

# Adsorption isotherms, kinetics and column operations for the removal of hazardous dye, Tartrazine from aqueous solutions using waste materials—Bottom Ash and De-Oiled Soya, as adsorbents

Alok Mittal\*, Jyoti Mittal, Lisha Kurup

*Department of Applied Chemistry, Maulana Azad National Institute of Technology, Bhopal 462 007, India*

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## Abstract

Adsorbents, Bottom Ash (a power plant waste) and De-Oiled Soya (an agricultural waste) exhibit good efficacy to adsorb a highly toxic dye, Tartrazine. Through the batch technique equilibrium uptake of the dye is observed at different concentrations, pH of the solution, dosage of adsorbents and sieve size of adsorbents. Langmuir and Freundlich adsorption isotherms are successfully employed on both the adsorbents and on the basis of these models the thermodynamic parameters are evaluated. Kinetic investigations reveal that more than 50% adsorption of dye is achieved in about 1 h in both the cases, whereas, equilibrium establishment takes about 3–4 h. The linear plots obtained in rate constant and mass transfer studies further confirm the applicability of first order rate expression and mass transfer model, respectively. The kinetic data treated to identify rate controlling step of the ongoing adsorption processes indicate that for both the systems, particle diffusion process is predominant at higher concentrations, while film diffusion takes place at lower concentrations. The column studies reveal that about 96% saturation of both the columns is attained during their exhaustion, while about 88 and 84% of the dye material is recovered by eluting dilute NaOH solution through exhausted Bottom Ash and De-Oiled Soya columns, respectively.

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*Keywords:* Tartrazine; Azo dye; Adsorption; Bottom Ash; De-Oiled Soya; Waste materials

## 1. Introduction

Today, almost every aspect of modern living poses potential health risks. Our environment is a complex and dynamic system, in which all forms of life are interdependent. However, man is constantly changing the basic characteristics of his environment by disposing hazardous materials like dyes into water. Unfortunately the toxic dyes once pass into the waste water cause detrimental effects on the human/animal health, which are not only limited to themselves but may be passed on to further generation by the way of genetic mutations, birth defects, inherited diseases and so on.

In order to remove hazardous materials, like dyes, adsorption is a method which has gained considerable attention in the recent past. Adsorption is such a useful and simple technique, which allows gathering of both kinetic and equilib-

rium data without needing any sophisticated instrument [1–3]. Although many mathematical models are available for predicting adsorption, the acquisition of equilibrium data remains fundamental for validating all such models. Consequently, there has been a growing interest in developing and implementing various potential adsorbents for the removal of specific organics from water [4–7] and researchers are always in a hunt for developing more suitable, efficient, cheap and easily accessible types of adsorbents, particularly from the waste materials.

The present work is an attempt to develop two waste materials—Bottom Ash and De-Oiled Soya, as efficient adsorbents for the removal of a hazardous dye, Tartrazine from aqueous solutions. As far as usage of Tartrazine is concern, it is used in drugs especially for the shells of medicinal capsules, syrups and cosmetics [8,9]. It is also used in variety of food materials and confectionary products as coloring material [10]. It possesses high water solubility, which maximizes its chance to be found as contaminant in industrial effluents. For the humans Tartrazine is considered highly toxic and can act as catalyst in

\* Corresponding author. Tel.: +91 942 5025427; fax: +91 755 2670904.  
E-mail address: aljymittal@yahoo.co.in (A. Mittal).

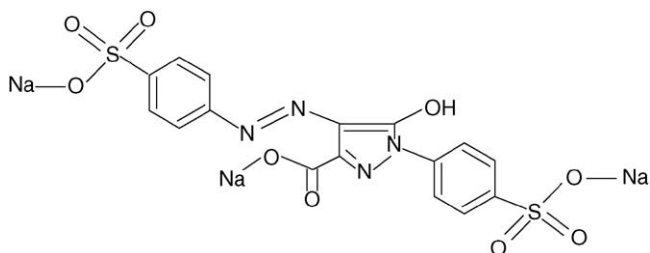
hyperactivity [11] and other behavioral problems [12]. It may also cause asthma, migraines, eczema, thyroid cancer and lupus [13–18].

It is therefore considered worthwhile to remove Tartrazine from the waste water by adsorbing it over two different types of waste materials. The waste material ‘Bottom Ash’ is an undesired collected material procured from thermal power generation plants after combustion of coke. Its disposal on the land gives rise to infertility of soil [19]. It has been successfully used as potential adsorbent for the removal of metals [20] as well as dyes [21,22]. The other adsorbent ‘De-Oiled Soya’ is a processed out waste material obtained from soya oil industries. De-Oiled Soya could be used as animal/bird food but the reports suggest that more than 170 ppm hexane residue in the De-Oiled Soya makes it toxic to the birds, animals and fishes [23,24]. It has also been used as an efficient adsorbent for the removal of few dyes by our laboratory [22,25,26].

## 2. Experimental

Tartrazine, IUPAC name trisodium-5-hydroxy-1-(4-sulfonatophenyl)-4-(4-sulfonatophenylazo)-H-pyrazole-3-carboxylate ( $C_{16}H_9N_4Na_3O_9S_2$ , molecular weight 534.4) was obtained from M/s Merck. All other chemicals used were of AR grade.

Throughout the studies all the solutions including the stock solution (1 mM) was prepared in doubly distilled water. The absorbance measurements for the solutions were recorded on UV–visible spectrophotometer, Model 117 (M/s Systronics, Ahmedabad, India) over the wavelength range of 200–500 nm.



The chemical analysis of the adsorbents was achieved by conventional methods as reported by Vogel [27]. For the surface studies of the adsorbents scanning electron microscopy was performed using SEM-501 electron microscopy and for calculating the surface area of the particles a Quantasorb surface area analyzer was used. Mercury porosimeter and specific gravity bottles were used to determine the porosity and density of the adsorbent materials, respectively. By applying Ni-filtered Cu  $K\alpha$  radiation, Philips X-diffractometer was used for X-ray measurement, whereas HP FT-IR was used for recording Infrared spectra of the adsorbents.

Adsorbent ‘Bottom Ash’ was obtained from thermal power station of M/s B.H.E.L., Bhopal, India. It is a grayish black dust, granules spherical in shape. The sub-bituminous coal used by TPS was obtained from M/s South Eastern Coal Field Limited, Chirmiri, Sarguja (India). The other adsorbent ‘De-Oiled Soya’ was a free gift from Surya Agro oils.

Both the adsorbents were first washed in doubly distilled water and then subjected to the treatment with hydrogen peroxide for 24 h, which oxidizes the organic components present in the adsorbents. The material was then filtered and washed with doubly distilled water and subjected to different temperatures for activation.

### 2.1. Adsorption studies

The batch technique was used for the adsorption studies. The investigations were performed at different concentrations and temperatures. After a good deal of investigations, concentration range of  $1 \times 10^{-5}$  to  $1 \times 10^{-4}$  M was chosen. Dye solutions of volume 25 mL each were taken in a series of 100 mL measuring flasks and a known amount of adsorbent was added into each flask. The mixture was agitated intermittently and then kept for 24 h for saturation. It was observed that the 3–4 h were sufficient for establishing the equilibrium. Thereafter the supernatant liquid was filtered using Whatmann filter paper No. 42 and uptake of dye was observed spectrophotometrically at  $\lambda_{max}$  426 nm.

### 2.2. Kinetic studies

For the kinetic investigations 25 mL of the dye solution was kept in different measuring flask with either 0.1 g of Bottom Ash or 0.05 g of De-Oiled Soya. The mixture was then subjected to intermittent shaking at different time intervals and 30, 40 and 50 °C temperatures. The solutions were then filtered and the filtrate was analyzed spectrophotometrically for the uptake of the dye.

### 2.3. Column operations

For the column operations, initially the slurry of different adsorbents was prepared by mixing a known amount of each adsorbent in distilled water in separate beakers and the mixture thus obtained was kept overnight. Then the glass column of length 30 cm and internal diameter 1 cm was filled with the selected adsorbent on a glass wool support. To avoid air entrapment, the column was first filled with water then the slurry of each adsorbent was introduced carefully in each column, which slowly settles down by displacing the heel of water. The dye solution of particular concentration was then allowed to percolate through each column at a flow rate of  $0.5 \text{ mL min}^{-1}$ . After almost 90–95% exhaustion the column operation was stopped.

### 2.4. Dye recovery and column regeneration

In order to retrieve the adsorbed dye as well as to reuse the exhausted columns column regeneration was carried out. The eluent selected for this process was NaOH solution of pH 11 due to exceptionally good solubility of Tartrazine in alkaline medium. The eluent was passed at a flow rate of  $0.5 \text{ mL min}^{-1}$  and it was observed that 12–20 aliquots of 5 mL each of the

NaOH solution was sufficient for complete recovery of the dye. Subsequently the column was washed with hot water.

### 3. Results and discussion

#### 3.1. Characterization of the adsorbent material

Chemical constituents of the Bottom Ash and De-Oiled Soya were determined using standard methods of chemical analysis and presented in Table 1. Physical characteristics like, surface area, porosity and density of both the adsorbents were determined by the methods given in the experimental section of this paper and are given on Table 2. To find out the nature of the adsorbents, 1 g sample of activated Bottom Ash and De-Oiled Soya were stirred separately with 100 mL de-ionized water of pH 6.8 for 2 h and left for 24 h in an air tight conical flask. These were then filtered and the pH of the filtrate was measured. It was observed that in both cases pH of the solution decreases indicating thereby acidic nature of Bottom Ash as well as De-Oiled Soya.

Fig. 1a and b presents the *d*-spacing values provided by X-ray diffraction (XRD) spectra of the activated Bottom Ash and De-Oiled Soya, respectively. Fig. 1a reflects the presence of mainly alumina ( $\text{Al}_2\text{O}_3$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), beaverite [ $\text{Pb}(\text{Cu},\text{Fe},\text{Al})_3(\text{SO}_4)_2(\text{OH})_6$ ], borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) and kaolinite [ $2\{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\}$ ] in Bottom Ash. In case of De-Oiled Soya the XRD spectrum does not give any major peak(s). This may be due to lack of inorganic substances, as also observed in the qualitative analysis (Table 1). X-ray diffraction analysis of both adsorbents also showed a predominance of poorly soluble minerals, which indicate a high chemical stability of Bottom Ash and De-Oiled Soya. The SEM photographs at different magnifications recognized the granules of the activated Bottom Ash

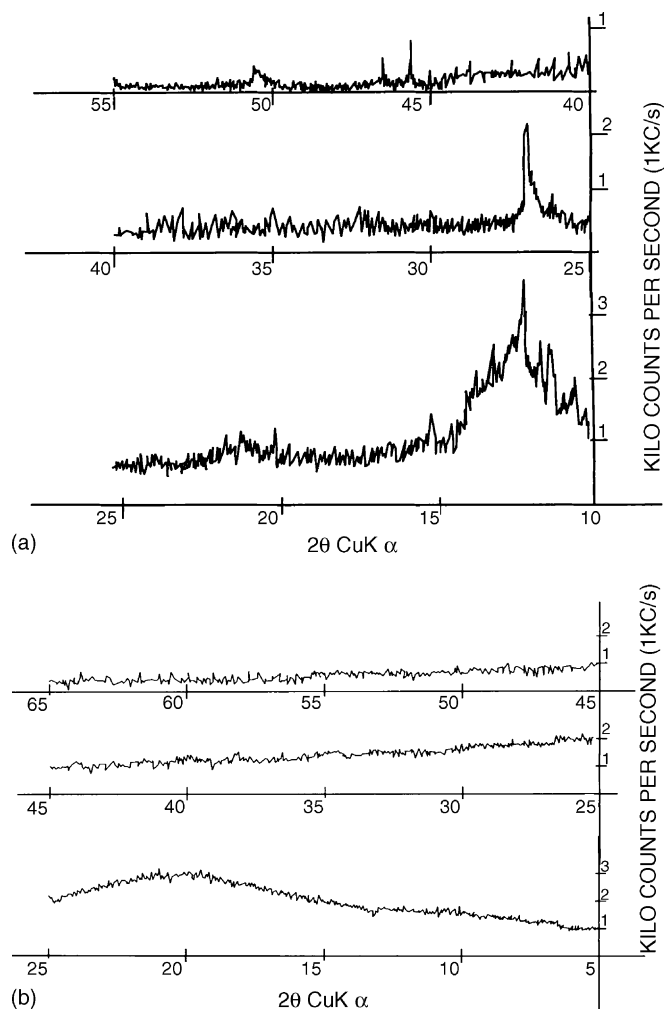


Fig. 1. (a) X-ray diffraction spectrum of the activated Bottom Ash. (b) X-ray diffraction (XRD) spectrum of the activated De-Oiled Soya.

and activated De-Oiled Soya almost spherical and are presented in Fig. 2a and b, respectively.

#### 3.2. Effect of pH

The adsorption studies of Tartrazine on Bottom Ash and De-Oiled Soya carried out at all the temperatures and varying pH range (pH 2–8) showed a decline in percentage removal of dye at higher pH values. A typical pH versus percentage removal of the dye at 30 °C is presented in Fig. 3, which depicts a constant decrease in the uptake of dye above pH 6.0 and thereafter no change in the adsorbed amount was observed. Maximum uptake of the dye about 77.30 and 85.31% was achieved at pH 2.0 for Bottom Ash and De-Oiled Soya, respectively. Therefore, pH 2.0 was selected as an optimum value for performing subsequent studies.

Fig. 3 shows maximum adsorption of the dye over both the adsorbents at low pH. This clearly indicates increase of protonation due to neutralization of negative charge at the surface of the adsorbents, which facilitates diffusion and provides more active surface of the adsorbents, resulting thereby greater adsorption at their surfaces. A decrease in the percentage removal with

Table 1  
Chemical constituents of Bottom Ash and De-Oiled Soya

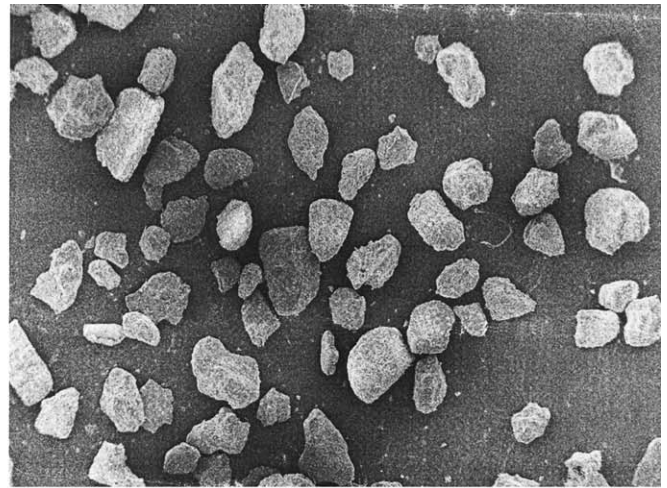
Bottom Ash		De-Oiled Soya	
Constituents	Percentage by weight	Constituents	Percentage by weight
Moisture	15	Moisture	11
SiO <sub>2</sub>	45.4	Fibre	6
Al <sub>2</sub> O <sub>3</sub>	19.3	SiO <sub>2</sub>	2
Fe <sub>2</sub> O <sub>3</sub>	9.7	Ca	0.2
CaO	15.3	P	0.7
MgO	3.1		
Na <sub>2</sub> O	1.0		

Table 2  
Physical parameters of Bottom Ash and De-Oiled Soya

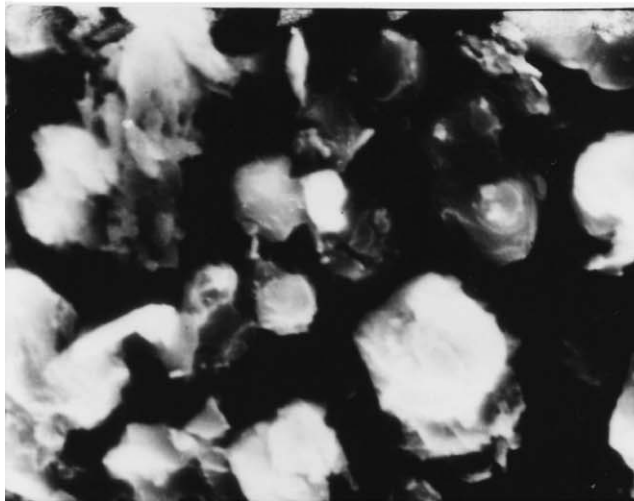
Parameter	Value	
	Bottom Ash	De-Oiled Soya
Surface area (cm <sup>2</sup> g <sup>-1</sup> )	870.5	728.6
Porosity (%)	46	67
Density (g mL <sup>-1</sup> )	0.6301	0.5614
Loss on ignition (%)	1.14	4.27



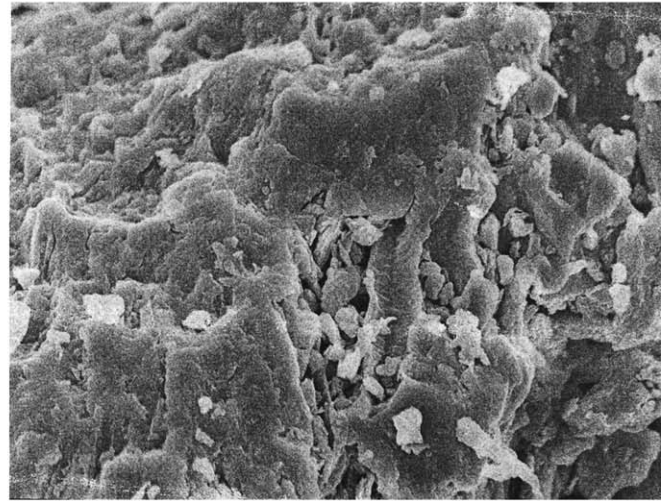
(i)



(i)

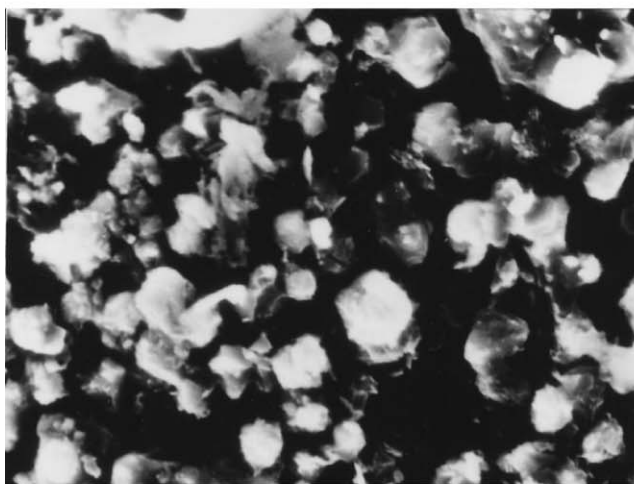


(ii)



(b)

(ii)



(a)

(iii)

Fig. 2. (a) Scanning electron microscopic photographs of the activated bottom ash particles at different magnifications: (i)  $1 \times 320$ ; (ii)  $1 \times 160$ ; (iii)  $1 \times 80$ . (b) Scanning electron microscopic photographs of the activated De-Oiled Soya granules at different magnifications (i)  $1 \times 320$  and (ii)  $1 \times 160$ .

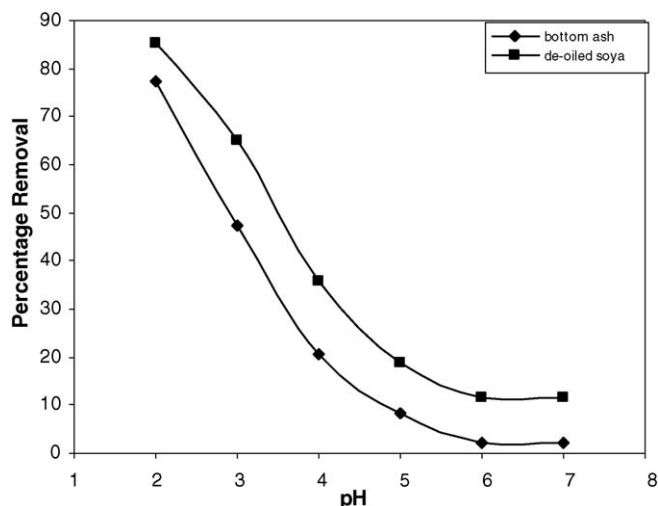
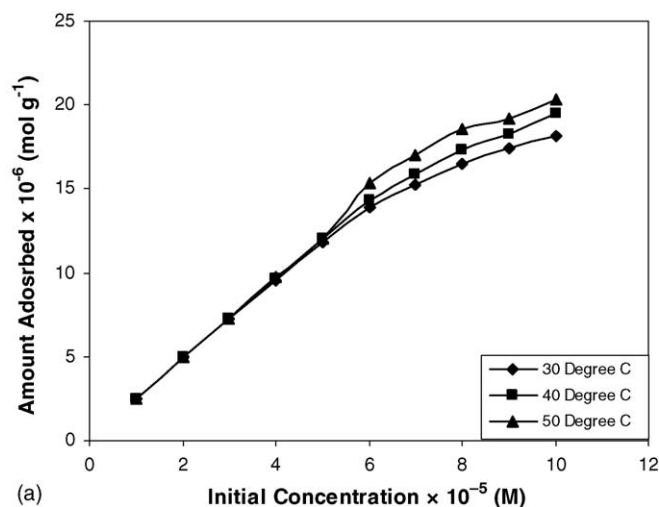


Fig. 3. Effect of pH on uptake of Tartrazine by Bottom Ash and De-Oiled Soya at 30 °C [Bottom Ash: concentration =  $9 \times 10^{-5}$  M, adsorbent dose = 0.1 g, particle size = 0.08–0.15 mm], [De-Oiled Soya: concentration =  $9 \times 10^{-5}$  M, adsorbent dose = 0.05 g, particle size = 0.30–0.425 mm].

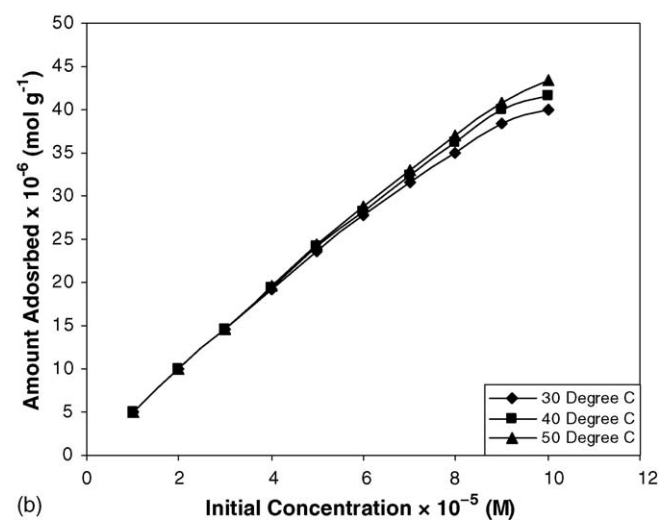
increase in pH may be due to deprotonation, which retards the diffusion.

### 3.3. Effect of concentration

By maintaining a fixed pH of 2.0 and volume of the dye solution 25 mL, the adsorption on Bottom Ash and De-Oiled Soya was carried out in the concentration range from  $1 \times 10^{-5}$  to  $1 \times 10^{-4}$  M solutions of Tartrazine at temperatures 30, 40 and 50 °C. Fig. 4a and b reveals that for both the adsorbents, at concentrations upto  $2 \times 10^{-5}$  M almost 100% removal of the dye is achieved and the amount of dye adsorbed increases with the increase in the concentration of the solution. It is found that the maximum uptakes of the dye  $2.033 \times 10^{-5}$  and  $4.348 \times 10^{-5}$  mol g<sup>-1</sup> were obtained for Bottom Ash and De-Oiled Soya, respectively, at concentration of  $1 \times 10^{-4}$  M in each case and at 50 °C. An increase in adsorption of dye with rising temperatures indicates the endothermic nature of the process in both the cases.



(a)



(b)

Fig. 4. (a) Effect of initial concentration and temperature on the removal of Tartrazine by Bottom Ash [adsorbent dose = 0.1 g, particle size = 0.08–0.15 mm, pH 2.0]. (b) Effect of initial concentration and temperature on the removal of Tartrazine by De-Oiled Soya [adsorbent dose = 0.05 g, particle size = 0.30–0.425 mm, pH 2.0].

Table 3  
Freundlich and Langmuir constants at different temperatures for the removal of Tartrazine

Adsorbent	Freundlich constants					
	<i>n</i>			<i>K<sub>F</sub></i>		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Bottom Ash	39.714	37.078	34.341	1.00	1.00	1.00
De-Oiled Soya	31.437	37.078	30.358	1.00	1.00	1.00
Adsorbent	Langmuir constants					
	<i>Q<sub>0</sub></i> × 10 <sup>-5</sup>			<i>b</i> × 10 <sup>5</sup>		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Bottom Ash	1.890	2.105	2.358	5.75	5.52	5.65
De-Oiled Soya	3.984	4.292	4.608	6.12	7.28	8.03

Bottom Ash: adsorbent dose = 0.1 g, particle size 0.08–0.15 mm, pH 2.0. De-Oiled Soya: adsorbent dose = 0.05 g, particle size = 0.30–0.425 mm, pH 2.0.



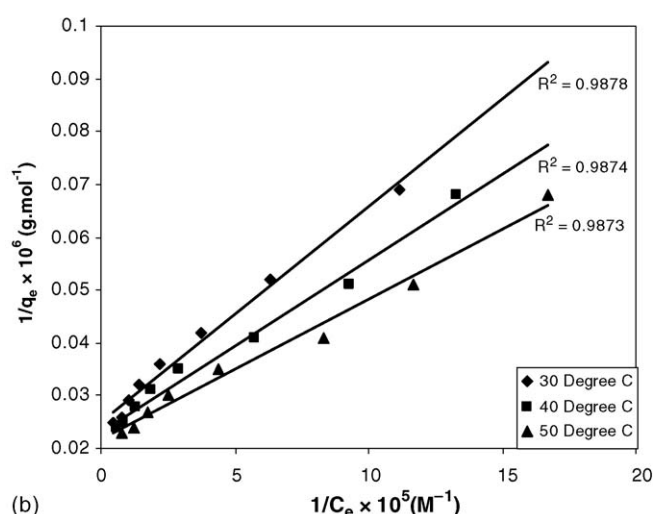
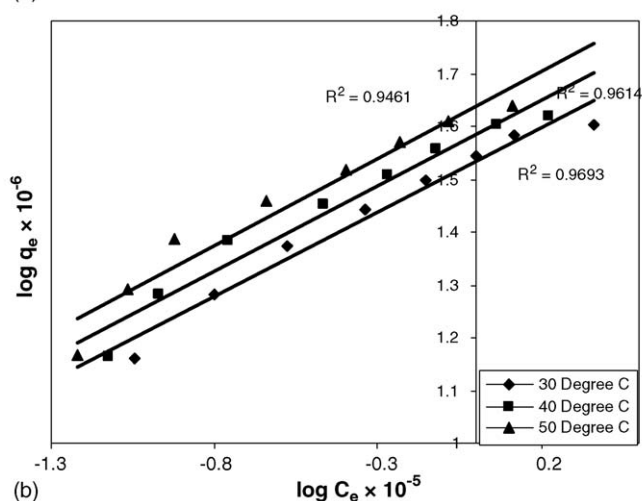
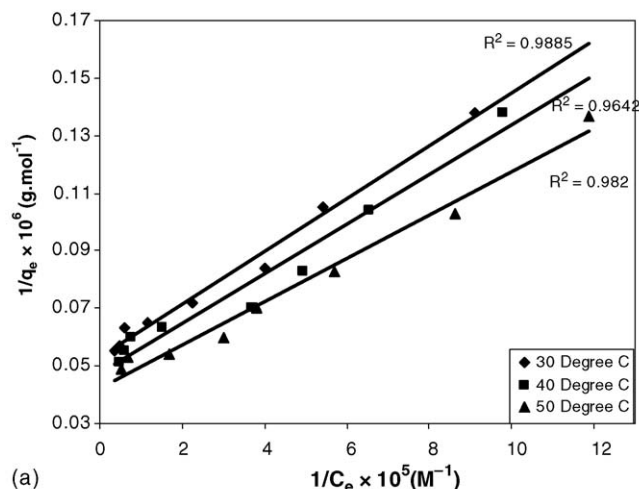
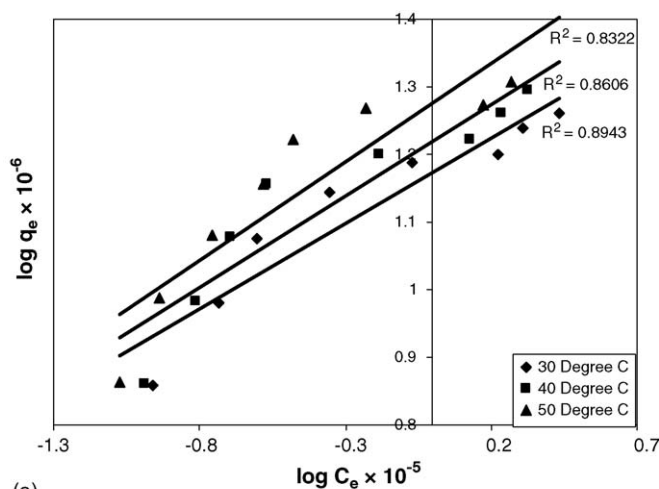


Fig. 5. (a) Freundlich adsorption isotherm for Tartrazine–Bottom Ash system [adsorbent dose = 0.1 g, particle size = 0.08–0.15 mm, pH 2.0]. (b) Freundlich adsorption isotherm for Tartrazine–De-Oiled Soya system [adsorbent dose = 0.05 g, particle size = 0.30–0.425 mm, pH 2.0].

Fig. 6. (a) Langmuir adsorption isotherm for Tartrazine–Bottom Ash [adsorbent dose = 0.1 g, particle size = 0.08–0.15 mm, pH 2.0]. (b) Langmuir adsorption isotherm for Tartrazine–De-Oiled Soya [adsorbent dose = 0.05 g, particle size = 0.30–0.425 mm, pH 2.0].

### 3.4. Adsorption isotherms

The validity of Freundlich and Langmuir isotherms were also confirmed by carrying out the adsorption of Tartrazine on both adsorbents at different temperatures. The Freundlich (Fig. 5a and b) and Langmuir (Fig. 6a and b) isotherms obtained at temperatures of 30, 40 and 50 °C are found linear in both the cases. These plots were then used to evaluate the values of respective constants, using well known Freundlich and Langmuir adsorption isotherm equations.

The values of Freundlich and Langmuir constants are listed in Table 3. For both the adsorbents, the adsorption capacity “ $K_F$ ” increases with increase in temperature and the same trend is shown by Langmuir constant “ $Q_o$ ”, which reflects the process to be endothermic in nature. The Langmuir constants were again used for calculating the thermodynamic parameters using well known equations and the values obtained are reported in Table 4.

The feasibility of the adsorption process is proved from the negative values of free energy ( $\Delta G^\circ$ ). The positive nature of the enthalpy change ( $\Delta H^\circ$ ) and the entropy change ( $\Delta S^\circ$ ) con-

Table 4  
Thermodynamic parameters for the uptake of Tartrazine over different adsorbents

Adsorbent	$-\Delta G^\circ$ (kJ mol <sup>-1</sup> )			$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )
	30 °C	40 °C	50 °C		
Bottom Ash	33.409	34.407	35.569	0.505	111.716
De-Oiled Soya	33.567	35.126	36.514	11.016	147.236

Bottom Ash: adsorbent dose = 0.1 g, particle size = 0.08–0.15 mm, pH 2.0. De-Oiled Soya: adsorbent dose = 0.05 g, particle size = 0.30–0.425 mm, pH 2.0.

Table 5  
Effect of sieve size on uptake of Tartrazine at different adsorbents

Adsorbent	Sieve size (mm)	Amount adsorbed (g)	Percentage adsorption	Half life ( $t_{1/2}$ ) ( $\text{h}^{-1}$ )
Bottom Ash	0.15–0.425	$7.256 \times 10^{-4}$	61.78	0.020
	0.08–0.15	$9.079 \times 10^{-4}$	77.30	0.011
	$\leq 0.08$	$10.200 \times 10^{-4}$	86.85	0.006
De-Oiled Soya	0.425–0.6	$7.300 \times 10^{-4}$	62.15	0.020
	0.3–0.425	$8.459 \times 10^{-4}$	72.02	0.014
	$\leq 0.3$	$10.020 \times 10^{-4}$	85.31	0.007

Bottom Ash: adsorbent dose = 0.1 g, concentration =  $9 \times 10^{-5}$  M, pH 2.0, temperature = 30 °C. De-Oiled Soya: adsorbent dose = 0.05 g, concentration =  $9 \times 10^{-5}$  M, pH 2.0, temperature = 30 °C.

firmly the endothermic nature of the process and affinity of the adsorbent towards adsorbate, respectively.

### 3.5. Effect of sieve size

The percentage removal of the dye is found to increase with the decrease in the size of the adsorbents (Table 5). The table also projects a decrease in the half life period ( $t_{1/2}$ ) with the decrease in the size of particles. For all the studies sieve sizes of 0.08–0.15 and 0.30–0.425 mm were opted for Bottom Ash and De-Oiled Soya, respectively. The selection of these granules was done on the basis of their sufficient adsorption capacity and availability.

### 3.6. Effect of amount of adsorbents

The effect of amount of adsorbents was studied by increasing the dosage from 0.01 to 0.35 g and from 0.01 to 0.30 g of Bottom Ash and De-Oiled Soya, respectively, at all the temperatures. It was found that at each temperature in both the cases with the increase in amount of adsorbents initially the adsorption increases steeply upto 0.05 g of the adsorbents and then gradual. The behavior obtained at 30 °C is presented in Fig. 7.

### 3.7. Kinetic studies

The preliminary investigations done for the uptake of Tartrazine by Bottom Ash and De-Oiled Soya at an optimum pH, adsorbate concentration and amount of adsorbents, indicate the process to be quite rapid particularly in the initial phases. The adsorption capacity for the first hour of contact was found between 50 and 65% in case of Bottom Ash and 47–56% in case of De-Oiled Soya and the saturation attained within 3–4 h (Fig. 8a and b). In general, it was found that percentage removal of adsorbate increases on raising the dosage of each adsorbent. It was also observed that there occurred a significant increase in adsorption, when dosage of each adsorbent is increased from 0.01 to 0.3 g and additional amount did not cause any substantial change in the amount of dye adsorbed. It was also found that in each case the rate of removal increases with the increase in the concentration of dye solution whereas, the time required for the removal of 50% dye is independent of the initial adsorbate concentration. Thus with the kinetic studies it can be safely

concluded that the ongoing adsorption over both the adsorbents is sufficiently rapid to recommend their use in the treatment of waste water polluted by Tartrazine.

### 3.8. Adsorption rate constant studies

For the determination of rate constant of adsorption ( $k_{\text{ads}}$ ) of Tartrazine on both the adsorbents following Lagergren's rate expression [28] was applied:

$$\log(q_e - q_t) = \log q_e - \frac{k_{\text{ads}}}{2.303} \times t \quad (1)$$

where  $q_e$  is the amount adsorbed at equilibrium and  $q_t$  is the amount adsorbed time  $t$ . Graph is drawn between time versus  $\log(q_e - q_t)$  at different temperatures for the adsorbents Bottom Ash (Fig. 9a) and De-Oiled Soya (Fig. 9b). The plots obtained are linear and thus confirm the applicability of the Lagergren's first order rate expression in both the cases. From the slopes derived from the straight lines, the values of the rate constants of adsorption ( $k_{\text{ads}}$ ) at different temperatures were calculated (Table 6).

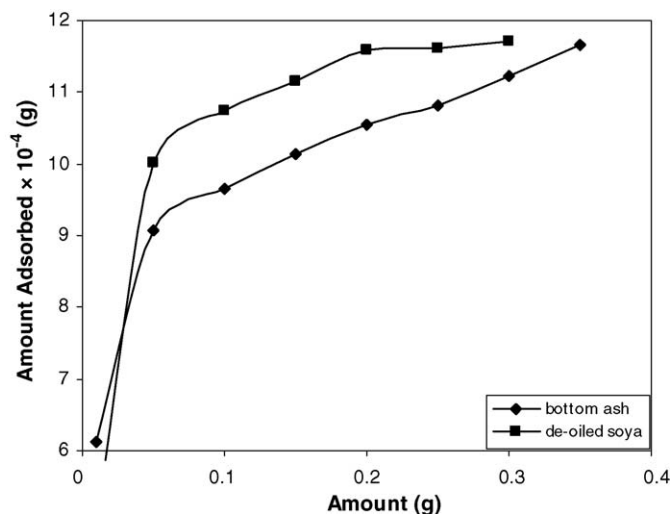
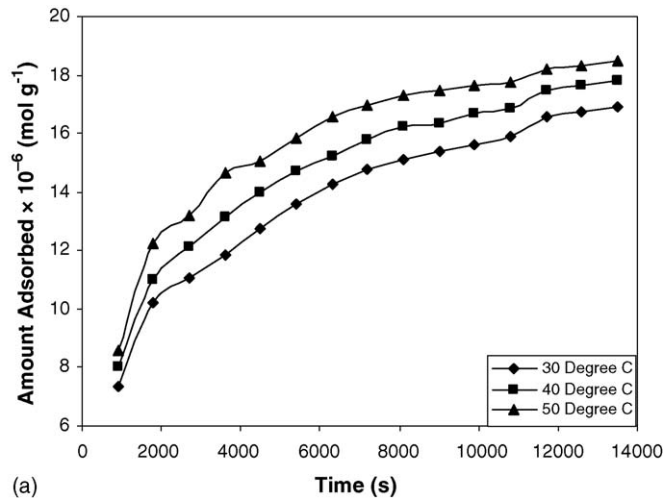
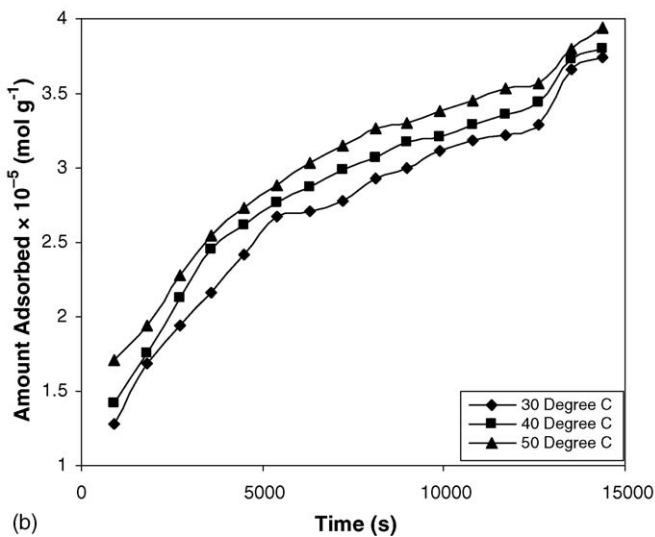


Fig. 7. Effect of amount of adsorbent for the removal of Tartrazine using Bottom Ash and De-Oiled Soya at 30 °C [Bottom Ash: concentration =  $9 \times 10^{-5}$  M, particle size = 0.08–0.15 mm, pH 2.0], [De-Oiled Soya: concentration =  $9 \times 10^{-5}$  M, particle size = 0.30–0.425 mm, pH 2.0].



(a)



(b)

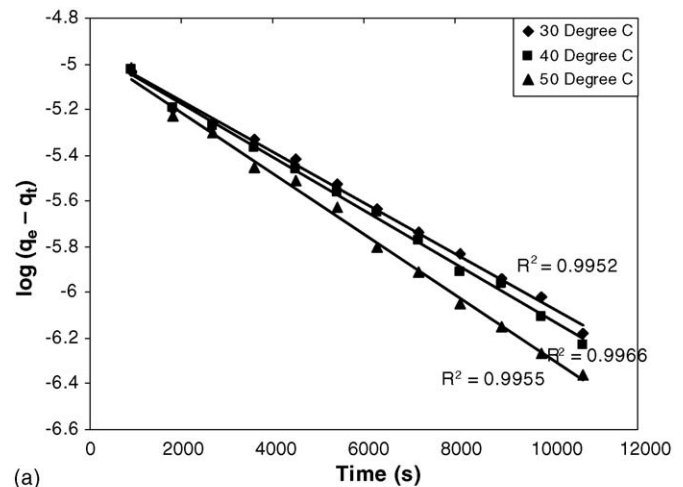
Fig. 8. (a) Effect of contact time for the uptake of Tartrazine by Bottom Ash at different temperatures and at a concentration of  $9 \times 10^{-5} \text{ M}$  [adsorbent dose = 0.1 g, particle size = 0.08–0.15 mm, pH 2.0]. (b) Effect of contact time for the uptake of Tartrazine by De-Oiled Soya at different temperatures and at a concentration of  $9 \times 10^{-5} \text{ M}$  [adsorbent dose = 0.05 g, particle size = 0.30–0.425 mm, pH 2.0].

### 3.9. Mass transfer studies

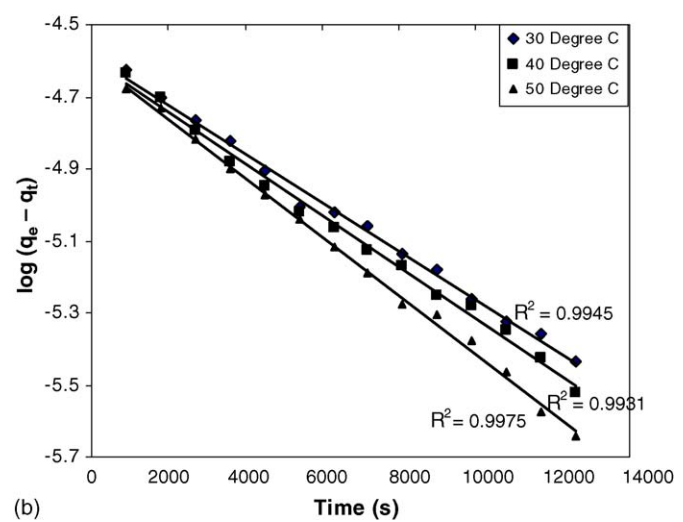
For the calculation of mass transfer coefficient ( $\beta_L$ ), McKay et al. [29] proposed following mass transfer model:

$$\ln \left( \frac{C_t}{C_0} - \frac{1}{1 + mk} \right) = \left( \frac{1 + mk}{mk} \beta_L S_S \right) t + \left( \frac{mk}{1 + mk} \right) \quad (2)$$

where  $C_t$  is the concentration of adsorbate ( $\text{mg L}^{-1}$ ) after time  $t$ ,  $C_0$  the initial concentration of adsorbate ( $\text{mg L}^{-1}$ ),  $m$  the mass



(a)



(b)

Fig. 9. (a) Lagergren's plot of time vs.  $\log(q_e - q_t)$  for Tartrazine–Bottom Ash system at different temperatures. (b) Lagergren's plot of time vs.  $\log(q_e - q_t)$  for Tartrazine–De-Oiled Soya system at different temperatures.

of adsorbent per unit volume of particle free adsorbate solution ( $\text{g L}^{-1}$ ) and  $k$  is the Langmuir constant ( $\text{L g}^{-1}$ ) obtained by multiplying adsorption capacity,  $Q_0$  and adsorption energy,  $b$ .  $S_S$  is the outer surface area of the adsorbent per unit volume of particle-free slurry ( $\text{cm}^{-1}$ ). The values of  $m$  and  $S_S$  are calculated using the following equations:

$$m = \frac{W}{V} \quad (3)$$

$$S_S = \frac{6m}{(1 - \epsilon_P)d_p \rho_p} \quad (4)$$

Table 6

Rate constants of adsorption ( $k_{ad}$ ) and mass transfer coefficient ( $\beta_L$ ) values of Tartrazine adsorption at different temperatures

Adsorbent	$k_{ad}$ ( $\text{s}^{-1}$ )			$\beta_L$		
	30°C	40°C	50°C	30°C	40°C	50°C
Bottom Ash	$2.563 \times 10^{-4}$	$2.724 \times 10^{-4}$	$3.047 \times 10^{-4}$	$8.192 \times 10^{-9}$	$1.045 \times 10^{-8}$	$1.343 \times 10^{-8}$
De-Oiled Soya	$1.555 \times 10^{-4}$	$1.647 \times 10^{-4}$	$1.880 \times 10^{-4}$	$1.016 \times 10^{-10}$	$1.020 \times 10^{-10}$	$1.039 \times 10^{-10}$



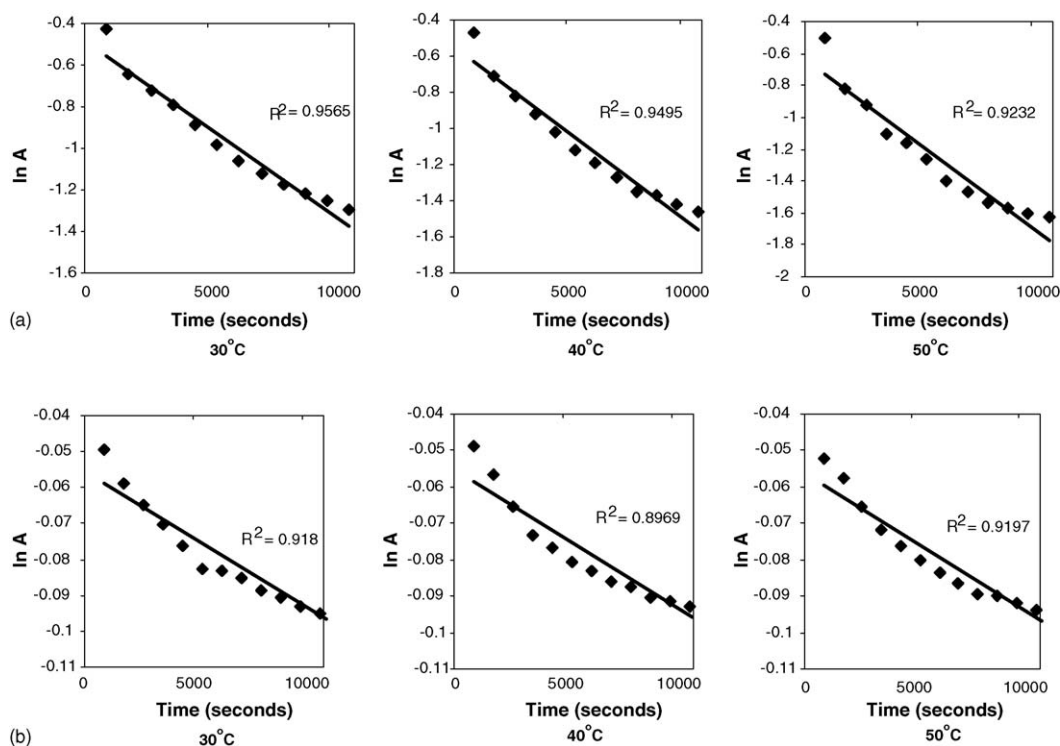


Fig. 10. (a) Plot of time vs.  $\ln A^*$  for the mass transfer of Tartrazine–Bottom Ash system at different temperatures [volume of aqueous solution of dye = 25 mL, concentration of adsorbate =  $9 \times 10^{-5}$  M]. (b) Plot of time vs.  $\ln A^*$  for the mass transfer of Tartrazine–De-Oiled Soya system at different temperatures [volume of aqueous solution of dye = 25 mL, concentration of adsorbate =  $9 \times 10^{-5}$  M].  $A^* = \frac{C_t}{C_0} - \frac{1}{1+mk}$ .

where  $W$  is weight of adsorbent (g),  $V$  the volume of particle free adsorbate solution (L),  $d_p$  the particle diameter (cm),  $\rho_p$  the density of adsorbent ( $\text{g cm}^{-3}$ ) and  $\varepsilon_p$  is the porosity of the adsorbent particle.

A graph was drawn between  $\ln \left( \frac{C_t}{C_0} - \frac{1}{1+mk} \right)$  versus time (Fig. 10a and b) and plots obtained were linear, which prove the validity of the model for both the adsorbents. From these plots the values of  $\beta_L$  for different systems were determined and are presented in Table 6. Fairly low values of  $\beta_L$  suggest a rapid transportation of the adsorbate from bulk to solid phase and reflect the good efficiency of both the adsorbent materials towards dye [29].

### 3.10. Rate expression and treatment of data

For the proper understanding of experimental data it is necessary to identify the rate controlling step of the adsorption process. Boyd et al. [30] gave the expression (Eq. (5)) for the treatment of kinetic data, which is in accordance with the observations of Reichenberg [31]:

$$F = 1 - \frac{6}{\pi^2} \sum_1^{\infty} \left( \frac{1}{n^2} \right) \exp(-n^2 B_t) \quad (5)$$

where  $F$  is the fractional attainment of equilibrium at time ' $t$ ' and is obtained by using Eq. (6) and  $n$  is Freundlich constant of

the on going adsorption process.

$$F = \frac{Q_t}{Q_{\infty}} \quad (6)$$

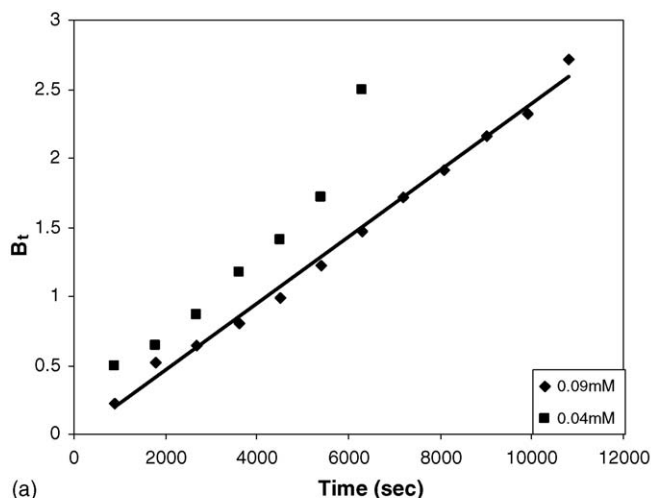
where  $Q_t$  and  $Q_{\infty}$  are the amount of uptake at time  $t$  and equilibrium, respectively. For every value of  $F$  corresponding calculated values of  $B_t$  was derived from Reichenberg's Table [31]. Thereafter time versus  $B_t$  plots were drawn at different concentrations for both the systems. Linearity in the time versus  $B_t$  plots at higher concentrations of the dye indicate that the particle diffusion process is operative in both the adsorbents, while film diffusion process is more pronounced at lower concentration due to deviation in linearity at all the temperatures. Typical time versus  $B_t$  plots at 30 °C are presented in Fig. 11a and b for the Bottom Ash and De-Oiled Soya, respectively.

To further evaluate the data the slopes of the straight lines obtained at  $9 \times 10^{-5}$  M of concentration of Tartrazine for both the systems was taken as  $B$ , the time constant, which was subsequently used for the evaluation of the values of  $D_i$  using Eq. (7):

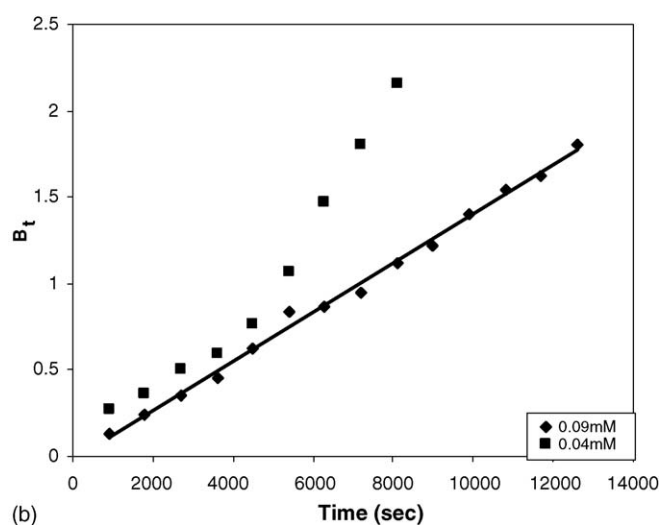
$$B = \frac{\pi^2 D_i}{r_0^2} = \text{time constant} \quad (7)$$

where  $D_i$  is the effective diffusion coefficient of adsorbate in adsorbent phases,  $r_0$  the radius of the adsorbent particle assumed to be spherical and  $n$  is an integer.

It was found that with the increase in temperature the contribution of the faster component of  $D_i$  increases and  $\log D_i$  versus



(a)



(b)

Fig. 11. (a) Plot of time vs.  $B_t$  for Tartrazine–Bottom Ash system at different concentrations and at 30 °C. (b) Plot of time vs.  $B_t$  for Tartrazine–De-Oiled Soya system at different concentrations and at 30 °C.

$1/T$  plots gave straight lines for both the adsorbents (Fig. 12). From the intercept of the straight line obtained in Fig. 12, corresponding value of  $D_0$  was calculated for each adsorbent and Arrhenius equation (Eq. (8)) was used to evaluate activation energy ( $E_a$ ). It was found that the  $E_a$  values for De-Oiled Soya–Tartrazine system and Bottom Ash–Tartrazine system are almost similar (Table 7):

$$D_i = D_0 \exp \frac{E_a}{RT} \quad (8)$$

Table 7  
Values of effective diffusion coefficient ( $D_i$ ), pre exponential constant ( $D_0$ ), activation energy ( $E_a$ ) and entropy of activation ( $\Delta S^\ddagger$ ) for the diffusion of Tartrazine in Bottom Ash and De-Oiled Soya

Adsorbent	$D_i$ ( $\text{m}^2 \text{s}^{-1}$ )			$D_0$ ( $\text{m}^2 \text{s}^{-1}$ )	$E_a$ ( $\text{J mol}^{-1}$ )	$\Delta S^\ddagger$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )
	30 °C	40 °C	50 °C			
Bottom Ash	$1.809 \times 10^{-9}$	$2.000 \times 10^{-9}$	$2.325 \times 10^{-9}$	$1.127 \times 10^{-7}$	10436.172	−336.835
De-Oiled Soya	$3.179 \times 10^{-13}$	$3.546 \times 10^{-13}$	$4.087 \times 10^{-13}$	$1.986 \times 10^{-11}$	10435.075	−408.699

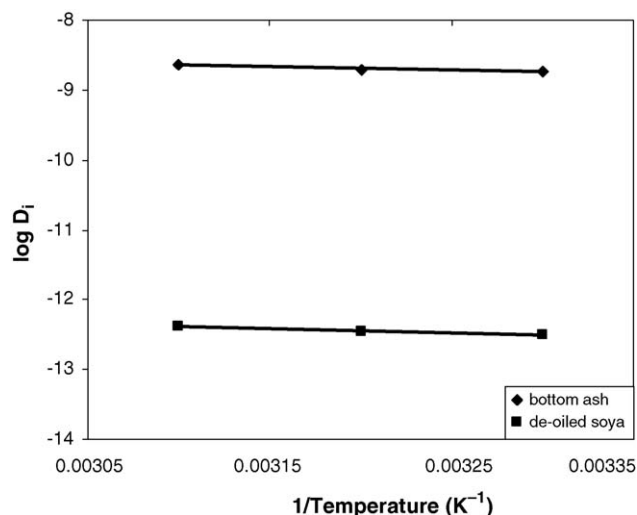


Fig. 12. Plot of  $1/\text{temperature}$  vs.  $\log D_i$  for Tartrazine–Bottom Ash system and Tartrazine–De-Oiled Soya system.

$$D_0 = (2.72d^2 \text{ kT/h}) \exp \left( \frac{\Delta S^\ddagger}{R} \right) \quad (9)$$

where  $d$  is the average distance between the two adsorption sites and has been taken as 5 Å for the particle sizes of the adsorbents chosen.

The values of  $E_a$ ,  $D_0$  and  $\Delta S^\ddagger$  for the diffusion of Tartrazine in Bottom Ash and De-Oiled Soya are listed in Table 7. The negative values of  $\Delta S^\ddagger$  obtained for both the systems reflect that no significant change occur in the internal structure of the adsorbents during the adsorption of Tartrazine.

### 3.11. Column studies

In practice the column type continuous flow operations have distinct advantages over batch treatment. For systems involving a spontaneous adsorption process a straight forward approach may be adopted for the design of a fixed bed adsorber [32], provided the rate of attainment of equilibrium of solute concentration between solution and adsorbed phase is known. Parameters evaluated for both the adsorbents are  $t_x$  (time involved in establishing the primary adsorption zone),  $t_f$  (time of initial formation of adsorption zone),  $t_\delta$  (time required by primary adsorption zone to move down its length),  $\delta$  (length of primary adsorption zone),  $f$  (fractional capacity of prepared column),  $F_m$  (mass rate flow of adsorbent) and percentage saturation of column at the break-

Table 8  
Fixed bed adsorber calculations

Adsorbent	$C_o$ (M)	$C_x$ (M)	$C_b$ (M)	$V_x$ (mL)	$V_b$ (mL)	$(V_x - V_b)$ (mL)	$F_m$ (mg cm <sup>-2</sup> )	$D$ (cm)
Bottom Ash	$1 \times 10^{-4}$	$9.902 \times 10^{-5}$	$0.640 \times 10^{-5}$	810	470	340	0.0332	1.5
De-Oiled Soya	$1 \times 10^{-4}$	$9.816 \times 10^{-5}$	$0.807 \times 10^{-5}$	190	120	70	0.0332	2.0

Table 9  
Parameters for fixed bed adsorber

Adsorbent	$t_x$ (min)	$t_\delta$ (min)	$t_f$ (min)	$f$	$\delta$ (cm)	Percentage saturation
Bottom Ash	5722.892	2108.434	240.00	0.886	0.577	95.61
De-Oiled Soya	24397.59	10240.96	940.00	0.908	0.873	95.98

point, by using the following equations:

$$t_x = \frac{V_x}{F_m} \tag{10}$$

$$t_\delta = \frac{V_x - V_b}{F_m} \tag{11}$$

$$\frac{\delta}{D} = \frac{t_\delta}{t_x - t_f} = \frac{t_\delta}{t_x + t_\delta(f - 1)} = \frac{(V_x - V_b)}{V_b + f(V_x - V_b)} \tag{12}$$

$$f = 1 - \frac{t_f}{t_\delta} = \frac{M_S}{(V_x - V_b)C_o} \tag{13}$$

$$\text{Percentage saturation} = \frac{D + \delta(f - 1)}{D} \times 100 \tag{14}$$

where  $M_S$  is the amount of adsorbate adsorbed in the primary adsorption zone from breakpoint to exhaustion,  $C_o$  is the initial concentration of adsorbate and  $D$  is the length of column.

The breakthrough curves expressed in terms of  $C_o$  and eluted volume for De-Oiled Soya–Tartrazine and Bottom Ash–Tartrazine systems are shown in Fig. 13. From the plot the values of  $V_b$ ,  $V_x$ ,  $C_b$  and  $C_x$ , were calculated, which were further used to evaluate the values of  $t_x$ ,  $t_f$ ,  $t_\delta$ ,  $\delta$ ,  $f$ ,  $F_m$  and per-

centage saturation of column at the breakpoint. The profile has been presented in Tables 8 and 9. The percentage saturation of the columns was found to be 95.61 and 95.98%, respectively, for the Bottom Ash and De-Oiled Soya columns.

### 3.12. Column regeneration and dye recovery

The elution of both the adsorbents was achieved by simultaneous chemical regeneration using suitable solvent. The solution of dilute NaOH of pH 12 was eluted through the exhausted column at a flow rate of 0.5 mL min<sup>-1</sup>. About 60–100 mL of dilute NaOH was sufficient for almost complete desorption of Tartrazine from both adsorbents. It is evident from Fig. 14 that in both the columns the major amount of the dye is recovered in the first 20 mL of the dilute NaOH. The percentage recovery is about 88% for Bottom Ash and 84% for De-Oiled Soya column. After desorption the columns were washed with hot water. To check the adsorption efficiency of columns, the columns were reloaded with the dye solution. The breakthrough capacities for the Bottom Ash–Tartrazine system was found to be 81, 72, 59 and 45% and for De-Oiled Soya–Tartrazine system 75, 65, 53 and 42% during their first, second, third and fourth cycles, respectively.

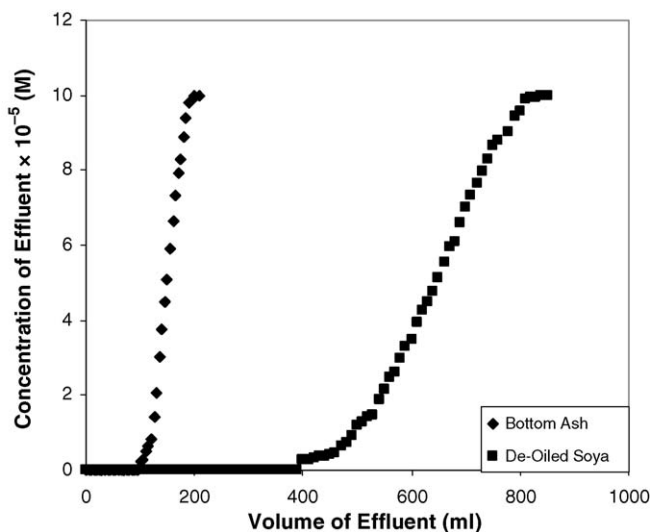


Fig. 13. Breakthrough curve for Tartrazine–Bottom Ash and Tartrazine–De-Oiled Soya columns.

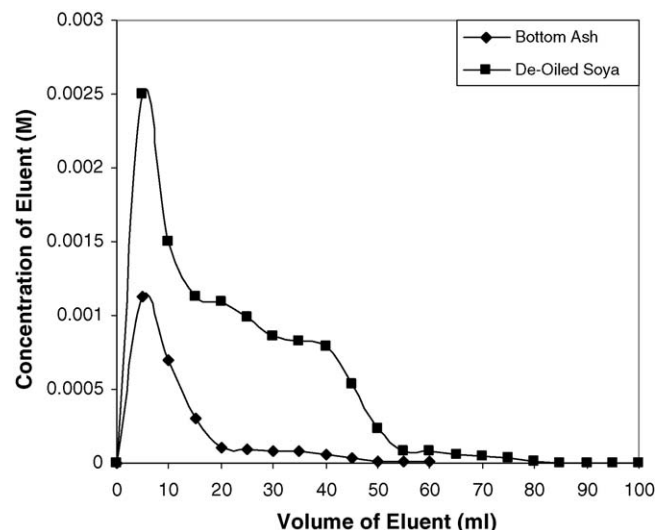


Fig. 14. Desorption of Tartrazine from Bottom Ash and De-Oiled Soya columns.

#### 4. Conclusion

Different operational parameters observed during the process of investigations reveal that adsorbents, activated Bottom Ash and De-Oiled Soya developed from the waste materials, can be effectively employed for the removal of the hazardous dye, Tartrazine. It was observed that the pH, temperature, contact time, sieve size, adsorbent dose and concentrations of the adsorbate govern the overall process of adsorption by both the adsorbents. Highest percentage removal of the dye could be obtained at pH 2.0 and at concentrations upto  $2 \times 10^{-5}$  M. Both the adsorbents satisfy the Langmuir and Freundlich adsorption isotherms and average values of free energy ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were found about  $-34$ ,  $0.5 \text{ kJ mol}^{-1}$  and  $112 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively, for the Bottom Ash and  $-35$ ,  $11 \text{ kJ mol}^{-1}$  and  $147 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively, for the De-Oiled Soya. The kinetic treatment predicts that the adsorption at lower concentration, takes place through film diffusion, whereas particle diffusion becomes active at higher concentration. The percentage column saturation was found around 96% for both the columns. It has also been possible to regenerate the adsorbents and to quantitatively recover the dye with dilute NaOH solution and about 84 and 88% of the dye was recovered from the Bottom Ash and De-Oiled Soya exhausted columns, respectively. Removal efficacy of each adsorbent clearly indicates that the developed method is cheaper and faster than commercially available methods.

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