g	K_1	R^2	q_e (cal) mg/g	K_2 (g/mg h)	R^2
200	40.05	19.95	0.0007	0.143	39.26	0.0189	0.9841
400	60.14	20.51	3.15E-05	0.724	58.89	0.01216	0.9909
600	79.36	21.24	2.59E-05	0.400	76.96	0.00341	0.472
800	86.03	21.58	4.83E-06	0.287	84.59	0.286733	0.999
1000	124.03	20.208	1.88E-07	0.211	120.75	3.1621	0.9971

3.8 Desorption studies

Desorption process was carried out to calculate the reusability and recovery of the adsorbent. The adsorbed 2, 4 D was removed from the prepared low cost activated carbon using distilled water, 1 M NaOH, and 1 M HCl as eluent.

The solution was filtered and then spectrometrically analyzed. The table shows the desorption percentage of 2, 4 D, the sequence was in the order of NaOH > HCl > Distilled water.

This implies that the phenol molecules are converted into phenolate anions by adding the NaOH, the adsorbed

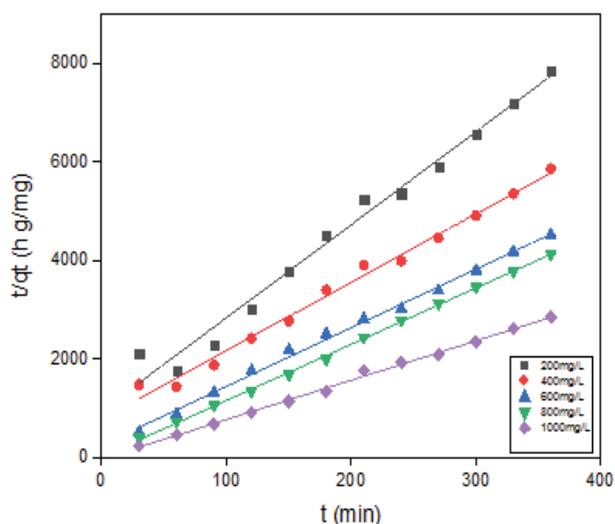


Fig. 9. Pseudo second order kinetic model for 2, 4 D on the prepared AC.

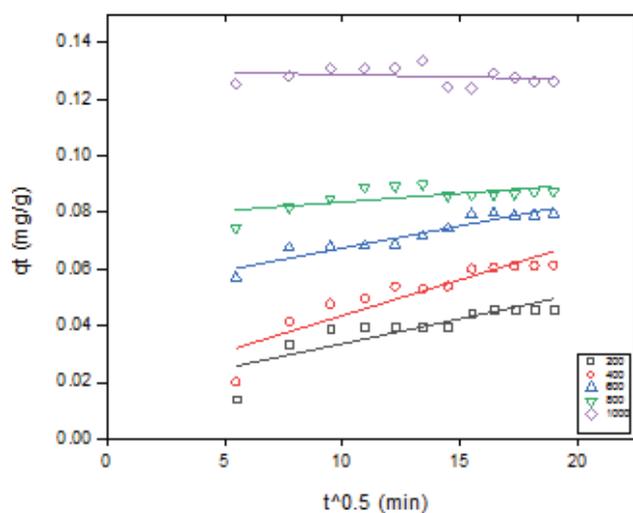


Fig. 10. Intra particle diffusion of 2, 4 D on AC.

molecules will be readily desorbed. From the above eluents, the NaOH showed a better result.

4. Conclusion

In the present study, activated carbon prepared from *Casuarina equisetifolia* residues (agricultural waste) by H_3PO_4 chemical activation was found to be significant in 2,4 dichlorophenol removal. The prepared activated carbon was characterized to know the significant properties of the AC for the removal of adsorbate. The equilibrium data best fits with Langmuir model than Freundlich, Temkin and Dubinin–Radushkevich and had high adsorption capacity of 125.75 mg/g at 30°C. The adsorption kinetics analysed using pseudo first order, pseudo second order and intra particle diffusion. The system found to follow pseudo sec-

Table 6
Intra particle diffusion

C_0 (mg/L)	Intraparticle diffusion model		
	K_p (mg/g h ^{1/2})	C	R ²
200	1.756	16.116	0.722
400	2.534	18.229	0.831
600	1.572	51.656	0.901
800	0.618	77.495	0.413
1000	0.735	85.952	0.426

Table 7
Thermodynamic parameters for removal of 2, 4 D

ΔH° (J/mol)	ΔS° (J/mol)	$-\Delta G^\circ$ (J/mol)		
		303 K	313 K	323 K
40.589	16.099	442.384	603.375	764.365

Table 8
Percentage desorption of removal of 2, 4 D in ACL

S.No	Eluent	Desorption %
1	Distilled Water	5.78
2	HCl	11.3
3	NaOH	90.75

ond order and the system was controlled by film diffusion. The thermodynamics studies confirm the process spontaneity and endothermic in nature. The regeneration study shows that NaOH has more ability to regenerate the adsorbent when comparing to other eluents.

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