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Removal of Reactofix golden yellow 3 RFN from aqueous solution using wheat husk—An agricultural waste

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Abstract

The wheat husk, an agricultural by-product, has been activated and used as an adsorbent for the adsorption of Reactofix golden yellow 3 RFN from aqueous solution. In this work, adsorption of Reactofix golden yellow 3 RFN on wheat husk and charcoal has been studied by using batch studies. The equibrium adsorption level was determined to be a function of the solution pH, adsorbent dosage, dye concentration and contact time. The equilibrium adsorption capacities of wheat husk and charcoal for dye removal were obtained using Freundlich and Langmuir isotherms. Thermodynamic parameters such as the free energies, enthalpies and entropies of adsorption were also evaluated. Adsorption process is considered suitable for removing color, COD from wastewater.

Keywords: Azo dyes; Reactofix golden yellow 3 RFN; Adsorption; Wheat husk

1. Introduction

The presence of the color in water is unpleasant; moreover, some dyes also toxic to human being and other animals. Many industries are releasing color constituents, i.e. dyes in watsewater which is contaminating our water resources. Azo dyes constitute a major class of environmental pollutants accounting for 60–70% of all dyes and pigments used. These compounds are characterized by aromatic moieties linked together with azo groups (–N=N–). The release of azo dyes into the environment is a concern due to coloration of natural waters, toxicity, mutagenicity and carcinogenicity of these dyes and their bio-transformation products [1]. Therefore, considerable attention has been given to evaluating the fate of azo dyes during wastewater treatment and in the natural environment. A range of conventional treatment technologies for dye removal have been investigated extensively [2–8], such as activated sludge, chemical coagulation, carbon adsorption, electrochemical treatment, reverse osmosis, hydrogen peroxide catalysis, etc. However, most of the above methods suffer from one or other limitations and none of them were successful in completely removing the color from wastewater [9].

Azo dyes require an effective treatment technique for their complete removal. Therefore, the aim of this work is to evaluate the adsorption treatment of azo dye. Adsorption hold promise in the treatment of wastewater, as it is inexpensive, simply designed, easy to handle and provides sludge-free cleaning operations. Commercially activated carbon has long been used as a standard adsorbent for color removal. In spite of its wide spread use in various cleaning procedures, activated carbon remains expensive; therefore, the development of low-cost alternative adsorbent has been the focus of recent research. About the selection of adsorbents, a literature survey reveals that materials such as commercially available activated carbon [10–14], zeolites [14] have been used in the past for the treatment of textile effluents. A number of non-conventional sorbent have been tried for the removal of chemical pollutant such as: peat [15,16], chitin [17], apple promace and wheat straw [18], sulfonated coal [19], organomontmorillonite [20], coir pith [21], slag from the manufacture of steel [22], fly ash [23,24] have been used for the removal of dyes. Recently Gupta and Ali [25] have reviewed the utility of the low-cost adsorbent for the removal of various pollutants including dyes. In present adsorption studies, wheat husk (agricultural waste) is converted into a cheap adsorbent and used

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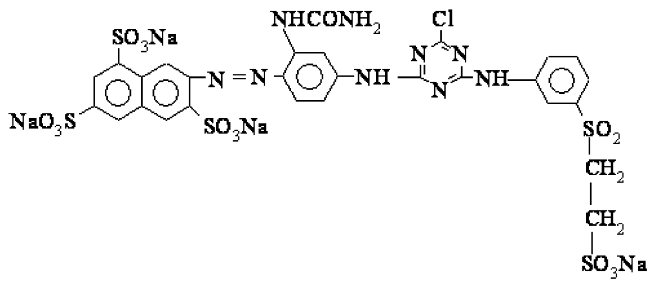

Scheme 1. Chemical name—(1,3,6-naphthalene trisulfo-[[4-chloro-6-[3-[2-(sulfoxy)ethyl]sulfonyl]phenyl]azo]-tetra sodium salt).

for the removal of dye. Efforts have been made to convert this waste into a potential and low-cost adsorbent. The present work reports the results of adsorption studies (with charcoal and wheat husk) on an azo dye Reactofix golden yellow 3 RFN (Scheme 1), with particular reference to color removal and wastewater treatment. It is an acid dye and the acidic group acts as auxochrome in this dye.

2. Materials and experimental methods

2.1. Adsorbent development

Two hundred grams of wheat husk was treated with hydrogen peroxide (30%) at 60 °C for 24 h to oxidize the adhering organic matter. The resulting material washed with double distilled water and filtered and again dried to 100 °C, powdered, grounded and sieved to the desired particle size. Physiochemical characterization of wheat husk has been carried out and the results are being shown in Table 1.

2.2. Adsorbate

Reactofix golden yellow 3 RFN was obtained from Aldrich chemical Co., USA. All other reagents were of AR-grade and were also obtained from Aldrich chemical Co USA and were used without any further purification process.

Table 1
Physical and chemical properties of adsorbent used in the experiments

Characteristics	Value
Chemical	
Moisture content (%)	6.40
Water-soluble components (%)	20.89
Insoluble components (%)	72.34
Ash (%)	2.58
Total loss of ignition (%)	88.45
C content (%)	44.59
H content (%)	6.56
pH	6.05
Physical	
Surface area (BET) (m^2/g)	0.67
Bulk density (g/mL)	0.36
Particle size (mm)	0.60

2.3. Equipments

pH measurements were made using a pH meter (Hach, Loveland, Co.). All color measurements were made on a Specord 200 UV–vis spectrophotometer (model UV–vis 1601) in the visible range in the absorbance mode. The spectrophotometer response time was 0.1 s, and the instrument has a resolution of 0.1 nm. Absorbance values were recorded at the wavelength of maximum absorbance (λ_{max}) for dye. The concentration of dye was measured in a 1 cm path length cell, with an absorbance accuracy of ±0.005 at λ_{max} of the dye. Biological degradation of the dyes was also taken into account by keeping different concentration solution of used dye at different time intervals and different temperature. It was observed that there was no change in concentration and λ_{max} values even after 24 h indicating the stability of this dye. Standard plots were made as a function of concentration.

2.4. Method

Stock solution (0.01 M) of Reactofix golden yellow 3 RFN was prepared in 250 mL distilled water. Solution of desired concentration 4.0×10^{-5} M was prepared from stock solution. A known amount of adsorbent was added. All the contents were agitated for a suitable contact time. Then the contents were filtered with Whattman filter paper no. 1, the supernatant solution was centrifuged and the concentration of dye was determined with UV–vis spectrophotometer at λ_{max} 427 nm.

3. Results and discussion

3.1. Sorption studies

Adsorption isotherms were determined for various dye-adsorbent systems. The distribution of dye between adsorbent and the dye solution at equilibrium is important in establishing the capacity of the adsorbent for the dye. Adsorption studies were carried out taking charcoal and wheat husk (biosorbent) as adsorbents. The effect of pH, concentration, adsorbent dose, temperature, and particle size of adsorbents were studied, in order to optimize each parameter for maximum uptake. Isotherms were run at three different temperatures.

3.2. Effect of adsorbent dose

The effect of adsorbent dose on removal of dye was studied by varying the dose of adsorbent for charcoal from 0.2 to 1.0 g/L and for wheat husk from 10.0 to 40.0 g/L at 30 °C, contact time (15 min for charcoal and 40 min for wheat husk) and adsorbate concentration 4.0×10^{-5} M. The adsorption increases from 0.2 to 0.8 g/L of charcoal and 10.0–35 g/L of wheat husk and then become almost constant in both the cases, indicating that a dose of 0.8 g/L of charcoal and 35 g/L of wheat husk are sufficient for maximum removal of dye (Fig. 1a and b). Therefore, these dosages were further used for successive experiments.

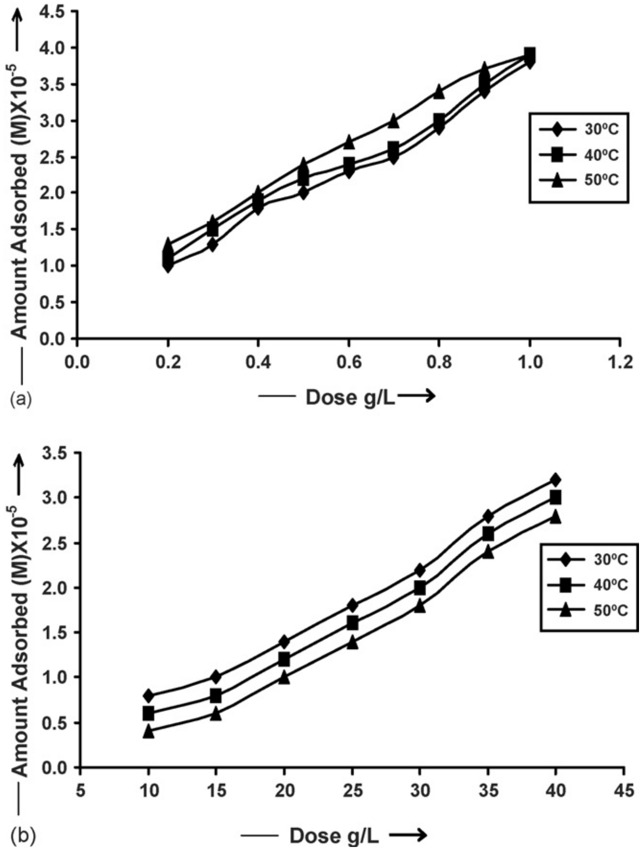

Fig. 1. Plots of adsorbent dose vs. amount adsorbed for Reactofix golden yellow 3 RFN: (a) charcoal (b) wheat husk. Experimental conditions: adsorbate concentration 4.0×10^{-5}, contact time 15 min for charcoal and 40 min for wheat husk.

3.3. *Effect of pH*

Since the efficiency of sorption processes is strongly dependent on the pH, which affects the degree of ionization of the sorbate (dye) as well as the surface properties of the sorbent, comparative experiments were performed over the pH range 2.0–10.0 at 30 °C and contact time (15 min for charcoal and 40 min for wheat husk). It is worth mentioning that the surface of the adsorbent changes its polarization according to the value of the pH of the solution. Thus, the pH influences at the same time both the surface state of the adsorbent; either the charcoal or wheat husk, or the ionization state of ionizable organic molecules. At lower pH the surface becomes positively charged and it is the opposite for higher pHs [26], It was observed that the maximum uptake of dye takes at pH 2.0 in case of wheat husk 86%. Since this dye exposes negatively charged sulfonate SO_3^- groups, it is conceivable that at low pHs, its adsorption is favored. On successive increase in pH the surface gets negatively charged which impede the approach of ionized dye molecule towards adsorbent. This probably explains the decrease in the rate of adsorption at higher pH. Where as the charcoal shows a constant; 88% removal in the pH range 2.0–6.0 (Fig. 2).

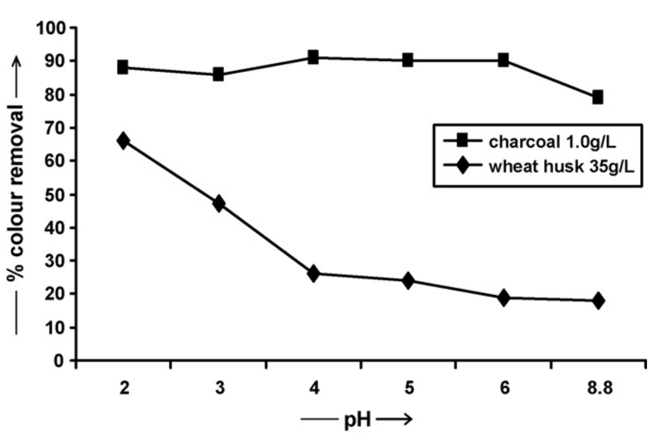

Fig. 2. Plots of pH vs. color removal (%) for Reactofix golden yellow 3 RFN for charcoal and wheat husk. Experimental conditions: temperature 30 °C, adsorbate concentration 4.0×10^{-5}, contact time 15 min for charcoal and 40 min for wheat husk, dose 0.8 g/L of charcoal and 35 g/L.

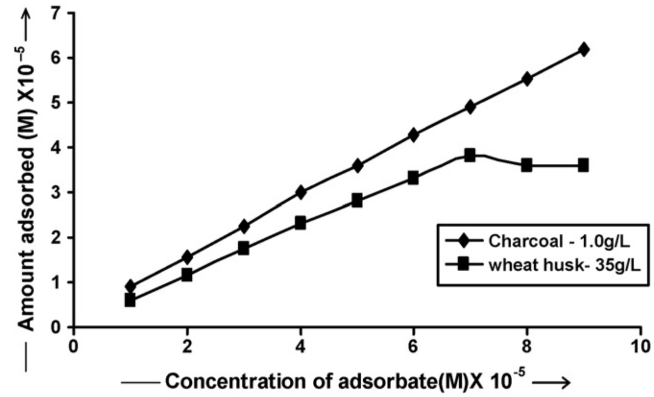

Fig. 3. Plots of concentration of adsorbate vs. amount adsorbed for Reactofix golden yellow 3 RFN for charcoal and wheat husk. Experimental conditions: temperature 30 °C, contact time 15 min for charcoal and 40 min for wheat husk, dose 0.8 g/L of charcoal and 35 g/L.

3.4. *Effect of adsorbate concentration*

For observing the effect of concentration of the adsorbate, the concentration range of 1.0×10^{-5} to 9.0×10^{-5} M was taken for the dye at 30 °C and contact time (15 min for charcoal and 40 min

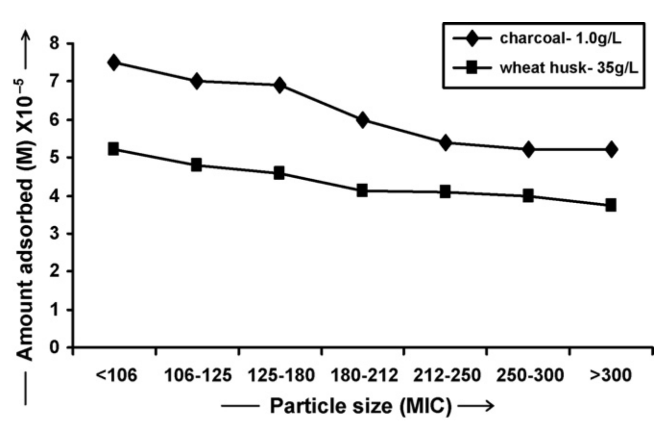

Fig. 4. Plots of particle size vs. amount adsorbed for Reactofix golden yellow 3 RFN for charcoal and wheat husk. Experimental conditions: temperature 30 °C, adsorbate concentration 4.0×10^{-5}, contact time 15 min for charcoal and 40 min for wheat husk, dose 0.8 g/L of charcoal and 35 g/L.

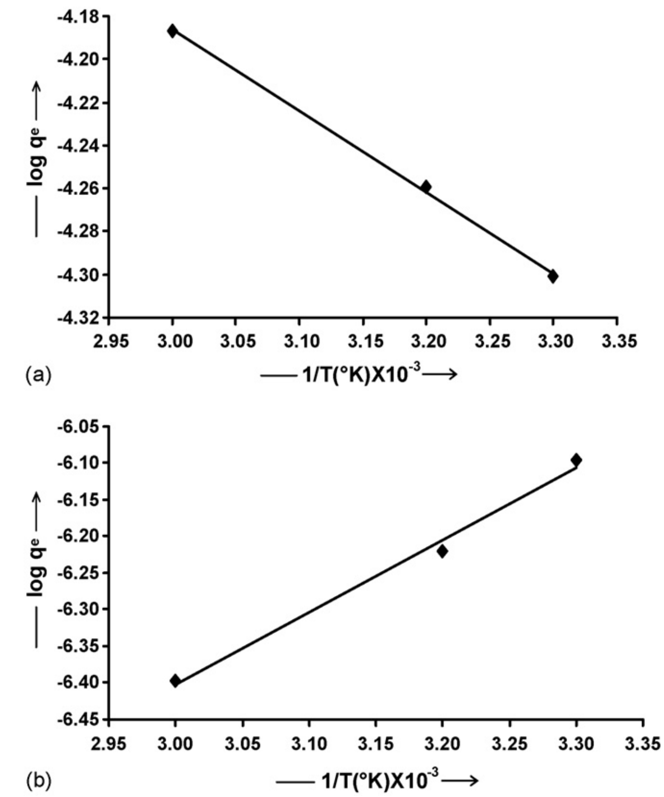

Fig. 5. Effect of temperature on adsorption of Reactofix golden yellow 3 RFN on (a) charcoal and (b) wheat husk. Experimental conditions: adsorbate concentration 4.0×10^{-5}, contact time 15 min for charcoal and 40 min for wheat husk, dose 0.8 g/L of charcoal and 35 g/L.

for wheat husk). Adsorption increases up to 6.0×10^{-5} M for wheat husk and 9.0×10^{-5} M for charcoal and then becomes almost constant for both the adsorbents (Fig. 3).

3.5. Effect of particle size

The adsorption studies were also carried out at seven different particle size at adsorbent dose (1.0 g/L for charcoal and 35 g/L for wheat husk), contact time (15 min for charcoal and 40 min for wheat husk) and at 30 °C. Maximum adsorption for charcoal 93% and for wheat husk 65% occur at a mesh size <106 MIC and for both the adsorbents adsorption decreases with increasing mesh size of adsorbent (Fig. 4).

3.6. Effect of temperature

The adsorption studies were also carried out at three different temperatures, 30, 40 and 50 °C. It is observed that for charcoal adsorption increases with increase in temperature. It was also observed that the maximum adsorption occurred at 50 °C and the order of adsorption follows the order 30 < 40 < 50 °C. It indicates that the process is endothermic in nature but in case of wheat husk adsorption decreases with increase in temperature. Maximum adsorption occurs at 30 °C and the order of adsorption follows the order 30 > 40 > 50 °C indicating exothermic nature of the process (Fig. 5a and b).

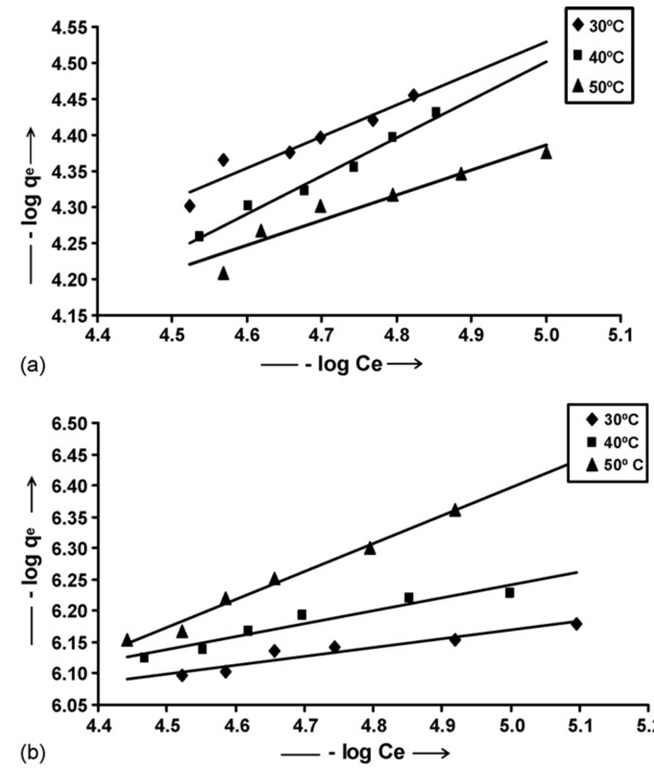

Fig. 6. Freundlich adsorption isotherms of Reactofix golden yellow 3 RFN for (a) charcoal (b) wheat husk.

3.7. Adsorption isotherm

3.7.1. Freundlich isotherm

The adsorption data of charcoal and wheat husk were fitted into the Freundlich model to observe the applicability of measured data. The logarithmic form of Freundlich model is given by the equation:

$$\log q_e = \log K_F + \frac{1}{n \log C_e} \quad (1)$$

where q_e is the amount adsorbed (mol/g), C_e the equilibrium concentration of adsorbate (mol/g) and K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. When $\log q_e$ was plotted against $\log C_e$, straight lines with slopes '$1/n$' were obtained (Fig. 6a and b for charcoal and wheat husk, respectively). The higher values of regression coefficients recommended the applicability of Freundlich model. The values on 'n' for both the adsorbents recline between 1 and 10 which also shows favorable adsorption. The Freundlich

Table 2
Freundlich constants for Reactofix golden yellow 3 RFN for charcoal and wheat husk

Temperature (°C)	Charcoal			Wheat husk		
	K_f (mmol g^{-1})	n	R^2	K_f (mmol g^{-1})	n	R^2
30	220.80	2.288	0.9179	29.6×10^4	7.173	0.9137
40	73.90	1.898	0.9836	15.6×10^4	4.775	0.9317
50	448.74	2.884	0.9174	14.9×10^3	2.242	0.9854

Table 3
Langmuir constants for Reactofix golden yellow 3 RFN for charcoal and wheat husk

Temperature (°C)	Charcoal			Wheat husk		
	b (L mmol^{-1})	Q_0 (mmol g^{-1})	R^2	b (L mmol^{-1})	Q_0 (mmol g^{-1})	R^2
30	6.690	0.707	0.9308	35.59	0.0832	0.9104
40	4.259	0.996	0.9731	16.94	0.0837	0.9146
50	11.71	0.756	0.9046	3.665	0.1158	0.9527

constant K_F calculated for charcoal and wheat husk, respectively, and the values of these at three different temperatures shows that theoretical capacity of wheat husk is much more then charcoal (Table 2).

3.7.2. Langmuir isotherm

The results of the adsorption of dye on charcoal and wheat husk were fitted into Langmuir isotherm. Langmuir isotherm has been used by various workers for the sorption of a variety of compounds, and the linear form of this isotherm is given by the equation:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \tag{2}$$

where q_e is the amount adsorbed (mol/g), C_e the equilibrium concentration of the adsorbate (mol/g) and Q_0 and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. When $1/q_e$ was plotted against $1/C_e$, straight line with slopes $1/bQ_0$ were obtained (Fig. 7a and b for charcoal and wheat husk, respectively). In these figures also higher vales of regression coefficient were observed, which advocate that adsorption of dye on charcoal and wheat husk also follows the Langmuir isotherm. The Langmuir constants 'b' and 'Q_0' were calculated for charcoal and wheat husk, respectively, from slop and intercept of figures, and their values at three different temperatures, are given in Table 3. The successive decrease in adsorption energy on increasing the adsorption temperature suggests the exothermic nature of adsorption. Where as relatively higher values of 'Q_0' again suggest the more adsorption capacity of wheat husk over charcoal.

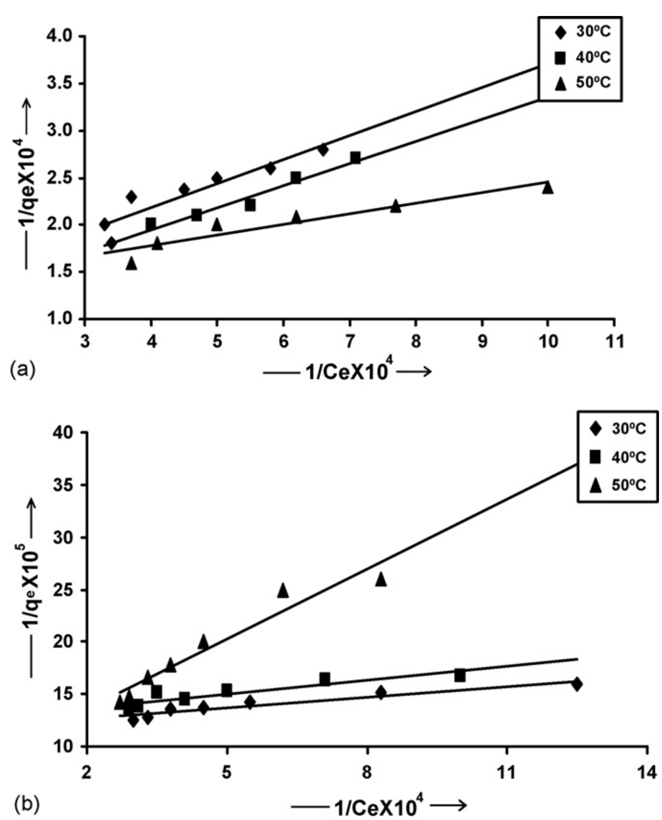

Fig. 7. Langmuir adsorption isotherms of Reactofix golden yellow 3 RFN for (a) charcoal (b) wheat husk.

3.8. Thermodynamic parameters

Thermodynamic parameters for the adsorption of dye on charcoal and wheat husk were calculated by the application of following equations, and the values are given in Table 4:

$$\Delta G^\circ = -RT \ln b' \tag{3}$$

$$\ln\frac{b_2}{b_1} = \left(\frac{\Delta H^\circ}{R}\right)\left[\frac{(T_2-T_1)}{T_1T_2}\right] \tag{4}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{5}$$

where b', b_1 and b_2 are the Langmuir constants at 30, 40 and 50 °C, respectively, and obtained from the Langmuir isotherm, other terms have their usual meanings. The negative free energy value shows the spontaneity of adsorption with both the adsorbents. The positive value of enthalpy in case of charcoal is due to endothermic nature of adsorption, where as the value was found negative in case of wheat husk which shows that the adsorption wheat husk was exothermic. The higher positive values of entropy contribute to feasibility of adsorption process (Table 4).

4. Chemical oxygen demand (COD)

COD of initial colored and treated filtrate of charcoal and wheat husk solutions was determined and it was observed that the COD values show (Table 5) a significant decrease from 1416

Table 4
Thermodynamics parameter of Reactofix golden yellow 3 RFN for charcoal and wheat husk

Adsorbent	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol)
Charcoal	−4.786.3	90408	282.57
Wheat husk	−8998.3	−19333.5	34.109

Table 5
COD values for 5.0×10^{-5} M Reactofix golden yellow 3 RFN before and after treatment

Treatment technique	COD in (mg/L)
Golden yellow dye before treatment	1416
Adsorption by wheat husk	320
Adsorption by activated charcoal	220

Table 6
Camparision with other low-cost adsorbent for dye removal on the basis of their adsorption capacity

Adsorbent	Dye	Maximum adsorption capacity, Q_0 (mg/g)	Ref.
Phanerochaete chrysosporium biomass	Reactofix golden yellow	5.64	[27]
Maize cob	Atrazon Blue	160	[6]
Maize cob	Maxilon Red	94.5	[6]
Peat	Basic BIue 69	233	[15]
Peat	Acid Bhre 25	8.84	[15]
Wheat husk	Reactofix golden yellow	0.1158 mmol/g	Present study

to 352, 220 and 320 mg/L, respectively, indicating less toxicity of the treated products in comparison to original dye.

5. Conclusion

Based on the results wheat husk was found to be an effective adsorbent for the removal of Reactofix golden yellow 3 RFN and it has good adsorption capacity which is comparable with the other low-cost adsorbent reported for the removal of similar and other ionic dyes using low-cost adsorbents (Table 6). Wheat husk is cheap and easily available material thus it is a better replacement of activated carbon. Wheat husk is a waste product hence its use as an adsorbent on one hand would solve its disposal problem and on the other hand would provide an effective adsorbent for the removal of dye. Thermodynamic parameters indicate that the process is spontaneous and feasible.

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