

Equilibrium and kinetic studies on the removal of Acid Red 114 from aqueous solutions using activated carbons prepared from seed shells

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Abstract

The use of low-cost and ecofriendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing dyes from wastewater. This paper deals with the removal of Acid Red 114 (AR 114) from aqueous solutions using activated carbons prepared from agricultural waste materials such as gingelly (sesame) (Sp), cotton (Cp) and pongam (Pp) seed shells. Optimum conditions for AR 114 removal were found to be pH 3, adsorbent dosage = 3 g/L of solution and equilibrium time = 4 h. Higher removal percentages were observed at lower concentrations of AR 114. The adsorption isotherm data were fitted to Langmuir and Freundlich equation, and the adsorption capacity of the studied adsorbents was in the order Sp > Cp > Pp. Kinetic studies showed that the adsorption followed both pseudo-second-order and Elovich equation. The thermodynamics parameters such as ΔG° , ΔH° , ΔS° were also evaluated. The activated carbons prepared were characterized by FT-IR, SEM and BET analysis.

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1. Introduction

The textile industry is characterized by its high water consumption and is one of the largest producers of industrial wastewater. The main pollution sources of textile wastewater are the dyeing and finishing processes. Wastewater containing dyes presents a serious environmental problem because of its high toxicity and possible accumulation in the environment. Many of these dyes are synthetic and contain aromatic rings, which make them carcinogenic and mutagenic [1]. The removal of dyes from textile effluents is currently of great interest [2]. Due to the large degree of organics present in these molecules and the stability of modern dyes, conventional physicochemical and biological treatment methods are not completely effective for their removal [3]. However, these processes are costly, need large land area and cannot be effectively used to treat the wide range of dye wastewaters [4]. Among the advanced chemical or physical treatments, adsorption is considered to be superior to other techniques. This

is attributed to its easy availability, simplicity of design, ease of operation, biodegradability, insensitivity to toxic substances and ability to treat dyes in more concentrated forms [3]. Activated carbon is the most popular and widely used adsorbent for the adsorption process [5] because it has a large surface area and high adsorption capacity. However, the price of activated carbon is relatively high, thus limiting its usage. This has led many workers to search for cheaper substitutes for the activated carbon [6]. A number of low-cost adsorbents have been examined for dye removal, including agricultural waste biomass [7], peanut hulls [8], almond shells [9], and wheat bran carbon [10]. Still, coloured wastewater treatment needs new adsorbents that are economical, easily available and effective.

In the present study, activated carbon prepared from seed shells of gingelly (sesame) (Sp), cotton (Cp) and pongam (Pp) were used as an adsorbent for the removal of Acid Red 114 (AR 114). The materials chosen are available in large quantities in most countries and at low-cost. The aim of the present work is to explore the possibility of using these carbonaceous materials as low-cost adsorbents for the removal of AR 114 from wastewater. Effective parameters such as adsorbent dosage, initial dye concentration, pH, kinetics and thermodynamic studies were carried

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Table 1
The physical chemical characteristic of AR 114 dye

Generic name	C.I. Acid Red 114
Colour index number	23,635
Abbreviation	AR 114
Commercial name	Acid Red 114
Molecular formula	C ₃₇ H ₂₈ N ₄ O ₁₀ S ₃ Na ₂
Purity	80%
Chromophore	Diazo
Molecular weight	830
λ _{MAX} (nm)	522 nm
Appearance	Dark red powder
Chemical name (IUPAC)	Disodium 8-((3,3'-dimethyl-4'-((4-(4-methylphenyl) sulphonyl) oxy) phenyl) azo)-(1,1'-biphenyl)-4-yl) azo)-7-hydroxy-1,3-naphthalenedisulphonate

out to evaluate the adsorption capacity of the activated carbons prepared from seed shells.

2. Experimental

2.1. Materials and methods

The seed pods of gingelly (sesame), cotton and pongam plants were collected from local agricultural fields. The seeds were removed from the seed pods and the shells were used for the preparation of adsorbents. The adsorbate AR 114 was obtained from Sigma–Aldrich (Bangalore, India). The dye was chosen as an adsorbate because it is commonly used in dyeing of silk fabrics (in and around Kancheepuram, Tamil Nadu, India) and is a dye contaminant in discharged effluents. The characteristics and chemical structure of AR 114 is shown in Table 1 and Fig. 1, respectively. All the other chemicals used were of analytical reagent grade and were purchased from Qualigens Fine Chemicals (Mumbai, India).

2.2. Preparation of activated adsorbents

The raw materials were repeatedly washed with distilled water to remove dirt, dust and other surface impurities. The washed seed shells were dried in the sun for 48 h, cut into small pieces, soaked in 18N sulphuric acid (1:2, w/v), and heated separately for 24 h at 80 °C in a muffle furnace (Gambaks Instru-

ments, Chennai, India). After treatment, all the treated samples were cooled to room temperature and washed with distilled water until the filtrates attained neutral pH. The resulting activated carbon materials (ACSS) were dried in a hot air oven at 105 °C, powdered and sieved through a 0.25 mm sieve.

2.3. Adsorption studies

To study the effect of parameters such as adsorbent dosage, pH and initial concentration for the removal of colour in AR 114, batch experiments were carried out in a thermostatic orbital shaker (Orbitek, Scigenics Biotech, Chennai, India) at a constant speed of 175 rpm at room temperature. The adsorption isotherm experiment was carried out by agitating 50-mL dye solutions of various concentrations. After agitation, the dye solutions were separated from the adsorbent by centrifugation for 10 min. Dye concentrations in the supernatant solutions were measured using a UV–vis spectrophotometer (ELICO, SL164, India). The effect of initial pH on dye removal was studied over a pH range of 3–11. The initial pH of the dye solution was adjusted by the addition of 0.1N solution of HCl or NaOH. To find the optimum amount of adsorbent per unit mass of the adsorbate, the dye solution (50 mL) was contacted with different amounts of ACSS till equilibrium was reached. The kinetic experiments were carried out using a known weight of adsorbent and employing AR 114 in the concentration range of 60–100 mg/L in a mechanical stirrer (Remi, India). The samples were withdrawn at predetermined time intervals and centrifuged. The effect of temperature on the adsorption characteristics was studied by determining the adsorption isotherms at 25, 30, 35, 40 and 50 °C with a fixed dye concentration and dosage. The dye removal percentage and amount adsorbed were calculated using the following relationships:

$$\text{Percentage removal} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

$$\text{Amount adsorbed (mg/g)} (q_e) = (C_0 - C_e) (V/m) \quad (2)$$

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).

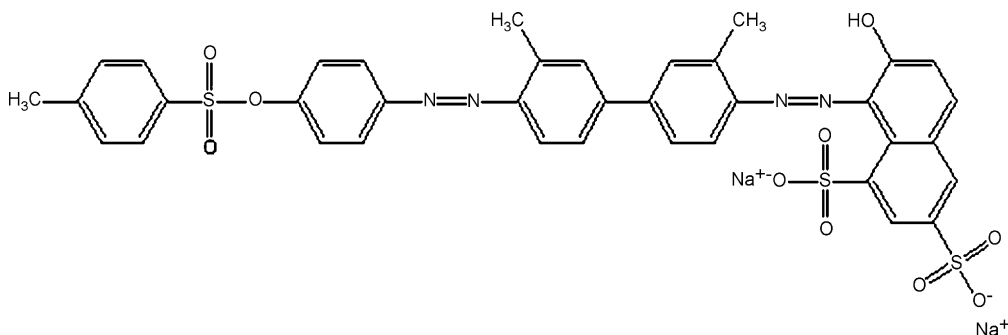


Fig. 1. Chemical structure of Acid Red 114.

Table 2
Physicochemical properties of various adsorbents

Adsorbent	$S_{\text{BET}}^{\text{a}}$ (m^2/g)	Pore volume ^b (cm^3/g)	Micropore volume ^c (cm^3/g)	Yield (%)
Sp	229.65	0.184	0.162	62
Cp	124.35	0.115	0.077	77
Pp	324.79	0.238	0.176	84

^a BET surface area.

^b Total pore volume, obtained at $p/p_0 = 0.992$.

^c Micropore volume calculated using BJH method.

3. Results and discussion

3.1. Characterization of the adsorbent

BET surface areas, pore volumes and pore size distributions were determined from N_2 isotherm data collected at 77 K (Quantachrome, USA) of ACSS are illustrated in Fig. 2 and Table 2. It is evident from Table 2 that the activated carbon Pp had high surface area and micropore volume. The identification of various forms of different constituents in activated carbon, viz., Cp, Sp and Pp, have been done with the help of

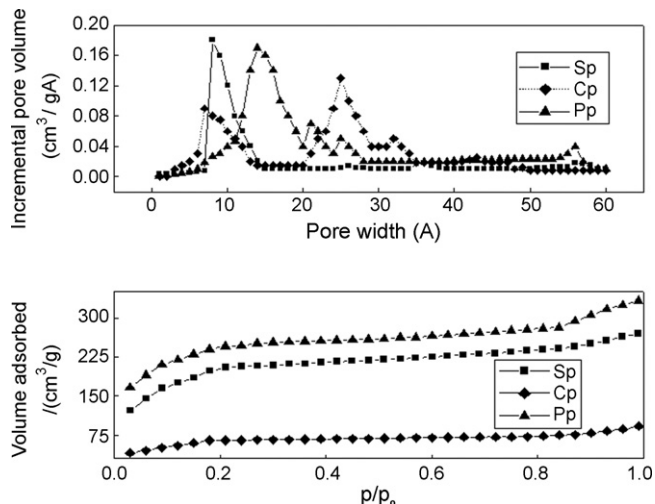


Fig. 2. Pore size distribution and adsorption isotherm of N_2 at 77K for ACSS.

FT-IR spectra (Fig. 4) in the range of $450\text{--}4000\text{ cm}^{-1}$. The bands around 3400 cm^{-1} (Sp, Cp, Pp) are due to self-associated O–H groups. The peak observed around 2925 cm^{-1} (Cp, Sp) displays various shoulders and represents asymmetric and sym-

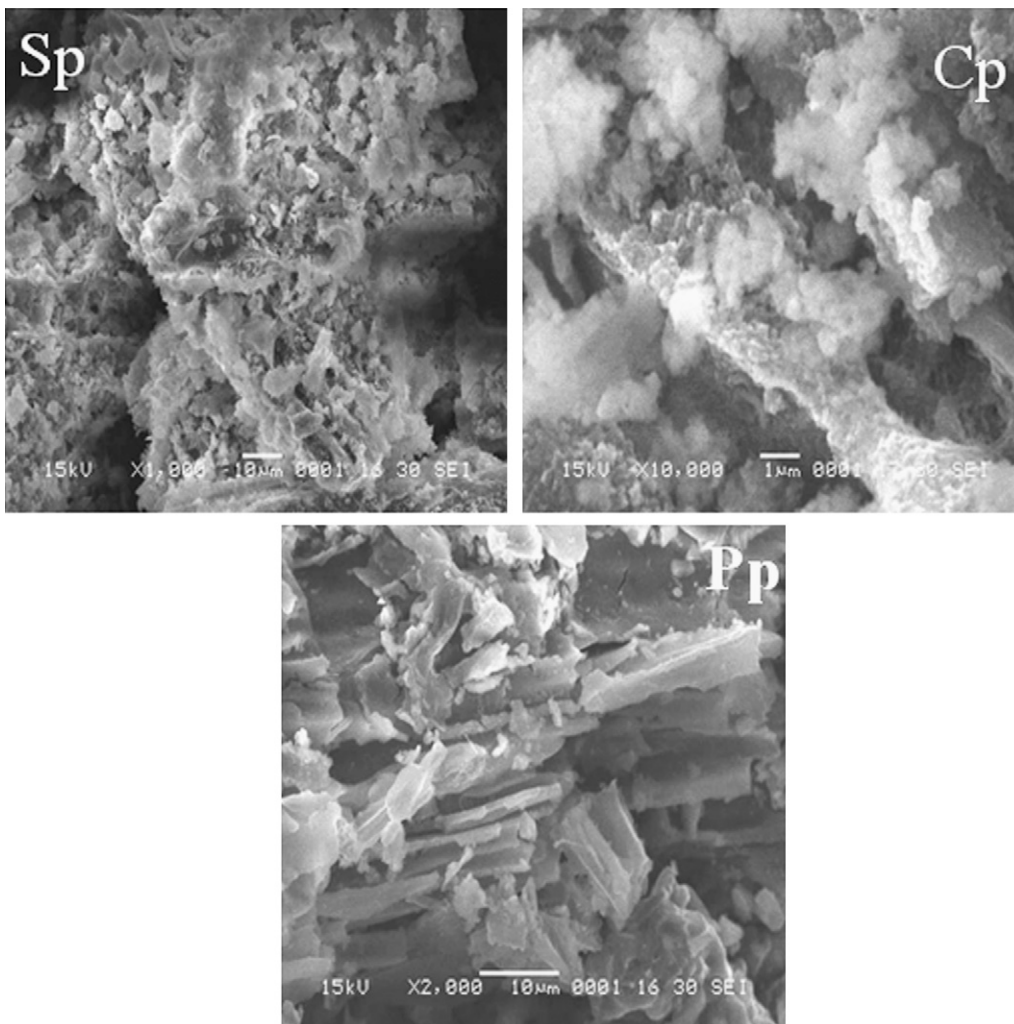


Fig. 3. Scanning electron micrograph (SEM) of various adsorbents.

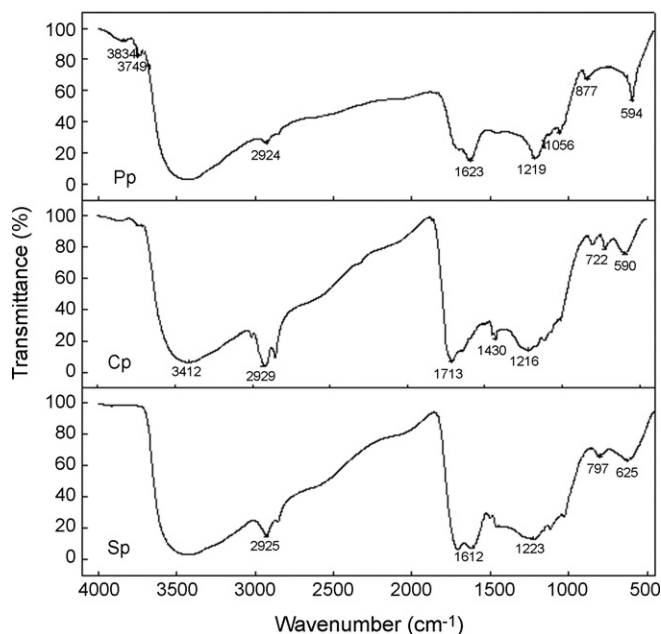


Fig. 4. FT-IR spectra of various adsorbents.

metric vibration modes of methyl and methylene groups [11]. The peak around 1650 cm^{-1} (Pp) can be assigned to symmetric and asymmetric stretching vibrations of the C=C group. In connection with this band assignment, it should be borne in mind that in the spectral region between 1700 and 1600 cm^{-1} there is overlapping of bands, resulting in the absorption maximum being shifted towards lower wave numbers [12]. The peaks around 1060 cm^{-1} (Pp) are due to OCH_3 groups, which may be attributed to the lignin aromatic groups. The intense peak around 600 cm^{-1} (Pp) can be assigned to the bending modes of the C-H group. Although some inference can be drawn about the surface functional groups from IR spectra, the broad and weak bands do not show any valuable information about the nature of the surface oxide groups. The presence of polar functional groups on the surface is likely to give considerable anion exchange capacity to the adsorbents. Scanning electron micrographs (SEMs) of ACSS are shown in Fig. 3. From Fig. 3, it is clear that Pp and Cp have considerable numbers of pores.

3.2. Effect of adsorbent dosage

The effect of changing adsorbent dosage on the adsorption rate of AR 114 was studied by varying the concentration of the adsorbent from 0.5 to 4 g/L while keeping the other experimental conditions constant. The percentage removal of AR 114 versus adsorbent dosage is shown in Fig. 5. An increase in the percentage of adsorption with increasing adsorbent dosage was observed in all the three adsorbents. This was due to the availability of more surface functional groups at higher concentrations of adsorbents [13]. 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

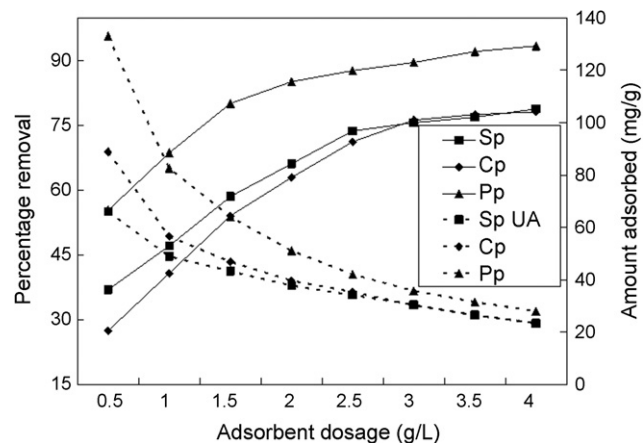


Fig. 5. Effect of adsorbent dosage on the removal of AR 114 by various adsorbents ($t = 8\text{ h}$, $C_0 = 120\text{ mg/L}$).

total surface area of the adsorbent and results in an increase in the diffusion path length [14].

3.3. Effect of initial pH

The effect of initial pH on the adsorption of dye by ACSS was studied by varying the initial pH of the dye solution from 3 to 11 under constant experimental conditions (as shown in Fig. 6). It is evident from Fig. 6 that all the adsorbents showed better adsorption capacity at the initial pH of 3. AR 114 is polar molecule (R-SO_3^-) 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 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 ACSS. At pH 3, there is high electrostatic attraction existing between the posi-

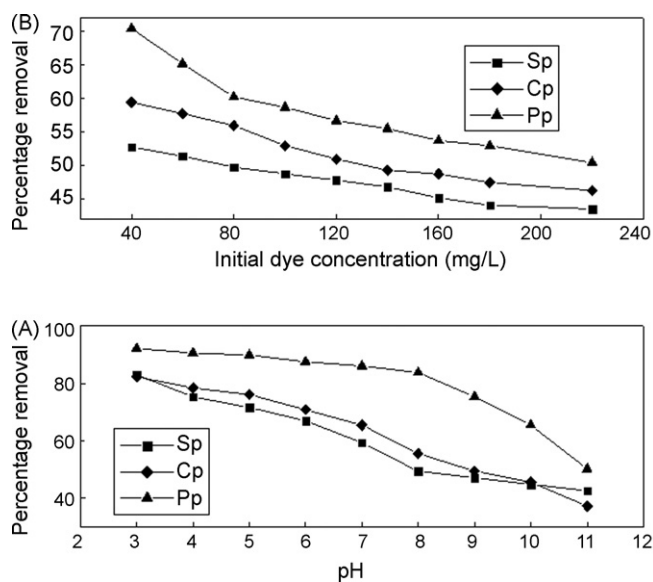


Fig. 6. (A) Effect of pH ($t = 8\text{ h}$, $C_0 = 100\text{ mg/L}$, $m = 0.1\text{ g/50 mL}$) and (B) initial dye concentration ($t = 8\text{ h}$, $m = 0.05\text{ g/50 mL}$) for the adsorption of AR 114 by various adsorbents.

tively charged surfaces of the adsorbent, due to the ionization of functional groups of adsorbent, 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 adsorbent does not favour the adsorption of anionic dye molecules due to the electrostatic repulsion. It is known that acid dyes, 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. A similar result was observed for the adsorption of Acid Red 14 by soy meal hull [15].

3.4. Effect of initial concentration (C_0)

The effect of C_0 on the removal of AR 114 by ACSS is shown in Fig. 6b. From the figure it is evident that the percent AR 114 removal decreased with the increase in C_0 , although the actual amount of dye adsorbed per unit mass of the adsorbent increased with the increase in C_0 . At lower concentrations, all AR 114 present in the adsorption medium could interact with the binding sites so higher percentage removals were obtained. At higher concentrations, lower removal percentage was observed because of the saturation of the adsorption sites.

3.5. 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 (Eq. (3)) [16], Freundlich (Eq. (4)) [17] and Temkin (Eq. (5)) [18] were tested.

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad \text{or} \quad \frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (3)$$

$$q_e = K_F C_e^{1/n} \quad \text{or} \quad \log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad \text{or} \quad q_e = B_1 \ln K_T + B_1 \ln C_e \quad (5)$$

where C_e is the concentration of the dye solution (mg/L) at equilibrium, q_e is the amount of dye adsorbed per unit weight of adsorbent (mg/g), K_L is the constant related to the free energy of adsorption (L/mg) and Q_m is the maximum adsorption capacity. K_F is a Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and $1/n$ is the adsorption intensity. $B_1 = RT/b$, K_T is the equilibrium binding constant (mg^{-1}) and B_1 is the heat of adsorption.

The isotherm constants for all the isotherms studied were calculated from the linear form of each model and the correlation coefficients are given in Table 3. Fig. 7 shows the comparative fit of Langmuir, Freundlich and Temkin isotherms with the equilibrium data plotted as q_e versus C_e . From Fig. 7 and the experimental results, it can be seen that the Langmuir model is the best-fit model for the adsorption of AR 114 onto ACSS.

Table 3

Freundlich and Langmuir constants for the removal of AR 114 by various adsorbents

Adsorbents	q_m (mg/g)	K_L (L/mg)	R_L	R^2
Langmuir				
Sp	102.04	0.011	0.327	0.9955
Cp	153.85	0.005	0.514	0.9903
Pp	204.08	0.010	0.461	0.9967
Adsorbents	K_F (mg/g)	n	R^2	
Freundlich				
Sp	2.2438	1.4004	0.9944	
Cp	1.2537	1.2109	0.9997	
Pp	3.3334	1.3051	0.9973	
Adsorbents	K_T (L/mg)	B_1	R^2	
Temkin				
Sp	0.093	21.492	0.9822	
Cp	0.128	20.253	0.9780	
Pp	0.130	35.8023	0.9868	

From the experimental results, it can be seen that the Langmuir and Freundlich models fit better than the Temkin model. Moreover, the dimensionless constant R_L lies within the favourable limit. The values of $1/n$ were also found to be between 0 and 1, indicating favourable adsorption of AR 114 on ACSS. Among the adsorbents studied, Pp showed the highest adsorption capacity (204.08 mg/g) when compared with the other two adsorbents Sp and Cp were 102.04 and 153.85 mg/g, respectively.

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 Pp contains large surface area compared to the other two adsorbents and it may contain proper pore size distribution to adsorb AR 114 (Fig. 2).

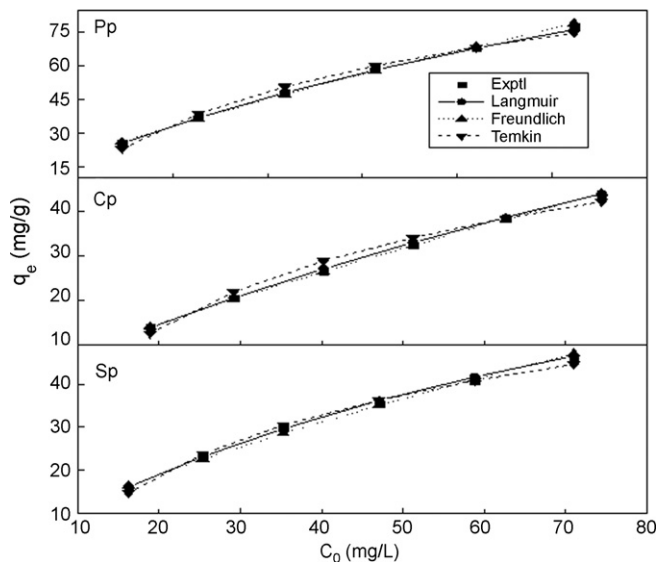


Fig. 7. The fit of experimental adsorption data to Langmuir, Freundlich and Temkin models for the removal of AR 114 by various adsorbents ($t=8$ h, $m=0.05$ g/50 mL).

Moreover, the presence of surface oxygen functional groups also imparts a polar character to the activated carbon surface, which can increase the preferential adsorption of anionic dye molecules by the electrostatic attraction process. The SEM of Pp (Fig. 4) shows a fibrous structure with large pore size with strands in each fibre. So there is a good possibility for dyes to be trapped and adsorbed into these pores.

The low adsorption capacity of Sp may be because the pore sizes generated on activation are smaller than the molecular size of AR 114; the resulting microporous structure making it inaccessible to the dye molecules [19] on the surface so that the adsorption capacity of Sp is reduced (as also evidenced by the textural properties and morphology given in Table 2 and Fig. 4, respectively). According to Wigmans [20], 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.

The adsorption capacity of Cp is higher than Sp even though it has low surface area, which may be because of the abundant formation of oxygen-containing functional groups and adequate pore size distribution (as also evidenced by Fig. 2 and Table 2). The SEM image of Cp also confirms the presence of heterogeneous pores on the surface. These differences in the adsorption capacities of the adsorbents studied will be due to their different origin, chemical surface properties and molecular pore size. According to the results obtained, Pp could be employed as an effective low-cost adsorbent and could be considered as an alternative to commercial activated carbon for the removal of colour.

3.6. Kinetic studies

The transient behaviour of the dye adsorption process was analysed by using pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich kinetic models.

The linear form of the pseudo-first-order equation is given by

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

The linear form of the pseudo-second-order model [21] is given by

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{1}{q_e t} \right) \quad (7)$$

The linear form of the Elovich equation [22,23] is given by

$$q_t = \left(\frac{1}{\beta} \right) \ln(\alpha\beta) + \left(\frac{1}{\beta} \right) \ln t \quad (8)$$

The rate constant for intra-particle diffusion (k_{id}) is given by Weber and Morris [24]

$$q_t = k_{ip} t^{1/2} + C \quad (9)$$

where q_t are the amounts of dye adsorbed on adsorbent at various time t (mg/g); k_1 is the equilibrium rate constant of pseudo-first-order kinetics (min^{-1}) and t is the contact time (min); k_2 is the

equilibrium rate constant of the pseudo-second-order kinetics ($\text{g}/(\text{mg min})$); α is the initial sorption rate ($\text{mg}/(\text{g min})$); β is the extent of surface coverage (g/mg); k_{ip} is the intra-particle diffusion rate constant ($\text{mg}/(\text{g min}^{1/2})$) and C (mg/g) is a constant that gives idea about the thickness of the boundary layer.

The rate constants, predicted equilibrium uptakes and the corresponding correlation coefficients for the three adsorbents are summarized in Table 4. The pseudo-first-order kinetics fits well for the first 30 min and thereafter the data deviated greatly from linearity. Thus, the model represents the initial stages where rapid adsorption occurs, but it cannot be applied for the entire adsorption process [25]. So, the pseudo-first-order model was inapplicable to this system. The correlation coefficients and the $q_{e,cal}$ values from the pseudo-second-order kinetic model are in good agreement with the experimental results. The Elovich equation assumes that the active sites of the adsorbent are heterogeneous and therefore exhibit different activation energies for chemisorption. When increasing the concentration of AR 114, it was observed that the constant α (related to the rate of chemisorption) increased and the constant β (related to the surface coverage) decreased (Table 4), which is due to the decrease in the available adsorption surface for the adsorbates. Therefore, by increasing the concentration, within the range studied, the rate of chemisorption can be increased.

A plot of q_t versus $t^{1/2}$ should be linear (figure not shown); if it passes through origin, intra-particle diffusion is the only rate-controlling step [26]. In the present study, all the adsorbents show the same general features of an initial curved portion followed by a linear portion and a plateau. The initial curved portion is attributed to bulk diffusion, the linear portion to intra-particle diffusion and the plateau to equilibrium. However, neither plot passed through the origin. When the plots do not pass through the origin, it indicates some degree of boundary layer control [27] and this further show that intra-particle diffusion is not the only rate limiting step but other kinetic models may also control the rate of adsorption, all of which may be operating simultaneously [28]. Values of k_{ip} and C are obtained from the slopes of the linear portion of the plots and are shown in Table 4.

Fig. 8 shows the fitting results using various kinetic models for the three adsorbents used for removing AR 114 with an initial concentration of 80 mg/L. From the pseudo-second-order model provides the best correlation for all the adsorption processes; the Elovich model also provides comparable fit to the experimental data (evident from the correlation coefficient values). The intra-particle diffusion model gives a linear fit over the first 50 min of the adsorption process. This suggests that the adsorption systems studied belong to the pseudo-second-order kinetic model, based on the assumption that the rate limiting step may be chemisorption involving electrostatic forces through sharing or exchange of electrons between the adsorbent and the adsorbate.

3.7. Evaluation of ACSS as adsorbent

Table 5 shows the comparison of the maximum monolayer adsorption capacities of various adsorbents for dyes. The values of q_{MAX} in this study (Cp = 153 and Pp = 204 mg/g) is larger

Table 4
Calculated and experimental q_e values and the pseudo-first-order, pseudo-second-order, intra-particle and Elovich rate constants

Adsorbent	C_0	$q_{e,exp}$ (mg/g)	Pseudo-first-order		Pseudo-second-order		Intra-particle diffusion			Elovich				
			q_1 (mg/g)	K_1 (min^{-1})	R_1^2	q_2 (mg/g)	$K_2 \times 10^{-3}$ (g/(mg min))	R_2^2	K_{id} ($\text{mg}/(\text{g min}^{1/2})$)	C (mg/g)	R_{id}^2	α (mg/(g min))	β (g/mg)	R_E^2
Sp	60	27.782	22.4957	0.0143	0.992	31.25	0.8759	0.9916	1.6717	4.1541	0.9701	2.2158	0.1637	0.9811
	80	43.977	26.7547	0.0127	0.9856	45.87	1.0473	0.9939	2.0266	14.711	0.9601	9.5806	0.1336	0.9924
	100	49.519	29.4917	0.0122	0.9586	51.28	0.9569	0.9908	2.0086	21.192	0.9826	12.4532	0.1235	0.9738
Cp	60	30.445	24.6774	0.0159	0.9774	33.55	1.0158	0.9947	1.7283	6.4623	0.9547	3.1818	0.1574	0.9781
	80	39.792	27.3779	0.0151	0.9712	42.19	1.1022	0.9934	1.8522	13.443	0.9763	9.3316	0.1491	0.9791
	100	47.616	32.0037	0.0159	0.9661	50.76	0.9072	0.9914	2.1581	16.795	0.9862	13.1684	0.1297	0.9838
Pp	60	43.229	32.0922	0.0154	0.9903	48.07	0.7117	0.9941	2.4558	9.3994	0.9582	4.6130	0.1106	0.9851
	80	49.684	29.4646	0.0143	0.993	52.63	0.9746	0.9962	2.3179	17.521	0.9546	11.8844	0.1168	0.9868
	100	54.846	30.2972	0.012	0.9779	57.14	1.0745	0.9971	2.2222	29.509	0.9672	18.2055	0.1127	0.9842

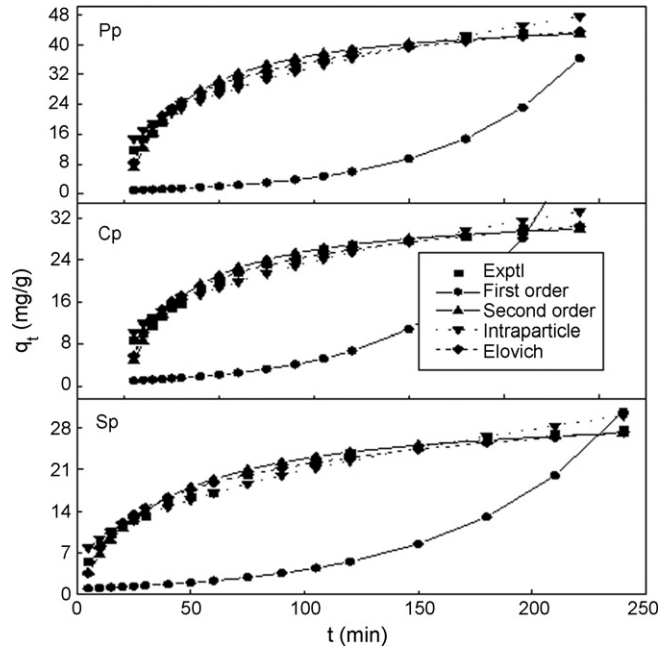


Fig. 8. Comparison between the measured and modelled time profiles for the removal of AR 114 by various adsorbents ($C_0 = 80 \text{ mg/L}$, $m = 1 \text{ g/L}$).

than those in most of the previous studies. The results showed that activated seed shells is effective for AR 114 dye and can be used as substitute for the commercial activated carbon.

3.8. Thermodynamic studies

The thermodynamic parameters reflect the feasibility and spontaneous nature of the adsorption process. Thermodynamic parameters of free energy change, enthalpy change and entropy change were determined from the following equations

$$K_d = \frac{C_a}{C_e} \tag{10}$$

$$\Delta G^\circ = -RT \ln K_d \tag{11}$$

$$\log K_d = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \tag{12}$$

where R is the gas constant, K_d is the distribution coefficient for the adsorption, C_a is the amount of dye adsorbed on the adsorbent of the solution at equilibrium (mg/L) and T is the solution temperature (K). Thus, a plot of $\log K$ versus $1/T$ should be a straight line (as shown in Fig. 9). The observed thermodynamic values are given in Table 6. The negative values of ΔG° indicate the feasibility and spontaneity of the adsorption process. The

Table 5
Comparison of adsorption capacities of various adsorbents for acid dyes

Adsorbent	ΔG° (kJ/mol)			ΔH° (kJ/mol)	ΔS° (kJ/mol)
	298 K	308 K	318 K		
Sp	-0.0400	-0.0414	-0.0427	86.6035	0.2767
Cp	-0.2586	-0.2673	-0.2760	67.1969	0.2119
Pp	-0.7372	-0.8197	-0.8463	103.9498	0.2210

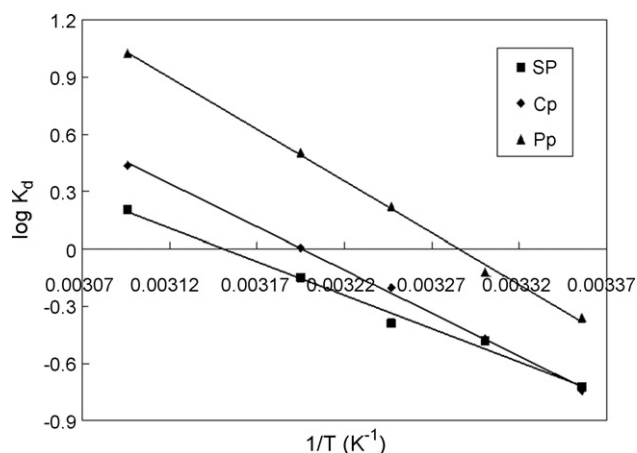


Fig. 9. The plot of $\log K_d$ vs. $1/T$ for various adsorbents ($t = 8$ h, $C_0 = 100$ mg/L, $m = 1$ g/L).

Table 6
Thermodynamic parameters calculated for the removal of AR 114 by various adsorbents ($C_0 = 100$ mg/L, $m = 1$ g/L)

Dyes	Adsorbents	q_{MAX} (mg/g)	Reference
Acid Red 114	Activated pongam seed shells	204	Present study
	Activated cotton seed shells	153	Present study
Acid Green 25	Activated palm ash	123.4	[29]
Acid Red 14	Soy meal hull	109.89	[15]
Acid Yellow 36	Activated rice husk carbon	86.9	[30]
Acid Blue 25	Hazelnut shells	60.2	[31]
Acid Yellow 23	Commercial activated carbon	56.5	[32]

high positive values of ΔH° confirm the endothermic nature of the overall adsorption process. The enhancement of adsorption at higher temperature may be due to the increase in the diffusion rate of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution [28]. The positive value of ΔS° suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbent. Similar results were observed for adsorption of Acid Green 25 on activated palm ash [29].

4. Conclusion

The results of this study show that the activated carbon prepared from the seed shells have suitable adsorption capacity with regard to the removal of AR 114 from its aqueous solution. Activated carbon prepared from pongam seed shells (204 mg/g) has better adsorption capacity than the activated carbons prepared from cotton (153 mg/g) and gingelly seed shells (108 mg/g). An initial pH of 3 was found to be optimum for maximum AR 114 removal by all the three adsorbents studied. All the three adsorbents are easily available materials and can be inexpensive

alternatives for more costly adsorbents for acid dye removal in wastewater treatment. Adsorption followed both Langmuir and Freundlich isotherms. Adsorption kinetics was found to follow pseudo-second-order rate expression. The negative values of ΔG° indicate spontaneous adsorption of AR 114 on ACSS. The study confirms that ACSS can be used as an alternative for more costly adsorbents used for dye removal in wastewater treatment processes.

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