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Alternative usage of edible deoiled cake for decolonization of Reactive Red dye

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ABSTRACT

The present study explores the feasibility of using cheap renewable materials such as deoiled cake as an adsorbent for the removal of reactive red dye from aqueous solutions. Adsorption studies were carried out (batch mode) at varying initial dye concentrations, pH values and contact times. The results showed the highest dye adsorption capacity at pH ~7, under a constant temperature of 30 ± 2˚C (the equilibrium state), at an optimized adsorption period of 6 h. On analysis of different equilibrium isotherms, Redlich–Peterson and Sip isotherms were found to be the best representatives for reactive red dye sorption on the deoiled cake adsorbent studied.

Keywords: Adsorption; Red dye removal; Deoiled cake; Isotherms

1. Introduction

Many industries use dyes and pigments to color their products, namely textile, tannery, food, paper and pulp, printing, carpet, mineral processing, etc., which leads to heavy dye-enriched effluents with high coloration, suspended solids, dissolved organics, and inorganic salts. In addition to their undesirable coloration, some of these dyes have been reported to undergo degradation, resulting in the production of carcinogens and toxic products, thus minimizing the effectiveness of isolated biological degradation [1,2]. Removal of these dyes from wastewater using adsorption techniques has received a considerable attention in recent years by dint of the increased magnitude of dye effluents as well as simplicity in analysis (as well as provision of a comparative physisorptive profile of various adsorbent characteristics) [3].

Thus, adsorption remains a promising technique that produces good-quality effluents with low levels of dissolved organic compounds such as dyes. There is a growing interest in using cheap renewable materials for the adsorption of dyes to replace activated carbon, which has led to investigations on numerous low-cost adsorbents, viz. products comprising agricultural residues (such as wood dust, bagasse, fruit peel, wheat straw, and apple pomance) to that of industrial residues (such as activated slag, bagasse flyash, etc.), which have been employed in the recent past [4–8].

The objective of the present study is to evaluate the effectiveness of deoiled castor oil cake for the adsorption of Reactive Red dye from aqueous solutions. The adsorption of red dye was studied in

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relation to varying initial pH values, adsorbent dosages, initial concentrations and contact times for the optimization of adsorption parameters. The kinetic and isotherm analysis studies of reactive red dye adsorption were studied using different isotherm models.

2. Materials and methods

2.1. Selection and characterization of the adsorbent samples

Deoiled castor oil cake was collected from the local oil mill. The sample was crushed properly, was treated with hydrogen peroxide and left for 24 h to oxidize the organic impurities present in it. The treated samples were then thoroughly washed with distilled water and dried in the oven at 110 ± 5˚C to remove the moisture present in it. The oven-dried sample was sieved to obtain the desired particle size, and desiccated and preserved for subsequent analysis and experiments.

2.2. Adsorbate

Reactive red dye of analytical reagent grade supplied by Ranbaxy Laboratories Ltd., India, was used for the preparation of synthetic adsorbate of various concentrations in the range of 100–700 mg/L. The required quantity of dye was accurately weighed and dissolved in distilled water and made up to 1 L. The structure of the dye is presented in Fig. 1.

2.3. Analysis of the dye

The equilibrium concentrations were determined using Systronics UV–Vis spectrophotometer (characteristic peak at spectrophotometric wavelength of ~535 nm).

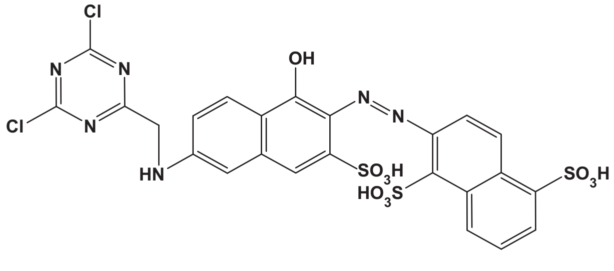

Fig. 1. Chemical structure of reactive red dye.

2.4. Adsorption studies (batch studies)

To study the effect of important parameters like pH, adsorbent dosage, initial concentration, and contact time, batch experiments were conducted at room temperature (30 ± 2˚C). For each experiment, 100 mL of dye solution of known concentration, at optimum pH (the pH of the adsorbate solution was adjusted using HCl and NaOH) and known concentrations of adsorbents, was taken in 250-ml conical flasks and agitated occasionally. The amount of red dye adsorbed by the adsorbent was calculated from the differences between the red dye concentration at initial time and equilibration time using the following equation:

$$Q = V\frac{C_0 - C_e}{M} \tag{1}$$

where C_0 is the initial sorbate concentration (mg/L), C_e is the equilibrium concentration in the solution (mg/L), V is the solution volume (L), and M is the mass of the adsorbent (g).

2.5. Effect of initial pH

The adsorption of dye was studied over a pH range of 2–10. The pH of the solution was adjusted using HCl and NaOH solution of 0.1 M at room temperature of 30 ± 2˚C and the studies were carried out for 24 h. The optimum dosage of the red dye solution was 500 ppm and the adsorbent dosage was kept at 5 g/L.

2.6. Adsorption isotherm study

The adsorption isotherm studies were carried out to compare the adsorption capacity at different adsorbent dosages. Two-parameter models, such as Langmuir and Freundlich and three parameter models such as Redlich–Peterson and Sip isotherms, were used to describe the equilibrium adsorption of the dye with deoiled cake.

2.7. Error analysis

In order to validate the isotherm models, different error functions of non-linear regressions had been used previously by a number of researchers in the field [9–13]. For the present study, to calculate the error function of non-linear regression, MATLAB (v 7.0) was used. In this version, the method of linear descent is used in early iterations and then gradually switched to the Gauss–Newton approach [14].

3. Results and discussion

3.1. Effect of pH

The surface charges of the adsorbents affect the pH of the dye solution. In fact, the functional groups present on the surface of the adsorbent were expected to be affected by change in the pH and the change in the functional groups, thereby leading to a shift in the kinetics of the reaction and the equilibrium characteristics of the adsorption process [15]. The adsorption of red dye was studied over the pH range of 2–10 and is shown in Fig. 2. Thus there is a distinct improvement of adsorption in the acidic range of pH, i.e. pH 2 (74.57%) and pH 4 (69.6%). However, a fairly high degradation was also achieved at pH 7 (65.5%), which is the highest adsorption of all the pH conditions, without extraneous pretreatment, and therefore pH 7 was taken for further studies.

3.2. Effect of adsorbent dosage

The effects of adsorbent dosage on the uptake of red dye by the deoiled castor cake were studied. The adsorbent dosage was varied from 0.5 to 5 g/L at a fixed initial red dye concentration of 500 ppm. The results are shown in Fig. 3. It can be observed that the removal of red dye increases with increase in adsorbent dosage due to higher increased surface area. However, the dye removal decreased after the adsorbent dosage of 4 g/L. It could also be due to clustering of deoiled castor cake at such high dosage. In fact, studies elsewhere reveal differential amounts of the adsorbate adsorbed (after equilibrium) per unit weight of the adsorbent for each adsorbate (dye) [15–17].

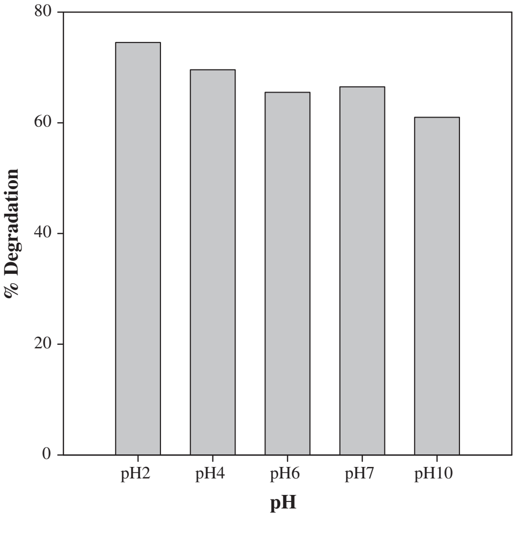

Fig. 2. Adsorption of reactive red dye by deoiled cake as a function of pH.

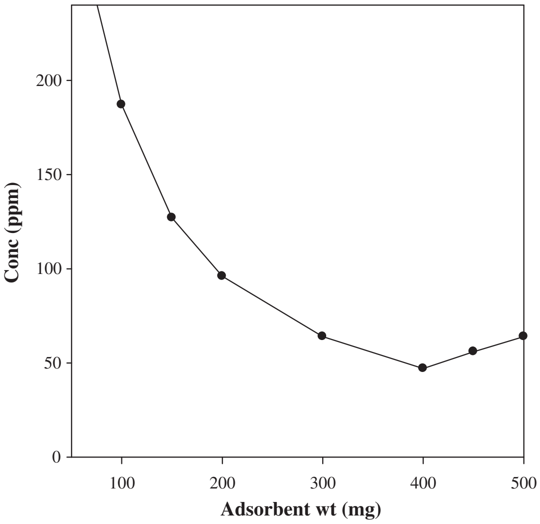

Fig. 3. Effect of deoiled cake dosage on the removal of dye.

3.3. Effect of initial concentration of red dye and contact time on adsorption by castor cake

Fig. 4 presents the effect of initial concentration of red dye adsorption on deoiled castor cake as a function of time. The plot shows that there is an increase in the adsorption of red dye per unit weight of adsorbent with increase in initial concentration. The uptake of red dye at initial stages of the contact time was rapid, and as it reached to equilibrium the uptake rate was found to decrease and remained almost constant at higher concentration. The equilibrium time is one of the important parameters for economical design of treatment unit. Based on the result, the contact time was fixed as 360 min for deoiled castor cake.

3.4. Infra red spectral analysis

The FTIR spectrums of the unreacted and reacted deoiled castor cake adsorbents are shown in Figs. 5(a) and 5(b). The broad band spectrums of these adsorbents fall in the range of 3,500–2,800 cm^{-1}, which is associated with the –OH group. The peaks at 1,659 and 1,541 cm^{-1} correspond to the C=C stretching vibration. The peak at 608 cm^{-1} can be attributed to the alkyl halides. This indicates the presence of several functional groups which can be effective for trapping the dye molecule.

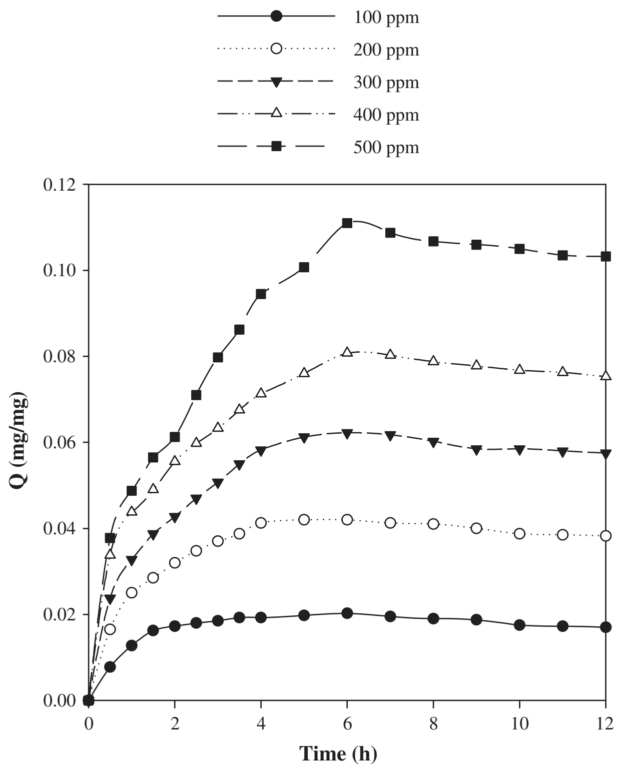

Fig. 4. Typical concentrations—time profile of dye adsorption on the deoiled cake.

3.5. Adsorption isotherm study

Various adsorption isotherm equations have been used to study the nature of adsorption. The most commonly used isotherms are Langmuir and Freundlich isotherms. The Langmuir isotherm equation [18] is valid for homogeneous surfaces. On the other hand, Freundlich isotherm equation [19] is highly suitable for heterogeneous surfaces over restricted ranges of concentrations. The Redlich–Peterson equation [20] is widely used as a compromise between Langmuir and Freundlich isotherms. The Redlich–Peterson equation is used to represent solute adsorption data on heterogeneous surfaces. Sip model [21] equation follows Freundlich isotherm at lower solute concentrations and follows Langmuir isotherm at higher solute concentrations.

In present study, the adsorption of the dye was evaluated and compared with two- and three-parameter single-solute isotherm models. The two-parameter models (Langmuir and Freundlich isotherm) can be easily linearized, and hence the parameters can easily be obtained by using least square method. For three-parameter models (Redlich–Peterson and Sip isotherms), MATLAB was used and the percent deviation was calculated as follows:

$$\text{Percent deviation} = \frac{q_{\text{e,exp}} - q_{\text{e,cal}}}{q_{\text{e,cal}}} \times 100 \tag{2}$$

where $q_{\text{e,exp}}$ is q_e observed under experimental conditions; $q_{\text{e,calc}}$ is q_e calculated using isotherm data.

Langmuir's equation is expressed as follows:

$$q_\text{e} = \frac{q_\text{m} b C_\text{e}}{1 + bC_\text{e}} \tag{3}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g), q_m is the maximum adsorption capacity (mg/g), and b is the constant related to the free energy of adsorption (L/mg).

The Freundlich equation is an empirical model that considers heterogeneous adsorptive energies on the adsorbent surface, and the equation is expressed as follows:

$$q_\text{e} = K_\text{F} C_\text{e}^{1/n} \tag{4}$$

where K_F is a constant, which indicates the relative adsorption capacity of the adsorbent ($(\text{mg}^{1-(1/n)}\,\text{L}^{1/n})/\text{g}$) and n is a constant intensity of adsorption.

The Redlich–Peterson equation is expressed as follows:

$$q_\text{e} = \frac{K_\text{RP} C_\text{e}}{\left[1 + (\alpha_\text{RP} C_\text{e})^{\beta}\right]} \tag{5}$$

where K_RP (L/g) and α_RP are Redlich–Peterson isotherm constants, and β is the exponent which lies between 0 and 1.

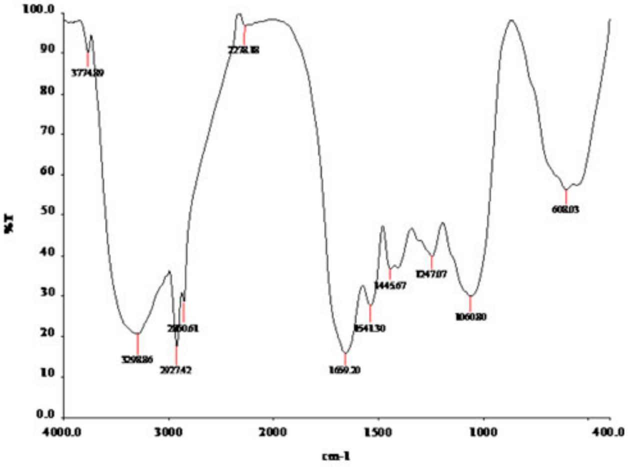

Fig. 5(a). FTIR spectrum of unreacted deoiled castor cake.

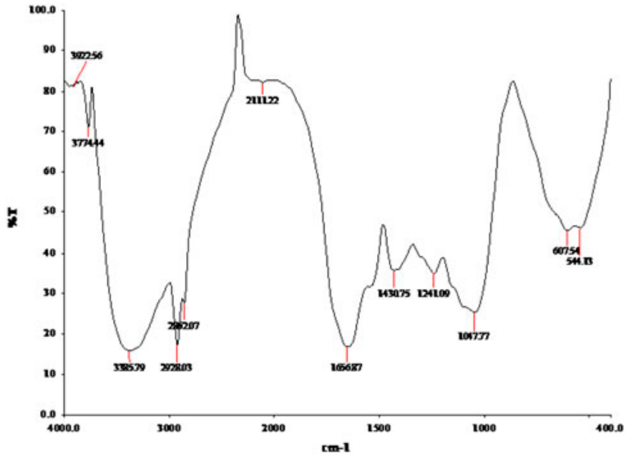

Fig. 5(b). FTIR spectrum of reacted deoiled castor cake.

Sip isotherm model equation is expressed as follows:

$$q_e = \frac{q_m (K_S C_e)^\beta}{\left[1 + (K_S C_e)^\beta\right]} \qquad (6)$$

3.6. Isotherm results interpretation

Figs. 6 and 7 represent the comparison of experimental and calculated amount of red dye adsorbed on deoiled castor cake. The criteria for selection of the isotherm model were based on correlation coefficient and standard deviation of residuals (Sy.x). The residual of a sample is the difference between the sample and the *estimated* value based on the prediction by isotherm models. Thus, the standard deviation of a residual is an effective measure of error between the estimated and predicted values. Based on these values, the Langmuir isotherm model could reasonably fit the data (correlation coefficient of 0.97 and standard deviation of residuals of 2.28). In order to further minimize the error, and hence to get best fit, three-parameter models were tried and compared [21]. The three to (Redlich–Peterson and Sip isotherms) and three-parameter models could best fit the data of red dye adsorption. Remarkable similarity was observed for the correlation coefficients, absolute sum of squares, and standard deviation of residuals (Sy.x) of these two models. The fitted parameter values for all the isotherms used are shown in Table 1.

3.6. Validation of adsorption isotherm models

All the four isotherm models studied show high correlation coefficient ($R^2 = 0.97$) indicating the possibility of simultaneous validity of multiple isotherm models. On comparison of the correlation coefficient and standard deviation of residuals of the four isotherm models, it can be observed that the three-parameter model provided the best fit. Fig. 8 also indicates that the distribution of percent deviation for three parameter models is reduced with increase in equilibrium concentration (1.688–0.2235%). The best fitting out of the two- and three-parameter isotherm models are the three-parameter isotherm models (with the order Sip > Redlich–Peterson > Langmuir > Freundlich).

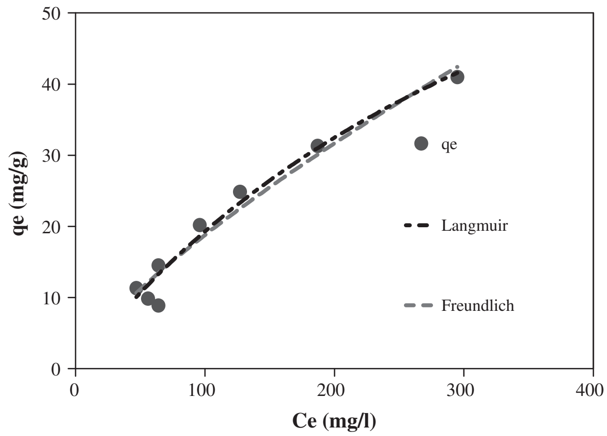

Fig. 6. The non-linearized Langmuir and Freundlich adsorption isotherms (two parameters) for dye with deoiled cake.

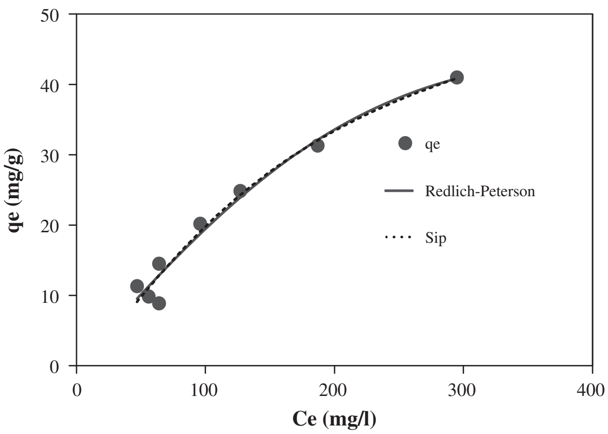

Fig. 7. The non-linearized Redlich–Peterson and Sip adsorption isotherms (three parameters) for dye with deoiled cake.

Table 1
The fitted parameters' values for all the isotherms used

Isotherms	Parameters	Values
Langmuir	q_m	102.1
	B	0.0232
	R^2	0.9662
	Sy.x	2.28
Freundlich	K_F	0.585
	N	1.328
	R^2	0.9562
	Sy.x	2.6
RP model	K_{RP}	0.205
	β	6.44×10^{-6}
	α_{RP}	1.975
	R^2	0.97
	Sy.x	2.34
Sip	q_m	60.91
	K_S	0.005776
	B	1.333
	R^2	0.972
	Sy.x	2.316

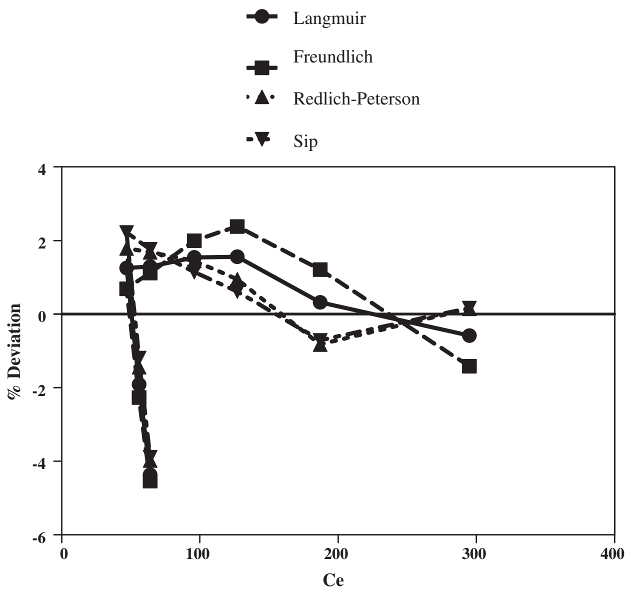

Fig. 8. Comparison of percentage deviation of isotherms for deoiled cake adsorption.

4. Conclusions

In the present study, adsorption (batch mode) of red dye on deoiled castor cake was investigated. It shows that deoiled castor oil cake is an effective adsorbent for the removal of red dye from aqueous solutions. The optimum conditions for red dye removal with respect to adsorbent dose (of deoiled castor), pH, equilibrium time and concentration were estimated to be 4 g/L, pH ~7, 6 h, and 500 ppm, respectively. Equilibrium adsorption data for red dye by the deoiled castor cake were also found to be best represented by the Sip model for its from aqueous solutions.

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