



Non-Commercial Agro Waste Product for the Removal of Acid Red-114 using *Ipomea carnea* Stem Waste

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ABSTRACT

Ipomea Carnea stem waste treated using phosphoric acid (ICAC) has been identified as low cost agro waste adsorbent for the removal of Acid Red-114 (AR-114) from the aqueous solution. The optimum condition adopted for dye removal was found to be pH 6, adsorbent dosage = 100 mg/L of solution and equilibrium time=240mins. Nearly 87% of the dye has been removed at a concentration of 20 mg/L. Pseudo Second order kinetic model has been obeyed. The adsorption isotherm data fitted well to Langmuir equation and the Q_0 Value obtained to be 80.86 mg/L. The results achieved clearly indicate that the chosen adsorbent is found to be a promising material for the adsorption of AR-114.

Keywords: *Ipomea Carnea* stem waste; Pseudo Second order kinetic; Langmuir equation

1. INTRODUCTION

Water is one of the most common substances on the Earth. Water covers over 70% of the surface of the Earth crust. Water has been studied since antiquity. It is the most familiar and abundant liquid on earth. Water is essential not only for survival but also contributes immeasurably to the quality of our lives. It is a raw material in the manufacture of chemicals, drugs, beverages, and hundreds of other products. It is an essential part of the manufacturing processes that produce everything from airplanes to zippers. In other words, we depend on water for most of our technology, comforts and conveniences, and of course for personal hygiene and to flush away our waste products.

Water is polluted due to the industrial developments in recent years which have left their devastating effect on the environmental. Dyes has been used in many of the textile industry which imparts effluent to the local water bodies and causes a very impact to the aquatic ecosystem. In case of aquatic plants which reduces the penetration of sunlight transmitting through water and reduces the photosynthesis process in water (Kadirvelu *et al.* 2003; Dinçer *et al.* 2007). It causes problems like mutagenic, carcinogenic and may cause severe damage to human beings, such as dysfunction of the kidneys, reproductive system, liver, brain and central nervous system (Shen *et al.* 2009). There are various technologies and methods which have adopted for the removal of dyes from effluent waste

water. One of the most promising technology is the adsorption process which has been used valiantly for the dye adsorption.

2. MATERIALS & METHODS

Ipomea Carnia stem has been collected from local source in Erode and treated with phosphoric acid. The precursor material to be carbonized was soaked with phosphoric acid in the ratio of 1:1 at 80 °C for 48 hrs. After 48 hrs, the material was crushed well using mortar and the crushed material was kept aside for 12 hrs. Further, the material was washed well with hot water until a neutral pH obtained and dried at 110 °C for 24 hrs. The dried mass, subjected to carbonization process at 800 °C for about 10 min was again thermally activated at 400 °C for about 10 min in the presence of nitrogen atmosphere. The final product was ground well and used for subsequent analytical assessment. The phosphoric acid hydrolysed powders sieved to various mesh size of 75-180, 180-250 and 250-355 microns was used for sorption studies. The adsorbent was prepared once in stock, stored and used throughout the experiment.

3. PREPARATION OF ACID RED 114 DYES SOLUTIONS

Acid Red 114 and other chemicals used were of analytical grade. The materials after purification were prepared using recommended methods (Vogel, 1961). Distilled water was employed for preparing all the

solutions and reagents. The stock solution was prepared by dissolving 1 gm of the dye in 1000 mL of double distilled water. The desired concentration of the dye can be prepared by diluting them to various concentrations. The characteristics of the dye are shown in table 1.

4. EXPERIMENTAL METHODS

4.1 Kinetics

The batch experiment was performed to obtain the rate and equilibrium data. Batch studies were performed for the dye concentration of 20, 40 and 60 mg/L at a particle size of 180-250 microns and at a temperature of 303K, the equilibrium time for ICAC was

200 min and the desired pH was 6 and pH_{ZPC} was 5.8. The dye concentration of the supernatant solution was analyzed using a spectrophotometer by monitoring the absorbance changes at wavelength of maximum absorbance (520 nm) in this adsorption experiments. The amount of dye adsorbed per gram of CPAC at equilibrium q_e (mg/g) and percentage dye removal were calculated with the following equation,

$$q_e = (C_o - C_e) / W * 100 \quad (1)$$

The percentage of dye removal (%R) in solution was calculated using equation 2.

$$\% \text{ of dye removal} = (C_o - C_e) * 100 \quad (2)$$

Table 1. Acid red 114 dye details

Class	Commercial Name	IUPAC Name	Empirical Formula	Molecular weight	Colour index number	Structure / Class	λ_{max} (nm)
Acidic	AcidRed -114	Disodium(8E)-8-[[[2-methyl-4-[3-methyl-4-[[4(methylphenyl)sulfonyloxyphenyl]diazanyl]phenyl]phenyl]hydrazinylidene]-7-oxonaphthalene-1,3-disulfonate	$C_{37}H_{28}N_4Na_2O_{10}S_3$	830.82	23635	Anionic Dye	520

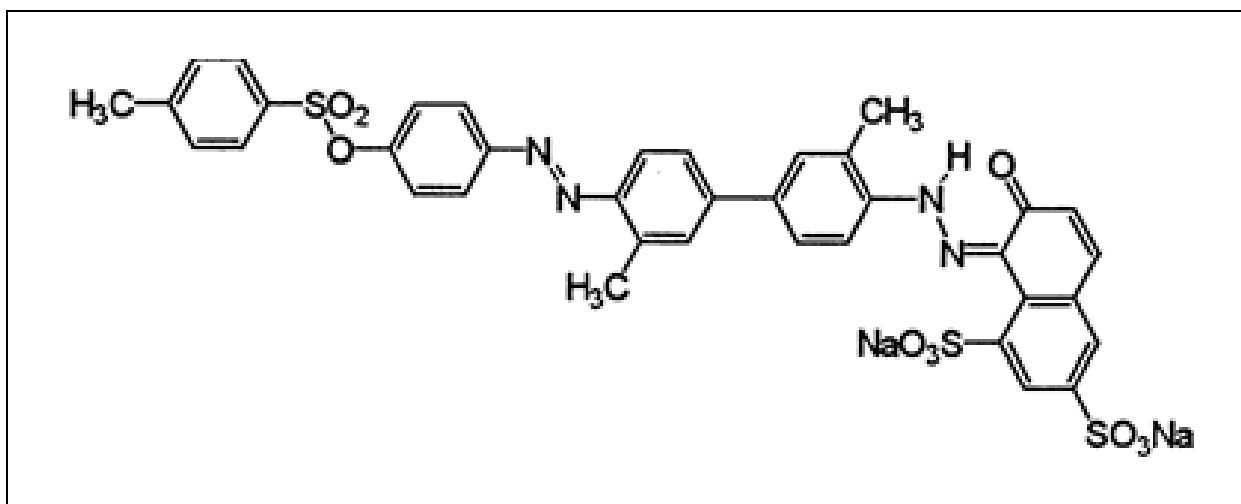


Fig. 1: AR-114

4.1.1 The Pseudo First-order Equation

The pseudo first - order equation (3) is generally expressed as follows.

$$dq_t / dt = k_1(q_e - q_t) \quad (3)$$

After integration and applying boundary conditions $t=0$ to $t = t$ and $q_t=0$ to $q_t = q_t$, the integration form of equation (4) becomes,

$$\text{Log} (q_e - q_t) = \text{log} q_e - k_1 / 2.303 * t \quad (4)$$

The value of $\log (q_e - q_t)$ were plotted against t . The plot of $\log (q_e - q_t)$ vs t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot respectively. The pseudo – first order kinetic constants are shown in Table 3.

4.1.2 The Pseudo Second-order Equation

The pseudo second – order adsorption kinetic rate equation is expressed as (5)

$$dq_t/q_e = K_2(q_e - q_t)^2 \quad (5)$$

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation (5) becomes,

$$1/(q_e - q_t)^2 = 1/q_e + K_2 t \quad (6)$$

which is the integrated rate law for pseudo second – order reaction. Equation 6 can be rearranged to obtain eq. 7, which has a linear form.

$$t/q_t = 1/K_2 q_e^2 + 1/q_e(t) \quad (7)$$

Equations (6) and (7) become,

$$(t/q_t) = 1/h + 1/q_e \quad (8)$$

The plot of (t/q_t) and t of equation (8) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively

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

4.2 Isotherm

4.2.1 Adsorption Isotherm

The Langmuir isotherm equations (Langmuir, 1918) have been used for the determination of adsorption isotherm to optimize the design of an adsorption system to remove basic dyes and also it is important to establish appropriate correlation from the equilibrium curves. The Langmuir adsorption, which is valid for monolayer adsorption, depends on the assumption that the intermolecular forces decrease rapidly with distance, and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The Langmuir equation is given in the following eq 10.

$$C_e/q_e = 1/Q_0 b + 1/Q_0 C_e \quad (10)$$

The constants can be evaluated from the intercepts and the slopes of the linear plots of C_e/q_e versus C_e (as shown in fig. 5). The adsorption data for ICAC states that it shows a monolayer of adsorption. From Table 3 the R^2 value (≥ 0.99) indicates that the adsorption

data of the dye onto the adsorbent at all the three temperatures studied a good fit for the Langmuir isotherm model. The maximum monolayer adsorption capacity of adsorbent onto the adsorbate decreased with increase in solution temperature from 303K to 333K, respectively. The Q_0 values shows that the adsorption capacity of ICAC adsorbent was highly

4.2.2 Freundlich Isotherm

At Equilibrium conditions, the adsorbed amount, q_e can also be predicted by using the Freundlich eq. (11).

$$q_e = K_f + C_e^{1/n} \quad (11)$$

A logarithmic form of the above equation is

$$\text{Log} q_e = \text{log} K_f + 1/n \text{log} C_e \quad (12)$$

The values of n and K_f were determined from the plot $\log C_e$ vs $\log q_e$, where, K_f is Freundlich constant related to the sorption capacity and $1/n$ is Freundlich constant related to the energy heterogeneity of the system and the size of the adsorbed, molecule ranges between 0 and 1, becoming more heterogeneous as its value gets closer to zero. The Freundlich equation (Freundlich, 1926) predicts that the dye concentration on the adsorbent will increase so long as there is an increase in the dye concentration in the liquid. The experimental evidence indicates that an isotherm is reached at a limiting value of the solid phase concentration. The equation itself does not have any real physical significance.

5. RESULTS & DISCUSSION

5.1 Effect of pH

The pH of the dye solution plays an important role in the whole adsorption process. As shown in fig. 2 consistent decrease in adsorption capacity of the ICAC was observed as the pH increased from 2 - 6, and a marginal decrease in uptake of dye was noticed at pH level beyond 6. As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which favours the adsorption of negative charged dye anions due to electrostatic attraction. In addition, adsorption of Acid Red-114 at acidic medium is higher due to the presence of excess H^+ ions competing with dye cations for the available adsorption sites.

5.2 Effect of Contact Time and Initial Concentration

The contact time between the adsorbent and adsorbate, play a vital role in the dye adsorption. The equilibrium isotherm of the dye depends on temperature

and pH of the adsorbent. The contact time is one of the major factors for the development of surface charge at the solid surface - interface. At lower concentration, the adsorption was more effective and as concentration increased, the adsorption decreased. At 20 ppm, the percentage of dye removed was found to be 87% and at 60 ppm, it was found to be 80%. Fig. 3 clearly shows that as concentration increases the adsorption starts decreasing. The adsorption of dye amount increased with an increase in initial dye concentration. The reason was that, at a higher initial concentration, the driving force between the aqueous and solid phase enhanced and also the number of collisions between dye ions and adsorbent increased. The reasons for decrease in adsorption at high concentration are due to low fractional adsorption. At low concentration, there was more number of sorption sites hence the adsorption increased. As the dye ratio increases, sorption sites becomes saturated, resulting in decrease in the sorption efficiency and a rapid uptake of dye at lower concentration are due to surface mass transfer. After a lapse of time, the remaining surface sites are difficult to be occupied because of repulsion between the solute molecules of the solid and bulk phase. The equilibrium time required for Acid Red -114 was 220 min.

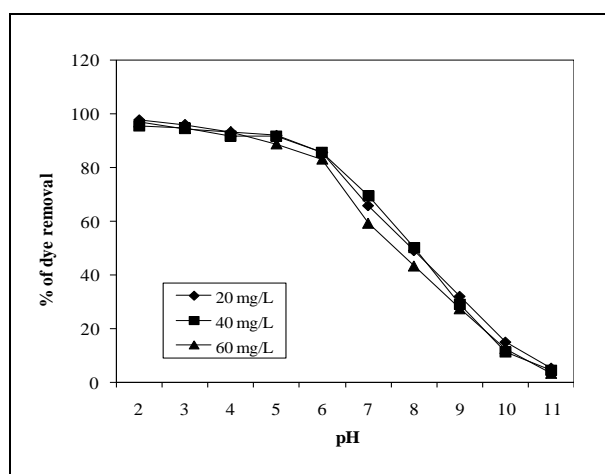


Fig. 2: Effect of pH on AR-114 adsorption by ICAC

5.3 Sorption Kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid-solution interface including the diffusion process. The models are explained as follows:

5.3.1 Pseudo First Order

The data obtained were analyzed with the Lagergren pseudo-first order kinetic model. The plot of $\log(q_e - q_t)$ versus t is shown in fig. 4. The values of k_1 and q_e were determined from the slope and intercept respectively as presented in table 3. The result indicated

that the data were not strongly correlated with R^2 ranging from 0.9929, 0.9954 and 0.9982 for the dose and or the concentration of 20 ppm. Also the theoretical values obtained from the equation did not yield reasonable values. Thus the rate of removal of Acid Red 114 from solution into the ICAC does not follow the pseudo-first-order equation. Indeed this is the general trend in most adsorption studies reported in the literature Oladoja ET I 2008.

Table 2. Effect of Agitation Time and Initial Dye Concentration on Acid Red 114 Adsorption onto ICAC

Volume of dye = 50 ml
Carbon dosage = 50 mg

pH = 6
Temp = 330K

S. No.	Time (min)	Dye concentration (mg/L)		
		20	40	60
1	5	28.01	21.43	11.11
2	10	37.40	28.57	20.40
3	20	48.40	36.80	28.90
4	40	56.10	46.20	41.41
5	60	63.30	53.20	49.14
6	80	67.80	60.20	55.10
7	100	73.35	64.30	57.91
8	120	76.66	68.00	61.62
9	140	80.05	72.00	63.89
10	160	83.90	75.00	68.00
11	180	86.90	79.40	71.30
12	240	86.90	82.63	74.99
13	220	86.90	84.00	76.78
14	240	86.90	84.00	80.00
15	260	86.90	84.00	80.00
16	280	86.90	84.00	80.00

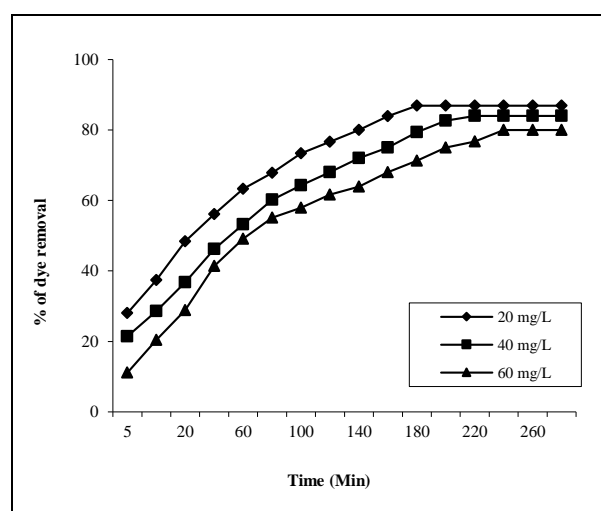


Fig. 3: Effect of initial dye concentration on AR 114 adsorption by ICAC

5.3.2 Pseudo Second Order

The results obtained when the data was subjected to the Pseudo-second-order equation are shown

in fig. 5 and the values are tabulated in table 4 which corresponds to the dosage and concentration respectively.

Table 3. Effect of Pseudo first order kinetics for AR 114 by CPAC and ICAC at varying initial dye conc.

Volume of dye = 50 ml pH = 6
 Temp. = 303 K
 Carbon dosage = 50 mg Particle size = 180 to 250 microns

Time (min)	ICAC		
	log (q _e -q _t)		
	C ₀ (mg/L)		
	20	40	60
5	0.77	1.11	1.32
10	0.69	1.06	1.25
20	0.59	0.99	1.19
40	0.49	0.90	1.06
60	0.37	0.81	0.97
80	0.28	0.71	0.87
100	0.13	0.63	0.82
120	0.01	0.55	0.74
140	-0.16	0.44	0.68
160	-0.52	0.33	0.56
180	-	0.10	0.42
200	-	-0.21	0.18
220	-	-	-0.02
240	-	-	-
slope	-0.0072	-0.0058	-0.0054
Intercept	0.795	1.156	1.3289
q _e (exp)	6.24	14.32	21.33
q _e (cal)	8.69	16.8	24
K _L	0.01662	0.01334	0.01248
R ²	0.9672	0.9554	0.9674

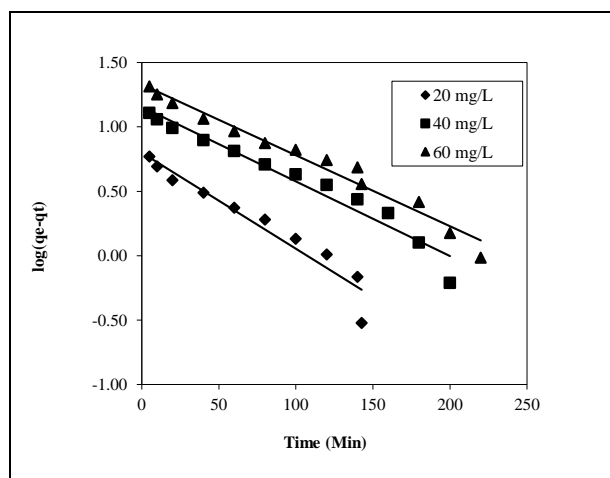


Fig. 4: Effect of initial dye concentration on Pseudo first order plot for AR 114 adsorption by ICAC

Table 4. Effect of Pseudo Second order kinetics for AR 114 by CPAC and ICAC at varying initial dye conc.

Volume of dye = 50 ml pH = 6
 Temp. = 303 K
 Carbon dosage = 50 mg Particle size = 180 to 250 microns

Time (min)	ICAC		
	t/q _t		
	C ₀ (mg/L)		
	20	40	60
5	1.3	1.2	1.5
10	2.4	1.8	1.6
20	4.1	2.7	2.3
40	7.1	4.3	3.2
60	9.5	5.6	4.1
80	11.8	6.6	4.8
100	13.6	7.8	5.8
120	15.7	8.8	6.5
140	17.5	9.7	7.3
160	19.1	10.7	7.8
180	20.7	11.3	8.4
200	23.0	12.1	8.9
220	25.3	13.1	9.6
240	27.6	14.3	10.0
260	29.9	15.5	10.8
280	32.2	16.7	11.7
Slope	0.1067	0.0529	0.0360
Intercept	2.2017	1.9001	1.7679
q _e (mg g ⁻¹)	9.3721	18.9186	27.8160
K ₂ × 10 ³	5.1710	1.4705	0.7311

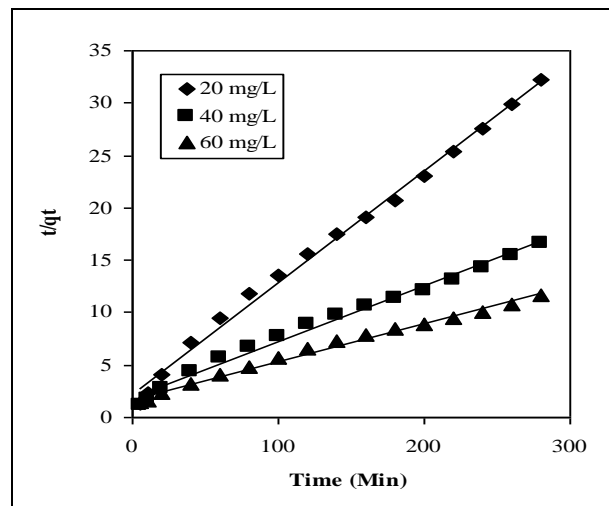


Fig. 5: Effect of initial dye concentration on pseudo second order plot for AR 114 adsorption by ICAC

The data applied shows very high correlation coefficients value. The calculated values of q_e are also close to the experimental data. This confirms that the adsorption process follows the pseudo-second-order model.

5.4 Adsorption Isotherm

The commonly used isotherms for non-linear equilibrium between amounts of acid dye on adsorbed the acid treated ICAC (q_e) and equilibrium concentration of solution (C_e) at a temperature of (303K) is investigated. Langmuir equation was found valid for monolayer sorption onto a homogeneous surface with a finite number of identical sites.

5.4.1 Langmuir Model

The adsorption isotherm for ICAC waste have been investigated. 100mg of the adsorbent was taken with 50 ml of the aqueous solution of the dye at various concentration (10-150 ppm) at a fixed pH of 6. The bottles were placed in orbital shaker at 200 rpm until equilibrium was obtained. The experiment was carried out at different temperature viz.303, 318 and 333K and the values are tabulated in table 5.

Table 5. Calculated Langmuir equilibrium isotherm of acid red 114 dye on ICAC

Temp K	Q_0 mg/g	K_L L/mg	R^2
303	80.86	7.67	0.995
318	85.22	11.51	0.998
333	95.24	13.90	0.995

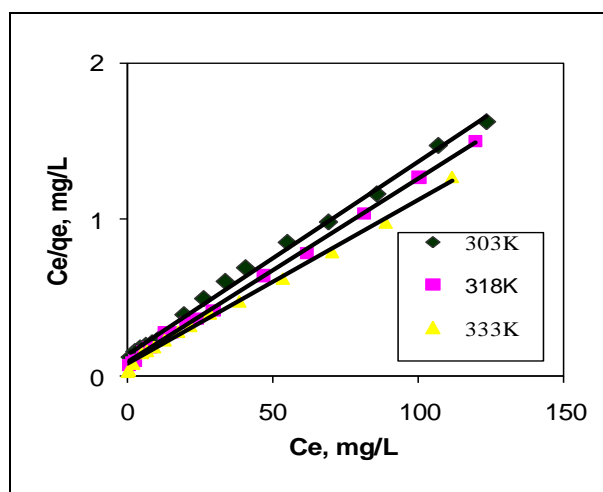


Fig. 6: Effect of Temperature variation on Langmuir plot for AR 114 adsorption by ICAC

5.4.2 Freundlich Model

Freundlich isotherm fits well into the observed data. The calculated Freundlich isotherm constants at 303, 318 and 333K shows that the value of Freundlich exponent are lying in the range of 1 - 10, indicate favourable adsorption process. But the regression coefficient values are found to be low which indicate that the adsorption process is lower and they follow only the monolayer of adsorption not the multilayer.

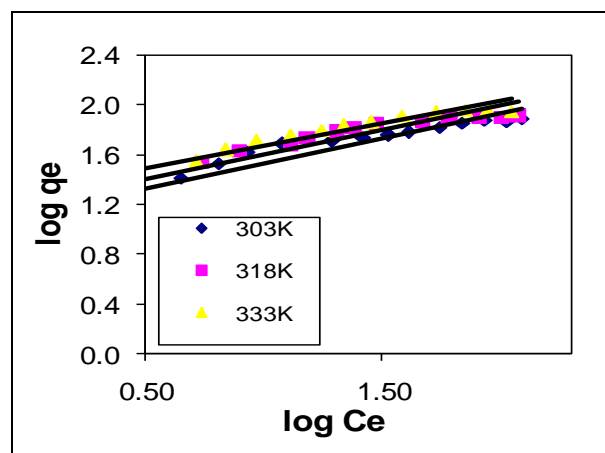


Fig. 7: Effect of Temperature variation on Freundlich plot for AR 114 adsorption by ICAC

6. CONCLUSION

- Ipomea Carnia stem waste (ICAC) is a promising adsorbent for the removal of the Acid red 114 from the water. About 100 mg of the CPAC removes 86% of the dye with the dye concentration of 20 ppm.
- The optimum pH adopted for the dye removal was 6 and their ZPC was 5.8. The dye reached the equilibrium time within 200 min.
- The experimental data observed perfect fit for Langmuir isotherm showing that the surfaces of the adsorbents were homogeneous, specific and uniform in nature for both the adsorbents.
- The values also had a good agreement with Freundlich isotherm model.
- The adsorption followed Pseudo second order kinetics for CPAC with the interaction over the first hour.

The above results clearly show that the adsorbent followed Pseudo second order model, Langmuir isotherm and are endothermic in nature.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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