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Adsorption of safranin dye from aqueous solutions using a low-cost agro-waste material soybean hull

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ABSTRACT

The present paper is aimed to develop a low-cost adsorption method using an agro-waste material soybean hull as an adsorbent for color removal from wastewater. The morphological characterization of soybean hull was done by Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction analysis, and zeta potential measurement. The soybean hull was utilized as an adsorbent for removal of safranin dye from the aqueous solutions. The effects of operating parameters such as pH, initial dye concentration, adsorbent dose, particle size of the adsorbent, and contact time were investigated. The adsorption data were modeled by the Freundlich, Langmuir, and Tempkin adsorption isotherm models. The thermodynamic parameters indicated that the adsorption process was spontaneous and endothermic. Also, the adsorption kinetics of dyes were found to follow the pseudo-second-order kinetics. Desorption study elucidates the mechanism of adsorption as well as recovery of adsorbent material. The results revealed that the soybean hull, a natural, eco-friendly, and low-cost adsorbent has a relatively large adsorption capacity and can be effectively used for removal of dyes from the wastewater.

Keywords: Adsorption; Agro-waste; Soybean hull; Safranin; Low-cost adsorbent; Desorption

1. Introduction

Dyes and pigments are widely used in industries such as textile, leather, food, cosmetics, paper, printing, and plastics to color the products. The dyes can be natural or synthetic; however, the synthetic dyes are largely used in industries. The annual production of synthetic dyes is over 7×10^5 tons [1]. The disposal of dye-laden wastewater from the industries is hazardous to human beings as it results in carcinogenic and mutagenic effects which can cause allergic dermatitis, skin irritation, cancer, and mutation [2–6]. The discharge of highly colored effluents into natural water bodies impedes light penetration, consequently retards the biological processes within streams and causes damage to aquatic life. Also, it is esthetically displeasing [7]. Thus, there is an urgent need for the decoloration and removal of dyes from industrial effluent.

Various methods, such as coagulation, flocculation [8], electrochemical oxidation, membrane filtration, ion-exchange, oxidation, and advanced oxidation [9,10], had shown potential for the decoloration or/and degradation of dyestuffs from wastewater. However, the nondegradable nature of dyes and their stability towards the light and oxidizing agents

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complicates the selection of a suitable method for their removal.

Adsorption is one of the most promising methods of color removal from wastewater due to its high efficiency, cost effectiveness, and simplicity [11]. Activated carbon is generally employed as an adsorbent due to its high adsorption capacity [12]. However, one of the major challenges associated with adsorption by activated carbon is its cost effectiveness. Therefore, research in the recent past has mainly focused on utilization of low-cost biodegradable agro-waste materials as an alternative to activated carbon [13]. Various types of agricultural/industrial solid-waste materials such as rice husk, coconut husk, and maize were investigated as the possible cost effective and eco-friendly alternative bioadsorbents [14,15].

Soybean hull is a by-product of the soybean process industries. It is a low-cost and easily available agro-waste material. Soybean hull is about 8–10% of the total mass of soybean [16] and due to its lower nutrient value (crude protein content of 11%, crude fibrin content of 36%, crude lipid content of 1%) it is usually used as animal feedstuff [17,18].

Previously, soybean hull were employed as a biosorbent for the removal of acid dyes from the aqueous solutions [19] and to remove heavy metal ions (Pb^{2+}) from contaminated wastewater [16]. Esterified soybean hulls were used for the removal of acridine orange and malachite green from the aqueous solution [20]. The stalks of soybean and canola were used as biosorbent for the removal of acid orange 7 and other hazardous reactive dyes from aqueous solutions [21–23].

In the present study, the adsorption potential of untreated soybean hull for a cationic dye safranin was investigated. Safranin (3,7-Diamino-2,8-dimethyl-5-phenylphenazin-5-ium chloride) is a basic azo dye [24] and it is among the oldest known highly water-soluble synthetic dye [25]. Generally, it is used for dyeing tannin, cotton, fibers, wool, silk, leather, and paper [26]. It is considered as the model compound to represent the dyes that are released in the effluents from the textile and food industries, due to its extensive use in food and textile industries as colorant [27].

Safranin was selected as the target dye contaminant because of its wide use in dyestuff industries. The adsorption characteristics of target contaminant safranin and its removal from aqueous solution by the soybean hull as an adsorbent was investigated. The surface morphology of the soybean hull was characterized and the mathematical adsorption isotherm models were used to fit the safranin adsorption data. A detailed morphological characterization of soybean hull is also presented.

2. Materials and methods

Safranin [Formula: $C_{20}H_{19}N_4^+Cl^-$, MW = 350.84 g mol^{-1}, λ_{max} = 520 nm, C.I. number = 50240] manufactured by M/s Glaxo was purchased from the market and used without further purification (Fig. 1). All chemicals used were of analytical reagent grade and used as received without further purification. All solvents were of HPLC grade. Deionized, double distilled water was used throughout the experiments.

2.1. Preparation of the adsorbent

The soybean hulls were obtained from a local oil extraction plant. It was cleaned, thoroughly washed with double distilled water to remove adhering foreign particles from the surface and then dried in sunlight. It was then dried in hot air oven at 70°C for about 24 h. After drying, the hulls were ground in ball mill and then sieved to a desired particle size as 355–210 μm (44–72 BSS mesh), 210–150 μm (72–100 BSS mesh), and <150 μm (<100 BSS mesh). Finally, these materials were stored in separate storage bottles for further experiments and characterization.

2.2. Morphological characterization of the adsorbent

Surface texture and elemental composition of the soybean hull samples (before and after adsorption of Safranin) were analyzed using a scanning electron microscope (SEM), (ZEISS EVO 18) equipped with an energy dispersive X-ray analysis (EDS attachment). The samples were coated with a thin gold film before observation in SEM.

The X-ray diffraction (XRD) pattern analysis of the sample was done at room temperature by PANalytical 3 kW X'pert Powder.

The Fourier transform infrared (FTIR) spectra of soybean hull samples were determined using FTIR

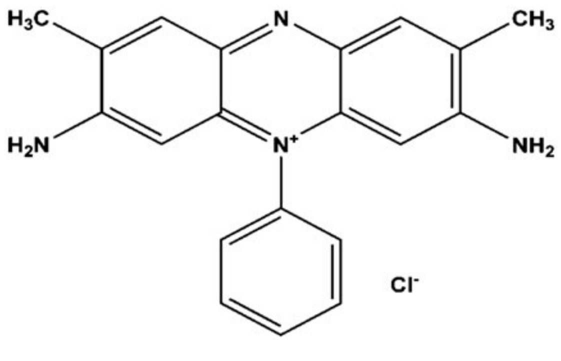

Fig. 1. Chemical structure of Safranin dye.

spectrometer (IR-Affinity-1, Shimadzu). The sample was ground with anhydrous KBr and the spectra were recorded between 4,000 and 400 cm^{-1}, by averaging 45 scans for each spectrum.

Zeta potential of soybean hull sample was determined by Malvern Zetasizer Instrument. The sample was dispersed in distilled water and sonicated before measurement of zeta potential.

2.3. Batch adsorption studies

Adsorption of Safranin was carried out batchwise in triplicate to study the adsorption characteristics of soybean hull in the aqueous solutions. Initially, the safranin stock solution of 1,000 mg L^{-1} was prepared by dissolving an accurately weighed amount of safranin in the double distilled water. The desired concentrations of the solution were obtained by diluting the stock safranin dye solution in accurate proportions to obtain the different initial concentrations.

The effects of the operating conditions (pH, adsorbent dosages, particle size of the adsorbent, contact time, initial dye concentration, and adsorption temperature) on safranin removal were studied. In all experiments, 50 mL of safranin solution with known amount of adsorbent was taken in 100 mL Erlenmeyer flasks. These flasks were stirred at 150 rpm in a thermostatic shaker. The pH of the solutions was maintained by adding 0.1 N NaOH or 0.1 N H_2SO_4.

After shaking, the adsorbent was separated carefully from dye solutions by filtration. The dye concentrations in the supernatant solutions were analyzed using a double beam UV–vis spectrophotometer (UV-1800, Shidmadzu, Japan) by measuring the absorbance at $\lambda_{\max}$ of 520 nm. The dye removal percentage and amount adsorbed were calculated using the Eqs. (1) and (2), respectively.

$$\text{Percent removal of dye} = \frac{(C_i - C_f)}{C_i} \times 100 \tag{1}$$

$$\text{Amount of dye adsorbed} = \frac{(C_i - C_f)V}{m} \tag{2}$$

where C_i and C_f are the initial and final concentrations (mg L^{-1}) of dye, respectively, m is the mass (g) of adsorbent, and V is the volume of dye solution (mL).

2.4. Desorption and recovery of adsorbents

After the dye adsorption, the dye-loaded adsorbent was dried and weighed for desorption experiment. It was then contacted with 100 mL distilled water at different pH values (2–12) and stirred in a thermostatic shaker for the fixed evaluated equilibrium time of adsorption process [19]. The desorbed dye concentration was estimated as discussed in Section 2.3.

3. Results and discussion

3.1. Morphological characterization of soybean hull

3.1.1. Scanning electron microscopy

SEM was used to characterize the surface morphology of soybean hull. SEM micrographs of soybean hull adsorbent, before and after adsorption, taken at different magnifications are presented in Fig. 2.

The soybean hull (Fig. 2(a) and (b)) had a rough surface with number of pores and cavities on its surface. This revealed a good possibility for the dye to be adsorbed and entrapped in the pores and cavities. The surface of soybean hull became comparatively smoother after adsorption of safranin dye, as the pores and cavities were occupied by the dye molecules (Fig. 2(c) and (d)).

The EDS analysis of the soybean hull before adsorption revealed the elemental composition as carbon—52.2 wt.%, oxygen—38.4 wt.%, nitrogen—7.9 wt.% with the trace amount of silicon (1.57 wt.%) and calcium (0.84 wt.%). Soybean hull did not reveal the presence of any chloride ion adsorbed on the surface. However, the EDS analysis of soybean hull after the adsorption of dye revealed the presence of the chloride ions (0.9 wt.%) in addition to other elements. It clearly indicates that the chloride ions from the safranin were adsorbed on the surface of the soybean hull.

3.1.2. FTIR analysis

The FTIR spectra of the soybean hull adsorbent in the range 4,000–400 cm^{-1} are presented in Fig. 3(a).

The peak at 3,622 and 3,304 cm^{-1} corresponds to N–H and O–H group stretching, respectively. A broad hump from about 3,600 to 3,200 cm^{-1} in the spectrum is probably due to surface-bonded water. The sharp peaks at 2,954 and 2,804 cm^{-1} correspond to –CH_2 asymmetric and symmetric stretching vibrations, respectively. The peak at 1,729 cm^{-1} represents the carbonyl group (–C=O) stretching. The peaks at 1,539 cm^{-1} and 1,514 cm^{-1} are due to aromatic –C=C– stretching which indicates the presence of aromaticity in the structure. The peaks at 1,454 cm^{-1} and 1,369 cm^{-1} are due to –C–O stretching vibrations. A broad band at 1,010 cm^{-1} corresponds to ether (–C–O–C–) stretch. A sharp band at 771 cm^{-1} indicated the presence of aliphatic chains and a band at 675 cm^{-1} is due to the presence of substituted

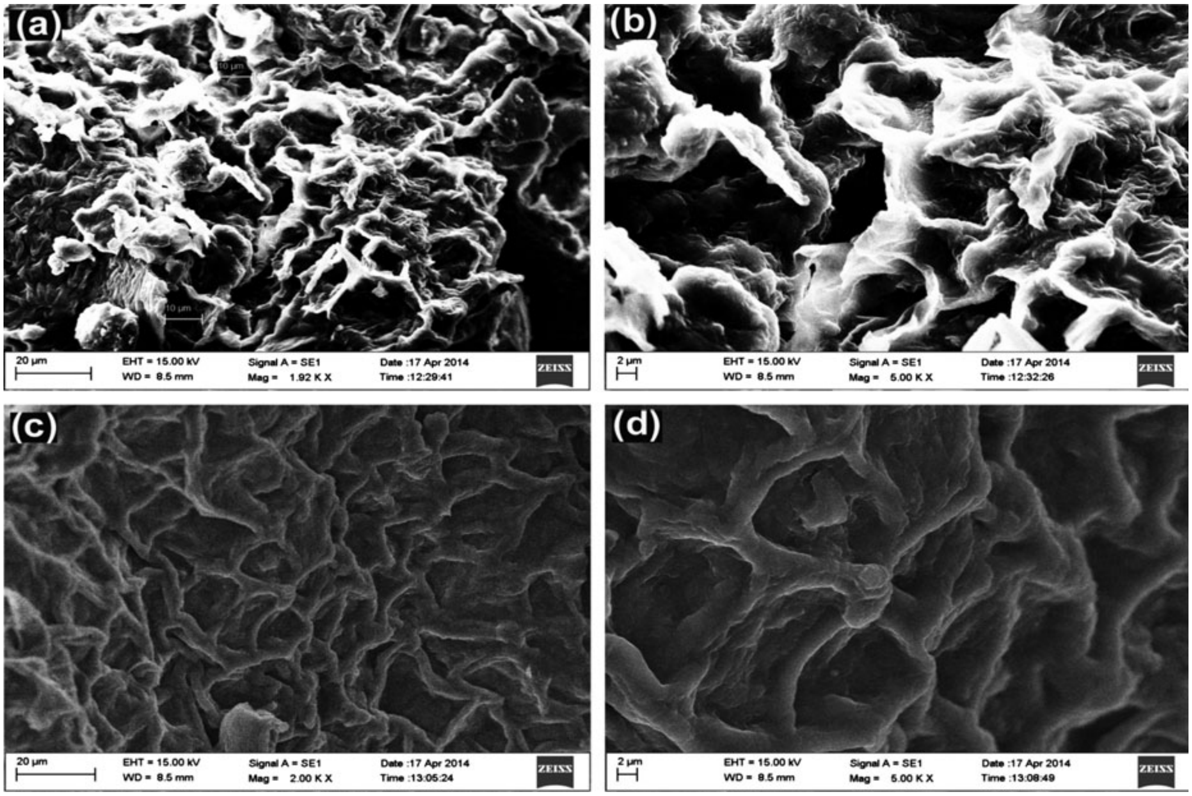

Fig. 2. Scanning electron micrographs of soybean hull at magnifications of (a) 1.92 K, (b) 5.00 K before the adsorption of dye, (c) 2.00 K, and (d) 5.00 K after adsorption of dye.

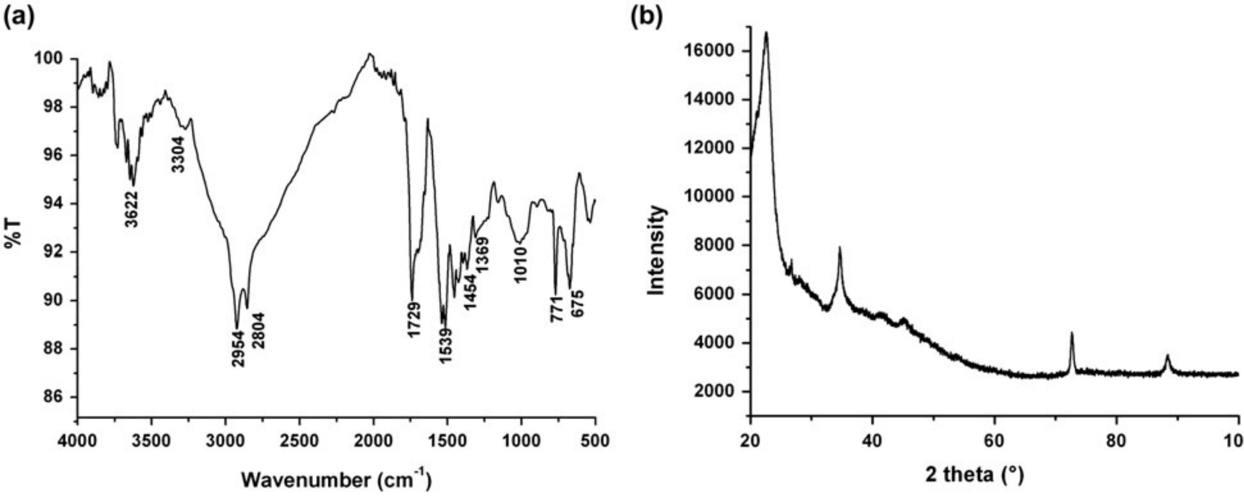

Fig. 3. (a) FTIR spectrum of soybean hull and (b) XRD pattern of soybean hull.

aromatic rings in the structure of soy hull adsorbent [28]. The –COOH groups present on the surface of soybean hull can significantly bind the cationic dye safranin (which remains as the positively charged ion in solution) through the electrostatic interactions. Moreover, –OH groups can bind with the ammonium ion (=N^+) of the dye molecule through the formation of hydrogen bonding interaction [11].

3.1.3. XRD analysis of soybean hull

The XRD patterns of soybean hull adsorbent are presented in Fig. 3(b). The broad nature of the peaks indicates a range of inter-atomic distances that are typical of amorphous structure. No sharp peak was observed due to the lack of inorganic material. The diffraction maxima at $2\theta = 22$ can be attributed to the characteristic crystalline form of cellulose [29].

3.1.4. Zeta potential of soybean hull adsorbent

Zeta potential is a measure of the magnitude of electrostatic interactions between charged surfaces [30]. A solution containing suspended adsorbent particles possesses a surface charge known as electrokinetic potential or zeta potential, which is important in determining the stability of the suspension.

The zeta potential of adsorbent was obtained to be −44.8 mV at an optimized pH value which showed that surface of soybean hull is negatively charged. Also, zeta potential in the range of ±40 to ±60 mV showed good stability of adsorbent material [31].

3.2. Effect of operational parameters on safranin adsorption

3.2.1. Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The effect of pH on the percent dye removal efficiency was observed over the pH range of 2 to 12 at a fixed adsorbent dose of 0.05 g and dye concentration of 50 mg L^{-1} (Fig. 4).

It was observed that the percent dye removal efficiency of adsorbent increased with an increase in pH from 2 to 8, and thereafter it became constant in the pH range from 8 to 12. Thus, all the succeeding investigations were performed at the optimized pH 8.

The presence of excess of H^+ at acidic pH (pH range 2–6) can compete with the dye cations for adsorption sites resulting in a lower percentage of dye removal. With the increase in pH, the acidic sites on the adsorbent surface are gradually neutralized and negative surface charge of adsorbents increased [32]. These negatively charged sites on the adsorbent particles may form an electrostatic interaction with the dye cations resulting in the increased percentage of dye removal [33]. Also, according to zeta potential value, the negative surface charge of adsorbent material can also enhance the adsorption properties through electrostatic forces of attraction [34].

3.2.2 Effect of particle size of adsorbent

The batch adsorption experiments were conducted with three different adsorbent particle sizes, viz 355–210 μm (44–72 BSS mesh), 210–150 μm (72–100 BSS mesh), and <150 μm (<100 BSS mesh). The effects of particle size on the adsorption capacity of the adsorbent are presented in Fig. 5.

The amount of dye adsorbed increased as the particle size of adsorbent decreased. The small particles had more surface area which facilitates the easy access to the particle pores for the adsorbate dye molecules. The breaking up of large particles to form smaller particles opened some tiny scaled channels,

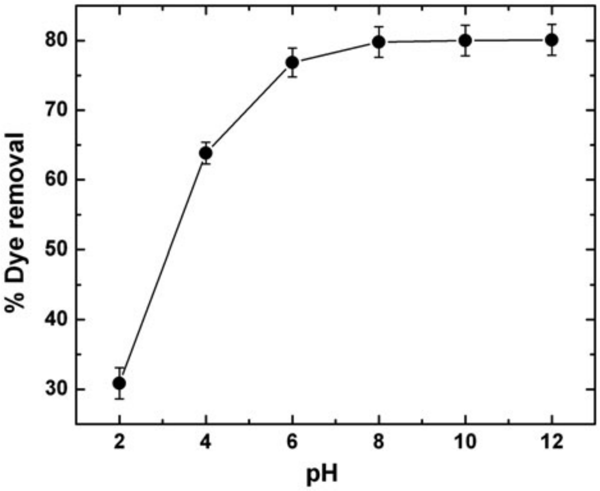

Fig. 4. Effect of pH on adsorption of safranin on soybean hull.

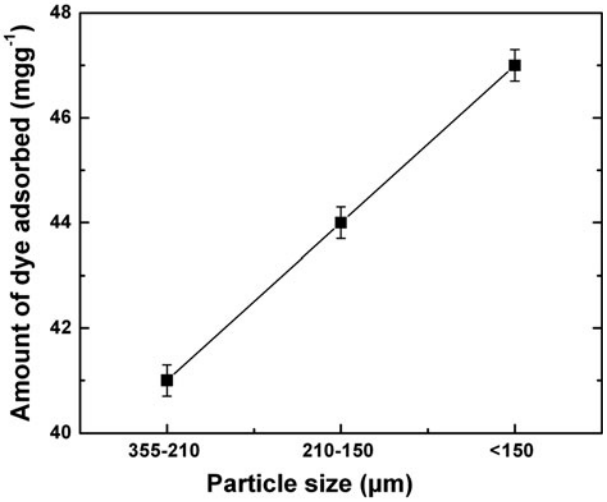

Fig. 5. Effect of particle size on adsorption of safranin on soybean hull.

which became available for adsorption, thus, the adsorption by smaller particles was higher than that by large particles [35]. The maximum quantity of dye i.e. 47 mg g^{-1} was absorbed by the adsorbent particle size <150 μm. Thus, this particle size fraction was used in further investigations.

3.2.3. Effect of adsorbent dose

Adsorbent dose is an important parameter in the adsorption studies which determines the capacity of an adsorbent for a given initial concentration of the adsorbate and helps to optimize a cost-effective dose [11]. The dye adsorption was carried out by varying the adsorbent dose from 0.02 to 0.1 g at three different temperatures (30, 40, and 50)°C for 90 min at the optimized pH. The amounts of dye adsorbed by varying the dosage of adsorbents at different temperatures are presented in Fig. 6.

The Fig. 6 reveals that the adsorption of safranin increased with an increase in the amount of adsorbent from 0.02 to 0.04 g, thereafter it remained constant. This trend was common at all temperatures; however, comparatively lower amount of dye was adsorbed at 30°C. The 0.04 g of dose per 50 mL of the solution was taken as the optimized dose for further experiments.

3.3. Effect of contact time and adsorption kinetics

Completion of the process within a short time is extremely important for industrial applications, in terms of cost-effectiveness and efficiency. Contact time plays a vital role in the adsorption studies as it suggests the necessary required time of contact for deriving maximum adsorption of the dye at the adsorbent surface. Fig. 7 presents graph for the variation in adsorption with respect to time.

The adsorption efficiency, increased gradually at first with the increase in contact time. The equilibrium was reached within 20 min of time. After attaining equilibrium, the adsorption gradually decreased for all temperatures, which indicated that desorption of the dye molecule from the surface of adsorbent started after equilibrium was reached. The adsorption process was governed by the physical adsorption and the dye molecules tend to revert back to the solution after attaining equilibrium. The aggregation of dye molecules around the adsorbent particles with time also resisted further adsorption of dye molecules [36].

Adsorption kinetics is an important step to investigate the adsorption process. Kinetics of adsorption of safranin onto the soybean hull adsorbent in aqueous medium was carried at three different temperatures (30, 40, and 50)°C. The adsorption kinetics of safranin on soybean hull was investigated by pseudo-first-order and pseudo-second-order kinetics models. The pseudo-first-order kinetic model expressed as Lagergren first-order rate equation (Eq. (3)) [37].

$$\log\,(q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303}t \qquad (3)$$

where K_{ad} is the first-order rate constant, q_e and q_t denotes the amount adsorbed at equilibrium and at time t, respectively. It is generally used for the periods before reaching equilibrium. K_{ad} ($\min^{-1}$) is

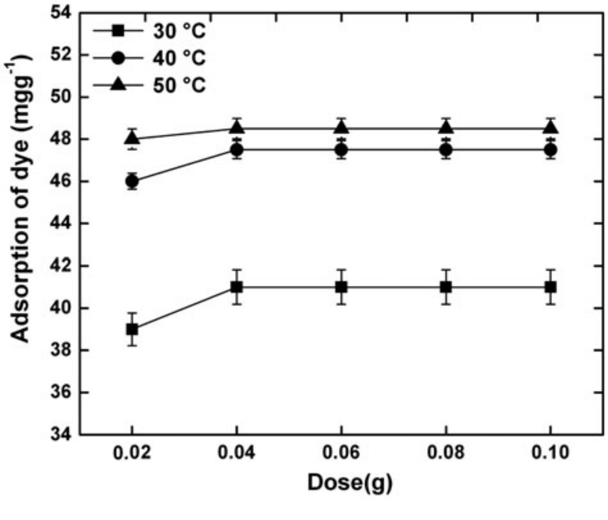

Fig. 6. Effect of adsorbent dose on adsorption of safranin on soybean hull.

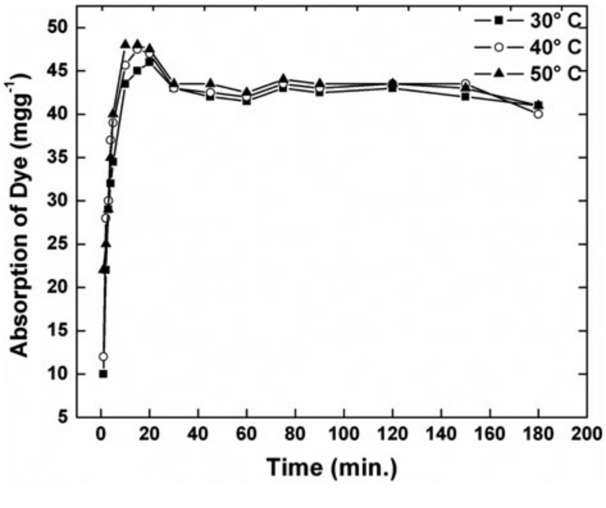

Fig. 7. Effect of contact time on adsorption of safranin on soybean hull.

pseudo-first-order rate constant. A plot of ln ($q_e - q_t$) vs. t is a line and q_e and K_{ad} are obtained from the intercept and slope of the graph, respectively.

The pseudo-second-order kinetic model is another model used for the adsorption kinetic data. This model is compatible with the mechanism of rate-controlling step throughout the adsorption contrary to the pseudo-first-order kinetic model. The pseudo-second-order kinetic model is given by the following equation.

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = K_2\ (q_e - q_t)^2 \tag{4}$$

when rearranged, it becomes Eq. (5),

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where K_2 (g mg^{-1} min^{-1}) is the second-order rate constant. The plot of t/q_t vs. t is a line, and q_e and K_2 are obtained from the slope and intercept of the graph, respectively.

Graph of ln ($q_e - q_t$) vs. t for the first-order kinetic model (Fig. 8) and graphs of t/q_t vs. t were plotted for second-order kinetic model (Fig. 9) and the constants obtained at different temperatures are given in Table 1.

As can be seen from the Table 1, the pseudo-second-order kinetic model represented the time-dependent function of equilibrium better than the pseudo-first-order kinetic model when R^2 values are considered. Therefore, the kinetic adsorption accords well with the pseudo-second-order model.

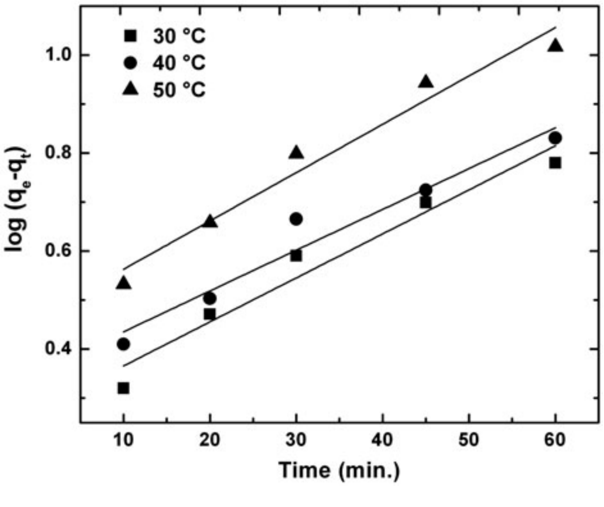

Fig. 8. Lagergren's plots for safranin–soybean hull adsorption at different temperatures.

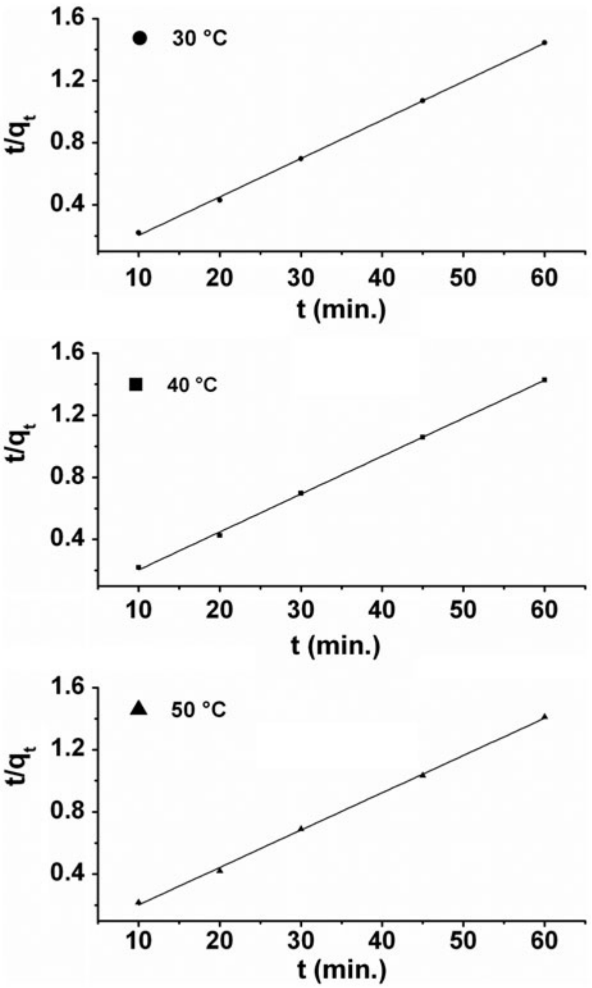

Fig. 9. Pseudo-second-order kinetic model for safranin–soybean hull adsorption at different temperatures.

Table 1
Rate constant for adsorption of safranin onto soybean hull

Temperature (°C)	K_{ad}	R^2	K_2	R^2
30	0.046	0.955	0.00015	0.999
40	0.030	0.953	0.00014	0.999
50	0.028	0.967	0.00013	0.999

3.4. Initial dye concentration and adsorption isotherms

There is a direct relationship between initial dye concentration and removal rate. The adsorption experiments were carried out in concentration ranges from 20 to 100 mg L^{-1} at a fixed adsorbent dose of 0.04 g and pH 8 at different temperatures (30, 40, and 50)°C. The results are presented in Fig. 10.

It was observed that the percent removal of dye increased up to 89.5% with the increase in the concentration of the dye for all the temperatures under investigation. This increase may be due to a greater degree of interaction between the adsorbate and the adsorbent soybean hull [38].

The adsorption isotherm models are widely used to describe the relativity between adsorption capacity and equilibrium concentration. The data for the adsorption of safranin by soybean hull adsorbent were analyzed by the Langmuir isotherm, Freundlich isotherm, and Temkin isotherm model.

The Langmuir isotherm (Eq. (6)) assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface and the adsorption of each molecule on the surface has equal adsorption activation energy [39]. The linear form of the Langmuir isotherm is expressed as:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \tag{6}$$

where q_e is the amount of adsorbate adsorbed per g of adsorbent (mol g^{-1}) and C_e is the equilibrium concentration of the adsorbate (mol L^{-1}). "Q_0" and "b" are the Langmuir constants related to maximum single-layer adsorption capacity (mg g^{-1}) and free energy or adsorption enthalpy (L mg^{-1}), respectively. A plot of C_e/q_e vs. C_e gives a linear graph and indicates the compatibility of adsorption with the Langmuir model. "Q_0" and "b" can be determined from the slope and intercept, respectively.

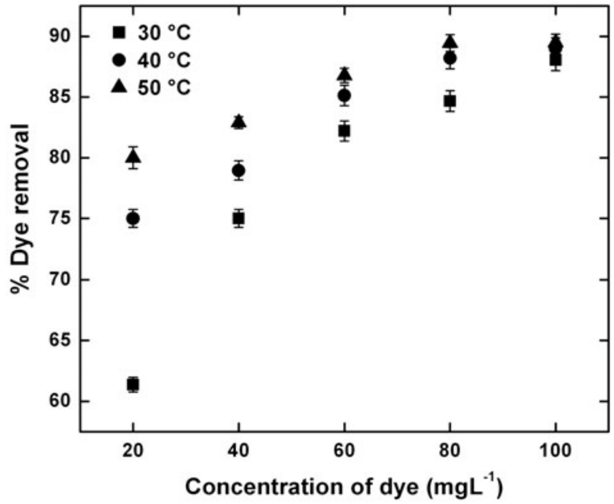

Fig. 10. Effect of initial dye concentration on adsorption of safranin on soybean hull.

The Freundlich isotherm supposes a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface and a multilayer adsorption [29]. The amount of material adsorbed by the adsorbent (q_e) increases quickly with pressure or concentration and then shows a slow increase with saturation of solid surface with adsorbed molecules. The variation of q_e with pressure or concentration is given by the linear form of the Freundlich model as Eq. (7).

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{7}$$

where q_e is the amount adsorbed (mol g^{-1}), C_e is the equilibrium concentration of the adsorbate (mol L^{-1}), K_f and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. High K_f values are indicative that adsorbent and the adsorbate are very close to each other. The n value changes with the heterogeneity of the adsorbate for the suitable adsorption process.

The Temkin isotherm model describes the behavior of adsorption heterogeneous systems. The derivation of the Temkin isotherm (Eq. (8)) assumes that the adsorption heat linearly decreases with increasing adsorption quantity, and the adsorption binding energy is distributed uniformly [29].

$$q_e = B_T \ln A_T + B_T \ln\ C_e \tag{8}$$

where $B_T = (RT)/b$ is the Temkin constant (J mol^{-1}) and $A_T = RT/bT$ is related to the heat of adsorption (mg L^{-1}). A graph of C_e vs. q_e is used in the derivation of various isotherms.

Fig. 11(a), (b), and (c) presents a linear Langmuir isotherm, a linear Freundlich isotherm, and a linear Temkin isotherm, respectively.

A parameter of the Langmuir isotherm can be expressed in terms of the dimensionless constant called separation factor R_L, to detect the favorability of adsorption process [11,29].

$$R_L = 1/(1 + bC_o) \tag{9}$$

where C_0 is the initial concentration of dye and b is the Langmuir constant. The values of R_L indicate the type of the isotherm, irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). The R_L values obtained from Eq. (9) are presented in Table 2.

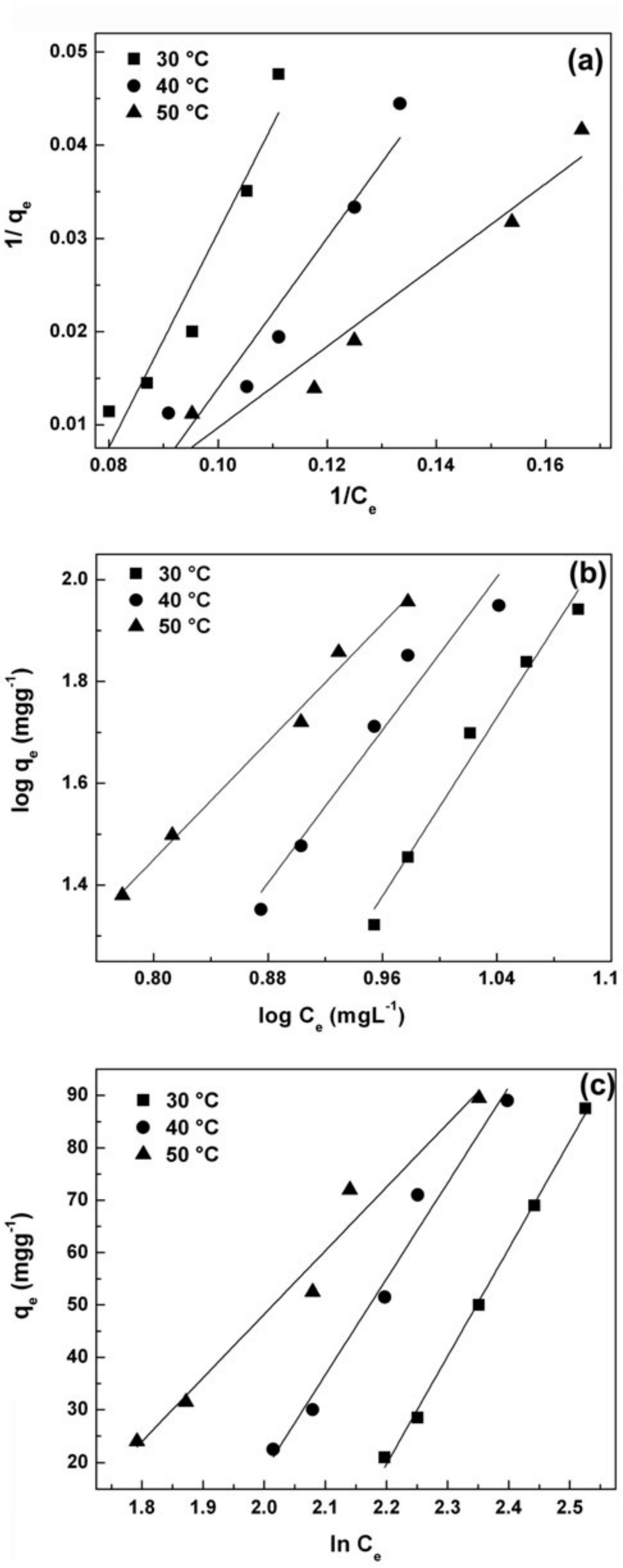

Fig. 11. Linear fits of the isotherm models (a) Langmuir model, (b) Freundlich model, and (c) Temkin model.

Table 2
R_L values at different temperatures

Temperature (°C)	R_L value
30	0.2048
40	0.1868
50	0.1745

The R_L values were found to be less than 1 which showed that safranin adsorption on soybean hull was extremely favorable. Moreover, the values of R_L decreased with an increase in temperature.

The fitting constants obtained from Langmuir, Freundlich, and Temkin isotherms are presented in the Table 3.

The fitting results showed that the Temkin model provided a better correlation than the Freundlich and Langmuir models when correlation coefficients (R^2) of the graphs are considered. The higher value of B_T indicated a strong bonding force between adsorbent and dye molecules. According to the values of B_T presented in Table 3, the heat of adsorption (RT/B_T) at 30, 40, and 50°C were 11.86, 14.21, and 22.14 J mol^{-1}, respectively, indicated that the contribution of chemisorption of safranin onto adsorbent gradually increased with the increase in temperature.

3.5. Effect of temperature on adsorption and adsorption thermodynamics

The effect of temperature on adsorption was investigated by performing adsorption experiments at 30, 40, 50, and 60°C with the optimized parameters and the results are presented in Fig. 12.

Fig. 12 revealed that the rate of uptake of dye on adsorbent increased with the increase in temperature. This is mainly due to the increased surface activity of adsorbent at higher temperature. The enhanced adsorption may be due to increase in availability of active surface sites and increased porosity at higher temperature. Furthermore, this may also be a result of rise in mobility of the dye molecules with rise in temperature. This suggested that safranin dye adsorption onto soybean hull was endothermic [40].

The thermodynamic parameters provide in-depth information about the energetic changes associated with adsorption process. The thermodynamic parameters, namely, the standard Gibbs energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) of the adsorption of the safranin dye onto the soybean hull were determined by using the Eqs. (10), (11), and

Table 3
Langmuir, Freundlich, and Temkin constants at different temperatures

	Freundlich Constants			Langmuir Constants			Temkin Constants		
Temperature (°C)	n	K_f (L g^{-1})	R^2	Q_0 (mg g^{-1})	b	R^2	A_T (L mg^{-1})	B_T (J mol^{-1})	R^2
30	0.3524	0.0014	0.9799	11.80	0.073	0.9928	205.38	8.20	0.9973
40	0.4120	0.3343	0.9580	14.99	0.082	0.9185	183.08	6.68	0.9779
50	0.7781	0.2665	0.9511	29.49	0.077	0.9430	121.25	4.96	0.9736

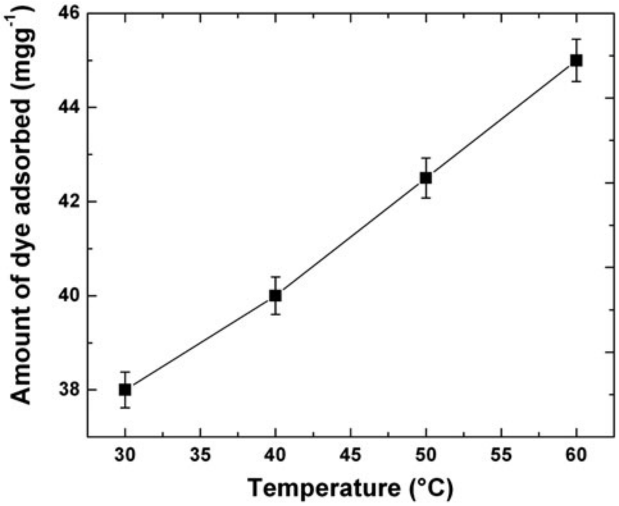

Fig. 12. Effect of temperature on adsorption of safranin on soybean hull.

(12) and the values for these parameters are presented in Table 4.

$$\Delta G = -RT\, ln\, b \tag{10}$$

$$\Delta H = R\left(\frac{T_2 T_1}{(T_2 - T_1)}\right) ln\left(\frac{b_2}{b_1}\right) \tag{11}$$

$$\Delta S = \frac{(\Delta H - \Delta G)}{T} \tag{12}$$

where T is the temperature, and R is the gas constant; b_1, and b_2 are Langmuir constants at (30, 40, and 50)°C, respectively, which were obtained from the slopes of the Langmuir isotherms.

The negative values of ΔG° revealed that the adsorption process was feasible and spontaneous. The ΔH° value was found to be positive which indicated that the process was endothermic in nature. The positive value of ΔS° showed the increased randomness at the solid- solution interface during the adsorption of dye. Also, from the Table 4 it can be noticed that the value for ΔH° is less than 40 kJ mol^{-1} which suggested the involvement of physical adsorption in the process [39]. The value for ΔG° ranges between 20 and 0 kJ mol^{-1} confirmed the physical adsorption dominates

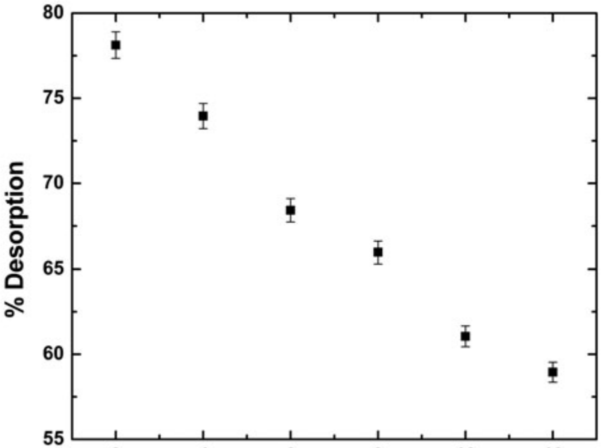

Fig. 13. Desorption plot for safranin from soybean hull.

Table 4
Thermodynamic parameters for adsorption of the safranin onto the soybean hull

ΔG° (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1})
30°C	40°C	50°C	19.24	66.41
−0.883	−1.155	−1.28		

the adsorption process of safranin dye on soybean hull adsorbent [41,42].

3.6. Desorption and recovery of adsorbents

After the dye adsorption, the materials (adsorbate and adsorbent) do not undergo any structural change, so they can be recovered and reused by desorption. Desorption study also helps to illustrate the mechanism and economical aspect of adsorption process.

The plot obtained in desorption study was inversely correlated with the pH effect in the adsorption process (Fig. 13). More number of positively charged sites at acidic pH favored desorption of cationic safranin dye. The percent desorption decreased from 78.12 to almost 59% as pH was increased from 2 to 12. This indicated that adsorption was mainly due to the ion-exchange mechanism [43,44].

4. Conclusions

The morphological characterization of soybean hull showed that it exhibited the presence of hydroxyl and carbonyl functional groups. Its porous and amorphous surface, as revealed by SEM and XRD studies and negative zeta potential assisted the process of adsorption. The removal efficiency was pH dependent and the adsorption equilibrium was obtained within 20 min. The removal efficiency of dye was found to be >80%. The various thermodynamic parameters were evaluated which suggested that the process was spontaneous, endothermic, and dominating mechanism involved was the physical adsorption. The kinetic experimental results suggested that the adsorption process obeyed pseudo-second-order kinetic model. Desorption study revealed that the adsorbent can be efficiently recovered. Based on these results it can be concluded that the soybean hull, a low-cost agro-waste material is a potential adsorbent for removal of safranin from the wastewater.

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Nomenclature

C_i — initial dye concentration
C_f — final dye concentration
C_e — equilibrium dye concentration
q_e — adsorption capacity
q_{eq} — adsorption capacity at equilibrium
q_t — amount of dye adsorbed at time, t
R_L — dimensionless constant separation factor
R^2 — correlation coefficient
K_{ad} — equilibrium rate constant of pseudo-first-order adsorption
K_2 — equilibrium rate constant of pseudo-second-order adsorption
λ_{max} — maximum wavelength
V — total volume of dye solution used
M — weight of adsorbent used
Q_o — Langmuir constant related to maximum single-layer adsorption capacity
b — Langmuir constant related to free energy or adsorption enthalpy
K_f — Freundlich constant related to adsorption capacity
n — Freundlich constant related to adsorption intensity
B_T — Temkin constant
A_T — Temkin constant related to the heat of adsorption
R — universal gas constant
ΔG° — Gibbs free energy
ΔH° — enthalpy
ΔS° — entropy
t — time
T — absolute temperature

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