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Adsorptive studies of hazardous dye Tropaeoline 000 from an aqueous phase on to coconut-husk

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Abstract

This contribution presents result pertaining to the adsorptive removal of water-soluble hazardous dye Tropaeoline 000, on to a low cost adsorbent—coconut-husk and its efficiency in the dye colour sorption was compared with activated carbon (AC). The results obtained from the batch experiments revealed the ability of the coconut-husk to remove the Tropaeoline 000 dye. The adsorption of dye was carried out at different pH, temperatures, amount of adsorbent, contact time, concentration of adsorbate (initial dye concentration) and particle size. The adsorption studies revealed that the ongoing adsorption validates both Langmuir and Freundlich adsorption isotherm at temperatures 30, 40 and 50 °C. The adsorption isotherm data was also employed to calculate thermodynamic parameters like $\Delta G°$, $\Delta H°$ and $\Delta S°$. The negative values of $\Delta G°$ indicate that the dye adsorption process is a spontaneous in nature. The positive value of $\Delta H°$ shows the endothermic nature of AC/coconut-husk system whereas negative value of $\Delta H°$ indicates that the exothermic nature of AC/coconut-husk. The adsorption was found to undergo via a pseudo-second order adsorption kinetics and the results revealed that coconut-husk, an agricultural waste, proved to be an excellent low cost adsorbent.
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1. Introduction

Wastewaters from dyeing and finishing operations in the textile industry are generally high in both colour and organic content. Effluents discharged from dyeing industries are highly coloured and they can be toxic to aquatic life in receiving waters [1,2]. Colour removal from textile effluents has been given much attention in the last few years, not only because of its potential toxicity, but mainly due to its visibility problems [3,4]. The total dye consumption of the textile industry worldwide is in excess of 10^7 kg/year, and an estimated 90% of this ends up on fabrics. Consequently, 1000 tonnes/year or more of dyes are discharged into waste streams by the textile industry worldwide [5].

Among several chemical and physical methods, the adsorption onto activated carbon has been found to be superior to other techniques in water-re-use methodology because of its capability for adsorbing a broad range of different types of adsorbates efficiently, and simplicity of design. However, commercially available activated carbon is still considered expensive [6]. Thus, many researchers researched for cheaper substitutes, which are relatively inexpensive, and are at the same time endowed with reasonable adsorptive capacity [7–15].

Among the various dyes, Tropaeoline 000 is a well known monoazo dye, which is widely used for colouring wool, cotton and silk as well as to synthetics like polyesters, acrylic and rayon. They are also used in paints, inks, plastics and leather. It is now well established that a prolong intake of Tropaeoline 000 can cause tumors, allergy and also cause eye, skin, respiratory and digestive tract irritation. Since Tropaeoline 000 possesses exceptionally good solubility in water, hence its removal by common chemical treatments or by physical treatments like coagulation, forth floatation, etc., is not easy. It is therefore considered worthwhile to employ adsorption technique, a tested method for the removal of hazardous organic compounds [16].

The object of the present investigations has been to evaluate the efficiency of removal of Tropaeoline 000 using activated coconut-husk and activated carbon. Activated coconut husks (ACHs) are an agricultural waste material, which is easily available, cheap and economically advantageous. In the present study application of activated coconut husks for the removal of dye

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from aqueous solution has been studied and activated carbon was used as a conventional adsorbent to compare the results. The effect of adsorbent dose, pH, particle size, temperature, initial dye concentration and equilibrium time has been studied and obtained results are discussed.

2. Materials and methods

For the present investigation water-soluble Tropaeoline 000 dye, (molecular formula $C_{16}H_{11}N_2NaO_4S$, molecular weight 350.33) (Scheme 1) was obtained from M/S Merck. To prepare various solutions at desired concentrations from the stock solution, double-distilled water was used for necessary dilutions. All reagents used in the present work were of analytical grade.

Adsorbent activated carbon (AC) was also purchased from M/S Merck and used as received. All pH measurements were carried out with a decibel DB 1011 digital pH meter, fitted with a glass electrode and COD digestion apparatus (Spectra Lab-2015 S) was used for determining COD of the solutions. Absorbance measurements were recorded on a Spectronic 20D+ Thermospectronic spectrophotometer over the wavelength range 200–800 nm.

2.1. Material development

Coconut-husk obtained was cleaned, thoroughly washed with distilled water, and then dried in an oven. This dried material was then control of husk with hydrogen peroxide solution for 24 h to oxidize adhering organic impurities and dried at 110 °C for 1 h in vacuum oven. The material was grounded and sieved to desired particle sizes such as <106, 106–125, 125–180, 180–212, 212–250, 250–300, >300 BSS (British standard size) mesh. Finally, granules of ACH thus obtained were stored in separate vacuum desiccators until required.

2.2. Adsorption and kinetic studies

All adsorption measurements carried out through batch technique at 30, 40 and 50 °C temperatures and desired pH. In each measurement, 30 mL of the dye solution of desired concentration and appropriate amounts of adsorbent of particle size 125–180 BSS mesh were taken in a 100 mL graduated airtight conical flask and mechanically agitated intermittently, till the equilibrium was established. However, in case of kinetic measurements the flask was shaked only for the desired time period. The adsorbents were now removed from the solution after carefully filtering by Whatmann filter paper (no. 41) and the concentration of the dye was determined on a spectronic 20D+ Thermospectronic spectrophotometer at λ_{max} 484 nm.
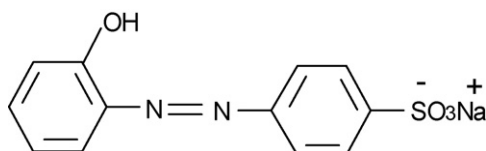
Scheme 1. Structure of Tropaeoline 000 dye.

3. Results and discussion

3.1. Adsorbent characterization

For structural and morphological characteristics IR and TEM of AC and ACH were carried out.

3.1.1. FTIR analysis

The FTIR spectra in the range 4000–400 cm^{-1} of AC and ACH, before and after treatment were recorded on a Simadzu Prestige 21 FTIR Spectrometer as KBr pellets. The FTIR measurement of AC and ACH, before and after adsorption shown in Fig. 1 presence of peak for large number of functional groups, viz, 3334.92 cm^{-1} –OH stretching, 2922.37 cm^{-1} C–H stretching vibration, 1207 cm^{-1} C–N stretching, 1037.70 cm^{-1} C–O stretching in primary alcohols, 1597.06 cm^{-1} –C=C– aromatic stretching frequency, 1620 cm^{-1} –N=N– stretching indicating the considerable dye adsorption capacity of AC and ACH.

3.1.2. TEM analysis

TEM studies for AC and ACH were performed on JOEL JEM 1230 microscope using an accelerating voltage of 115 kV. TEM studies are widely used to study the morphological features and surface characteristics of the adsorbent materials. In the present study, TEM photographs (Fig. 2) of AC and ACH reveals surface texture and porosity.

3.2. Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process [17,18]. To study the influence of pH on the adsorption capacity of AC and ACH for Tropaeoline 000 dye, experiments were carried out using different initial solution pH values, varying from 2.5 to 9.2. The obtained results are presented in Fig. 3, which shows that the adsorption capacity increases significantly with a decrease in the pH and maximum adsorption was observed at pH 2.5 (95% for AC and 82% for ACH). At acidic pH, the positively charged species start dominating and the surface tends to acquire a positive charge, while the adsorbate species are still negatively charged. As the adsorbent surface is positively charged the increasing electrostatic attraction between negatively charged adsorbate species and positively charged adsorbent particles would lead to increased adsorption of Tropaeoline 000 dye. Hence, all the succeeding investigations were performed at pH 2.5 for both the adsorbents.

3.3. Effect of adsorbent dose

To optimize the adsorbent dose for the removal of Tropaeoline 000 from its aqueous solutions, adsorption was carried out at different temperatures (30, 40 and 50 °C). The amounts of the dye adsorbed by adsorption on AC and ACH are presented in Figs. 4 and 5. The dose of adsorbent was varied from 0.06 to 0.23 g/L for AC and from 1.67 to 8.33 g/L for ACH at fixed pH and adsorbate concentration. It was observed from Figs. 4 and 5 that at all temperatures, for AC adsorption increases

with increase in the amount of adsorbent from 0.06 to 0.23 g/L and for ACH adsorption increases with increase in the adsorbent dose from 1.67 to 6.67 g/L. This is due to the fact that the number of available adsorption sites increases by increasing the adsorbent dose and consequently better adsorption takes place [19]. However, it was observed that the efficiency did not increase linearly with the increase in adsorbent dose. After that, even though the adsorbent dosage increases in the adsorption system, because of the unavailability of the adsorbate, the percentage adsorption remains constant [20]. The further increase in the amount of adsorbent from 0.23 to 0.26 g/L for AC and 6.67 to 8.33 g/L for ACH did not affect the uptake capacity significantly.

3.4. Effect of initial dye concentration

The dependence of concentration of the adsorbate dose on the rate of adsorption is used to define the rate-limiting step in the reaction. For adsorptive reaction, the rate varies directly with the concentration of adsorbate. The extent of adsorption depends on the size, shape, mobility and charge of molecules or ion present in solution. The uptake of the dye Tropaeoline 000 was studied over AC and ACH at dye concentrations ranging from 3×10^{-5} to 9×10^{-5} M at fixed dose of adsorbent, temperature and time. It was observed that the extent of adsorption of Tropaeoline 000 on both adsorbents increases linearly with the increase in concentration of the adsorbate. This is due to increase in driving force of the concentration gradient with increasing initial dye concentration [21]. It was also observed that the percent removal of dye decreases from 97 to 55% for AC and 87 to 30% for ACH.

3.5. Effect of particle size

The variation of the rate of adsorption of the substrate with different particle size of adsorbent is another method that
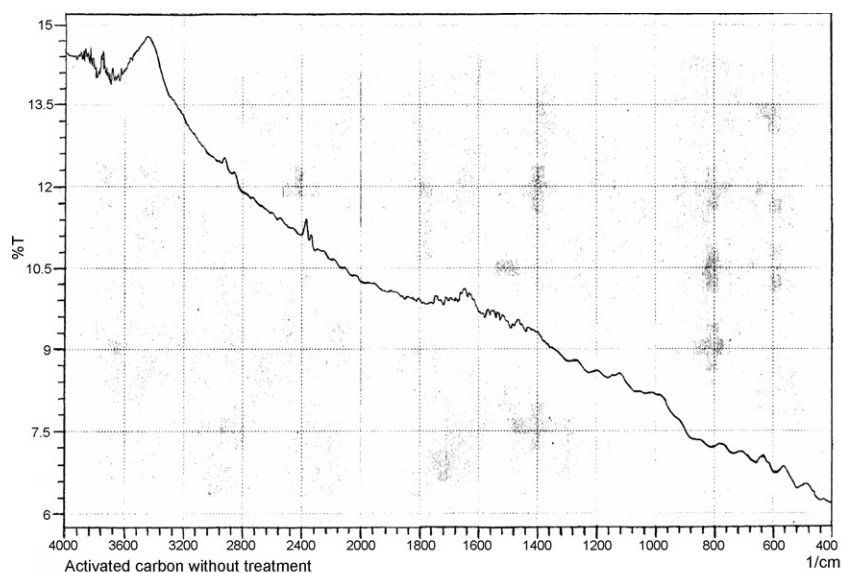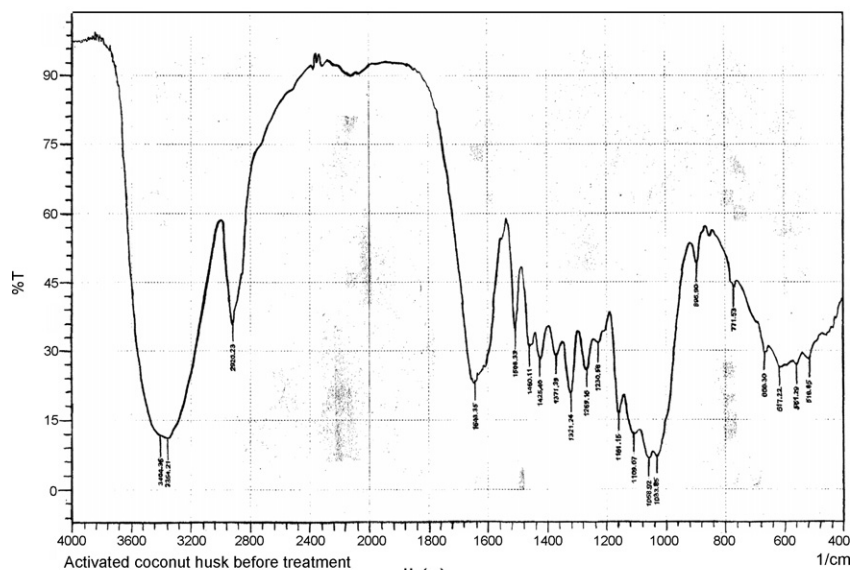
Fig. 1. FTIR spectra of (I-a) AC before adsorption (II-a) ACH before adsorption and (I-b) AC after adsorption (II-b) ACH after adsorption.
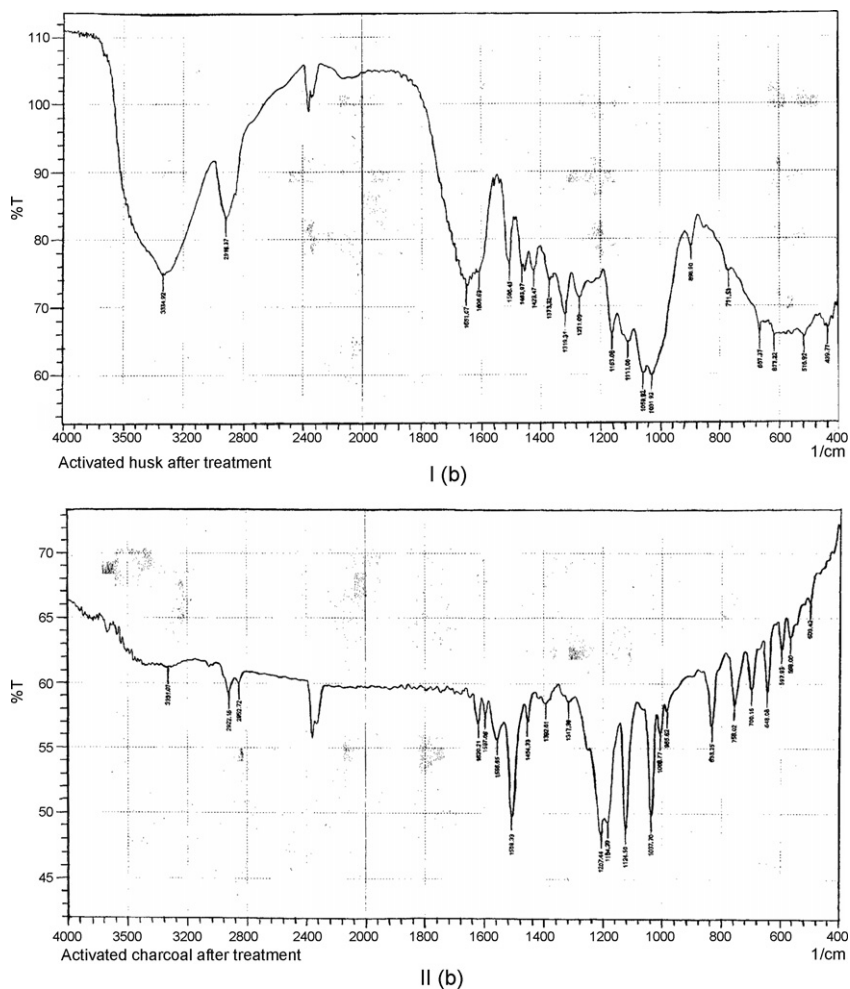
Fig. 1. (*Continued*).

is useful for the characterization of the rate-limiting mechanism of a particular system. The adsorption studies were also carried out at seven different particle sizes at fixed adsorbent dose (0.16 g/L for AC and 3.33 g/L for ACH), contact time (10 min for AC and 60 min for ACH), adsorbate concentration (6×10^{-5} M) and temperature (30 °C). The selected particle sizes were <106, 106–125, 125–180, 180–212, 212–250, 250–300, >300 BSS mesh size. It was observed that as the par-
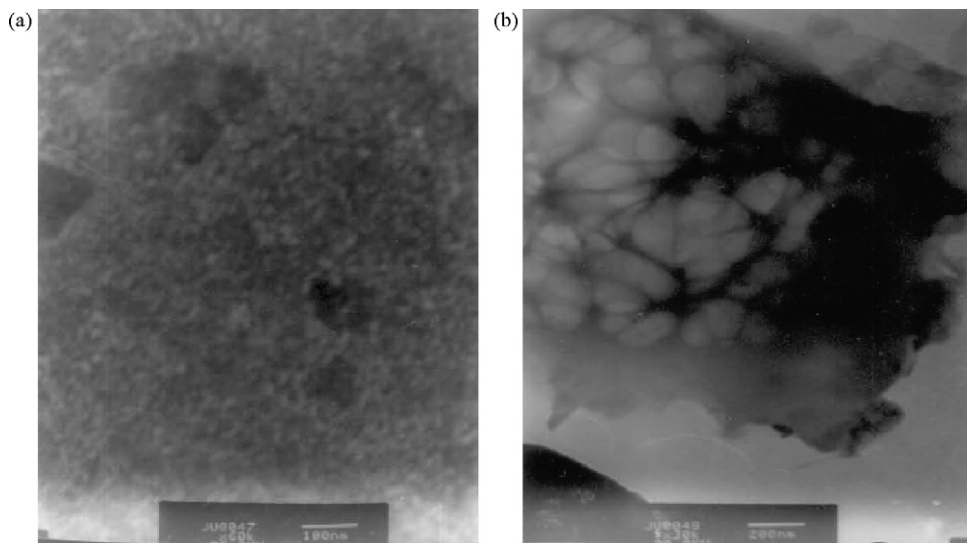
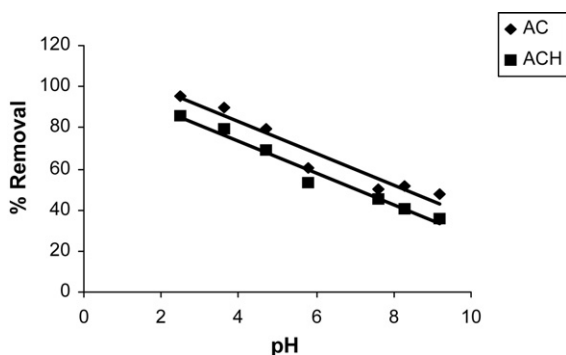

Fig. 2. TEM micrographs of (a) AC and (b) ACH adsorbents.

Fig. 3. Effect of pH on the adsorption of Tropaeoline 000 over AC and ACH. Dye concentration 6×10^{-5} M, temperature 30 °C, amount of AC 0.16 g/L and amount of ACH 3.33 g/L, sieve size 125–180 BSS mesh (for each).

Fig. 4. Effect of adsorbent dose on the uptake of Tropaeoline 000 over AC. Dye concentration 6×10^{-5} M, temperatures 30, 40 and 50 °C, pH 2.5, sieve size 125–180 BSS mesh.

ticle size decreases, the adsorption of the dye increases and hence the removal of the dye increases. This is due to larger surface area that is associated with smaller particles. For larger particles, the diffusion resistance to mass transport is higher and most of the internal surface of the particle may not be utilized for adsorption and consequently, the amount of dye adsorbed is small [22]. Whereas the breaking of large particle tends to open tiny cracks and channels on the particle surface, providing added surface area (for small particles) removes more dye in the initial stages of the adsorption process than the large particles [23]. Maximum adsorption about 94.55% for AC and 90.4% for ACH could be achieved at the particle size <106 BSS mesh.
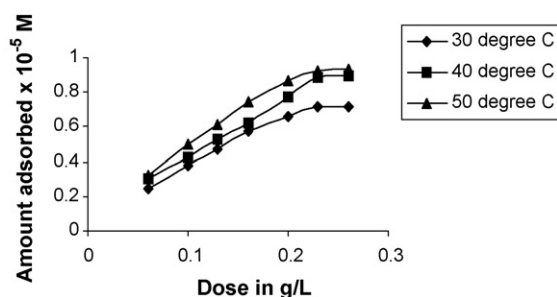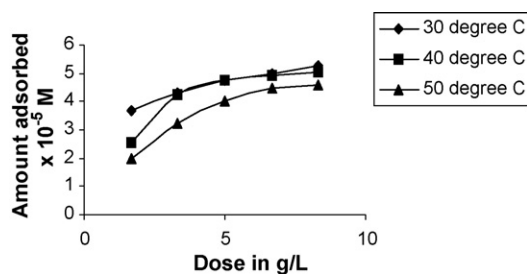

Fig. 5. Effect of adsorbent dose on the uptake of Tropaeoline 000 over ACH. Dye concentration 6×10^{-5} M, temperatures 30, 40 and 50 °C, pH 2.5, sieve size 125–180 BSS mesh (for each).

3.6. Effect of contact time

For both the adsorption processes, adsorption experiments were now carried out for different contact times with a fixed adsorbent dose (0.16 g/L for AC and 3.33 g/L for ACH), at pH (2.5), conc. (6×10^{-5} M) and temperature 30 °C. From the experiment it was found that the adsorption gradually increases with increase in contact time for both the adsorbents. For AC the adsorption increases up to 30 min and after that it remains constant. However, for ACH the adsorption increases up to 120 min and above which it remains constant. This is due to, for a particular experiment, the rate of adsorption decreased with time, it gradually approached a maximum adsorption and owing to continuous decrease in the concentration driving force and it also indicate that the adsorbent is saturated at this level [24].

3.7. Effect of temperature

Adsorption studies were carried out at 30, 40 and 50 °C for AC and ACH. The rate of uptake of dye with AC was found to increase with increase in temperature, thereby indicating the process to be endothermic in nature. For ACH an increase in adsorption with decrease in temperature was observed, signifying the process to be exothermic.

3.8. Adsorption isotherms

The relationship between the amount of dye adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The equilibrium data were analyzed by Langmuir and Freundlich isotherms. These isotherms are useful for estimating the total amount of adsorbent needed to adsorb a required amount of adsorbate from solution.

3.8.1. Langmuir isotherm

The Langmuir adsorption isotherm has been successfully applied to many other real sorption processes [25]. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Theoretically, therefore a saturation value is reached beyond which no further sorption can take place. The saturated monolayer curve can be represented by the linear form of the isotherm as

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \tag{1}$$

In the above equation q_e is the amount adsorbed (mol/g), C_e is the equilibrium concentration of the adsorbate (mol/L), and Q_0 and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. When $1/q_e$ is plotted against $1/C_e$, a straight line with slope $1/bQ_0$ and intercept $1/Q_0$ at temperature 30, 40 and 50 °C is obtained. There by confirming that the adsorption of the dye follows the Langmuir isotherm. Table 1 shows that the value of Q_0 increases with increase in temperature in case of AC and accounts for endothermic nature of the ongoing process. However, in case of ACH the

Table 1
Langmuir constants of Tropaeoline 000 over activated carbon (AC) and activated coconut-husk (ACH)

Temperature (°C)	Activated carbon			Activated coconut-husk		
	b ($\times 10^3$ mol g^{-1})	Q° ($\times 10^5$ L mol^{-1})	R^2	b (mol g^{-1})	Q° ($\times 10^5$ L mol^{-1})	R^2
30	1.427	0.041	0.9736	1.122	0.725	0.9699
40	8.249	0.042	0.9684	12.906	0.061	0.9103
50	3.310	0.053	0.9360	16.077	0.031	0.9462

Table 2
Freundlich constants of Tropaeoline 000 over activated carbon (AC) and activated coconut-husk (ACH)

	Activated carbon			Activated coconut-husk		
	K_f	n	R^2	K_f	n	R^2
30 °C	362.1	4.902	0.9727	1.092	0.9876	0.9818
40 °C	1229.4	14.577	0.9078	51.844	1.4573	0.9169
50 °C	488.3	7.062	0.9693	74.903	1.4482	0.9564

value of Q_0 decreases with increase in temperature indicating that the process is exothermic. The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor for equilibrium parameter, R_L [26], defined as follows:

$$R_L = \frac{1}{1 + bC_0} \tag{2}$$

where C_0 is the initial concentration of dye and b is the Langmuir constant. The values of R_L indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). Values of separation factor for both the adsorbents are found to be less than unity, confirming thereby the favorable adsorption process in both cases.

3.8.2. Freundlich isotherm

The adsorption data for adsorption over AC and ACH were also found to be fitted to the linear form of the Freundlich equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

where K_f and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively and the values of these constants are given in Table 2.

3.9. Thermodynamic parameters

Thermodynamic parameters for the adsorption of Tropaeoline 000 on AC and ACH were calculated using the following

equations and the values are given in Table 3:

$$\Delta G^\circ = -RT \ln b \tag{4}$$

$$\Delta H^\circ = -\frac{R(T_2 T_1)}{T_2 - T_1} \ln \frac{b_2}{b_1} \tag{5}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{6}$$

where ΔG° is the change in Gibb's free energy, ΔH° is the change in enthalpy and ΔS° is the change in entropy, b, b_1 and b_2 are Langmuir constants at 30, 40 and 50 °C, respectively. The negative values of ΔG° (Table 3) indicate that adsorption of Tropaeoline 000 over both the adsorbents was spontaneous. The positive value of ΔH° confirms the endothermic nature of adsorption of dye over AC, while the negative value of ΔH° shows the exothermic nature of adsorption of dye over ACH. The positive value of entropy shows the increased randomness at AC/Tropaeoline 000 interface and good affinity of AC towards dye, while negative value of entropy shows that decreased randomness at ACH/Tropaeoline 000 interface and reflects the affinity of ACH towards dye and also suggests the probability of favorable adsorption. The values of ΔG°, ΔH° and ΔS° are in consistent with the results presented in Table 3.

3.10. Kinetics of adsorption

In order to examine the controlling mechanism of the adsorption process, pseudo-first order and pseudo-second order equations were used to test the experimental data. A simple kinetic analysis of adsorption is the pseudo-first order rate expression of the Lagergren equation [27,28]. The first order kinetics only describes the sorption sites and not the adsorption process as a whole. The rate constants of adsorption, k_{ad}, for the removal of dye Tropaeoline 000 by AC and ACH at temperatures 30, 40 and 50 °C were determined using following first order rate expression:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

Table 3
Thermodynamic parameters of Tropaeoline 000 over activated carbon (AC) and activated coconut-husk (ACH)

	$-\Delta G^\circ$ (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})
	30 °C	40 °C	50 °C	30 °C	30 °C
Activated carbon	18.3×10^3	23.47×10^3	21.76×10^3	8.962×10^3	$.089 \times 10^3$
Activated coconut-husk	0.29×10^3	6.657×10^3	7.459×10^3	-18.46×10^3	-1.018×10^3

Table 4
Rate constants k_{ad} for pseudo-first order of Tropaeoline 000 over activated carbon (AC) and activated coconut-husk (ACH)

Temperature (°C)	k_{ad} ($\times 10^{-2}$ min^{-1}) (AC)	R^2	k_{ad} ($\times 10^{-2}$ min^{-1}) (ACH)	R^2
30	11.39	0.8723	2.27	0.8818
40	9.60	0.9455	3.56	0.8484
50	14.12	0.9372	3.34	0.8485

Table 5
Rate constants k_{ad} for pseudo-second order of Tropaeoline 000 over activated carbon (AC) and activated coconut-husk (ACH)

Temperature (°C)	k_{ad} ($\times 10^{-2}$ g/mg min) (AC)	R^2	k_{ad} ($\times 10^{-2}$ g/mg min) (ACH)	R^2
30	32.63	0.9912	39.68	0.9938
40	38.57	0.9955	40.95	0.9914
50	37.84	0.9980	40.37	0.9912

where k_1 is the rate constant of pseudo-first order adsorption (min^{-1}), and q_e and q_t are the amount of dye adsorbed per gram of adsorbent at equilibrium and time t, respectively.

A straight line of $\ln(q_e - q_t)$ versus t suggests the applicability of this kinetic model to fit the experimental data. The first order rate constant k_1 and equilibrium adsorption density q_e were calculated from the slope and intercept of this line.

The k_1 values and equilibrium adsorption density q_e for AC and ACH at 30, 40 and 50 °C are listed in Table 4. A comparison of results with the correlation coefficient (R^2) is shown in Table 4. The correlation coefficients for the pseudo-first order kinetic model are all <0.95, indicating a poor pseudo-first order fit to the experimental data.

The pseudo-second order kinetic model [29] is based on adsorption equilibrium capacity and can be expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e\, t} \tag{8}$$

where k_2 (g/mg min) is the rate constant for pseudo-second order adsorption. The slope and intercept of (t/q_t) versus t were used to calculate the pseudo-second order rate constant k_2 and q_e. It is likely that the behaviour over the whole range of adsorption is in agreement with the chemisorption mechanism being the rate-controlling step. From Table 5, the adsorption of Tropaeoline 000 on to AC and ACH are considered to be pseudo-second order with high correlation coefficients above 0.99 as shown in Fig. 6(a) and (b). This suggested that the pseudo-second order adsorption mechanism is predominant.

And that the over all rate of the Tropaeoline 000 adsorption process is most likely to be controlled by the chemisorption process for both the adsorbents [30]. Similar phenomena are observed in the adsorption of dyes [31,32].

3.11. Determination of activation energy for the adsorption process

The rate constant k_2 at different temperatures listed in Table 5 was then applied to estimate the activation energy of the adsorption of Tropaeoline 000 dye on to AC and ACH by the Arrhenius
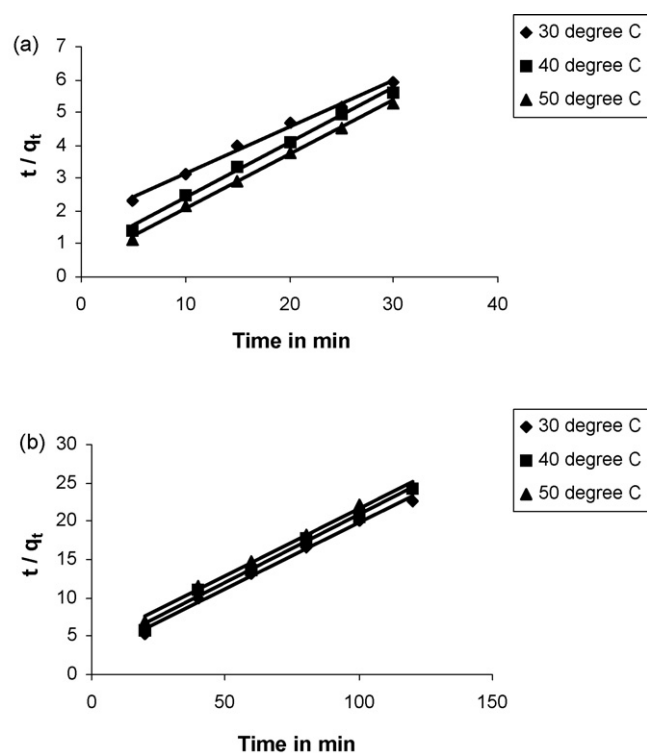

Fig. 6. Pseudo-second order plots for (a) Tropaeoline 000-AC and (b) Tropaeoline 000-ACH adsorption system at different temperatures.

equation [33]:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{11}$$

where E_a, R and A refer to the Arrhenius activation energy, the gas constant and the Arrhenius factor, respectively. The slope of the plot of $\log k$ versus $1/T$ was used to evaluate E_a and the value of E_a was found to be 3575 kJ/mol for AC and 872.97 kJ/mol for ACH, which shows that both the adsorbents have strong binding sites.

4. Chemical oxygen demand

The chemical oxygen demand test is widely used as an effective technique to measure the organic strength of wastewater.

To evaluate the toxicity of the adsorbed solutions, their initial and final COD values were determined. For carrying out the COD experiments, reagents were prepared as per standard methods [34]. Usual 2 h open reflux method was applied for the COD determination. It was found that for the dye solutions adsorbed by AC and ACH, the COD decreases from 1480.0 to 112.8 and 208 mg/L, respectively, indicating the lower toxicity of the solutions left after adsorption.

5. Conclusion

On the basis of the results obtained, it can be safely concluded that both AC and ACH act as potential adsorbents for the removal of Tropaeoline 000 from wastewater. ACHs are a cheap and easily available material that thus can act as a better replacement for AC. Being a waste product, the use of ACH as adsorbent would also solve their disposal problem.

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