Studies on the adsorption kinetics and isotherms for the removal and recovery of Methyl Orange from wastewaters using waste materials

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Abstract

De-Oiled Soya a waste of Soya oil industries and Bottom Ash a waste of thermal power plants have been used as effective adsorbent for recovery and removal of hazardous dye Methyl Orange from wastewater. During the studies effects of amount of dye and adsorbents, pH, sieve sizes, column studies etc. have been carried out. Adsorption of the dye over both the adsorbents has been monitored through Langmuir and Freundlich adsorption isotherm models and feasibility of the process is predicted in both the cases. Different thermodynamic parameters like Gibb's free energy, enthalpy and entropy of the undergoing process are also evaluated through these adsorption models. The kinetic studies confirm the first order process for the adsorption reaction and also play an important role in finding out half-life of the adsorption process and rate constants for both the adsorbents. It is also found that over the entire concentration range the adsorption on Bottom Ash takes place via particle diffusion process, while that of De-Oiled Soya undergoes via film diffusion process. In order to establish the practical utility of the developed process, attempts have been made for the bulk removal of the dye through column operations. For the two columns saturation factors are found as 98.61 and 99.8%, respectively, for Bottom Ash and De-Oiled Soya with adsorption capacity of each adsorbent as 3.618 and 16.664 mg/g, respectively. The dye recovery has been achieved by eluting dil. NaOH through the exhausted columns.
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1. Introduction

Increasing environmental pollution caused by toxic dyes due to their hazardous nature is a matter of great concern. Even small traces of the non-biodegradable and highly toxic dyes can prove harmful to the mankind. Effluents from dye production and dying mills are highly objectionable if discharged into open water without any proper treatment. The presence of coloring material in water system also reduces penetration of light and thereby affecting photosynthesis in aquatic planktons. Dyes are also major component of the laboratory wastes, which are then led into the soil and water bodies and also need to be removed.

Over last one decade it has been established that for the removal of dyes from wastewaters adsorption technique has proved more advantageous [1,2] over other physico-chemical methods like electrochemical treatment [3], photochemical method [4,5], biodegradation [6,7], etc., due to its effectiveness and economy. In the past few years efforts have been made to remove toxic substances from wastewaters by using low cost adsorbents like hardwood mulch [8], rice husk [9], feather [10], crushed brick [11], cedar saw dust [11], clay [12], fibrous clay minerals [13], etc. Literature survey also reveals that Gupta et al. have significantly contributed in this area of research and used different adsorbents to eradicate various dyes from waste water [14–21]. In last 2 years our laboratory has developed fast, versatile and cost effective methods for eradicating some hazardous dyes using waste materials like Bottom Ash and De-Oiled Soya [22–26]. In the present study, waste materials Bottom Ash and De-Oiled Soya are now exploited as effective adsorbents for the removal of Methyl Orange.

Methyl Orange is a water-soluble azo dye, which is widely used in the textile, printing, paper manufacturing, pharmaceutical, food industries and also in research laboratories. In the Analytical Chemistry Laboratories it is mainly used as an acid base indicator due to its ability to function as weak acid as the

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aqueous solution of the dye has a pH value of approximately 6.5 (5 g/l, H_2O, 20 °C) [27]. Microbial succession and intestinal enzyme activities in the developing rat has also been studied for the Methyl Orange [28] and the dye is found to increase their nitro reductase and azo reductase activities significantly with the appearance of anaerobes in the large intestine. Azo dyes are well known carcinogenic organic substances. Like many other dyes of its class Methyl Orange on inadvertently entering the body through ingestion, metabolizes into aromatic amines by intestinal microorganisms. Reductive enzymes in the liver can also catalyze the reductive cleavage of the azo linkage to produce aromatic amines and can even lead to intestinal cancer [29,30]. The toxic nature of the dye is still not quantified much but its high content in living systems can prove to be harmful. Thus, the safe removal of such a dye is the prime aim of our present research and this is accomplished by using an industrial waste material—Bottom Ash and an agricultural waste material—De-Oiled Soya, as potential adsorbents.

$$(CH_3)_2N \!\!-\!\!\bigcirc\!\!-\!\!N\!\!=\!\!N\!\!-\!\!\bigcirc\!\!-\!\!SO_3Na$$
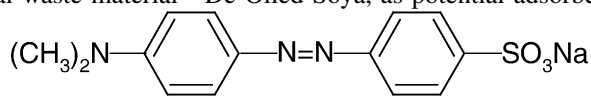
Methyl Orange (I)

2. Materials and methods

Methyl Orange (I), chemical name Sodium *p*-dimethyl-aminoazobenzenesulphonate (Molecular Formula $C_{14}H_{14}N_3NaO_3S$; Molecular weight 327.33) was procured from M/s Merck. All the studies were done using double distilled water and reagents of A.R grade. Adsorbent, Bottom Ash, was procured from thermal power station (TPS) of M/s Bharat Heavy Electrical Limited (B.H.E.L.), Bhopal (India) in the form of greyish black dust spherical granules. The coal used by TPS, BHEL, Bhopal was obtained from M/s South Eastern Coal Field Limited, Chirmiri, Sarguja (India). The De-Oiled Soya was a gift from M/s Sanwaria Agro Oils Limited, Bhopal, India.

All pH measurements were performed using a microprocessor-based pH meter; Model HI 8424 (M/s Henna Instruments, Italy). Absorbance measurements were carried out on UV/visible Spectrophotometer model number 117 (M/s Systronics, Ahmedabad, India). Philips SEM 501 electron microscope was used for scanning electron microscopy and Philips X-ray Diffractophotometer was used to carry out X-ray measurements using Nickel-filtered Cu Kα-radiation. Surface area of the adsorbent particles was calculated using Quantasorb model QS-7 surface area analyzer. The density and porosity of the adsorbent material were determined using Mercury Porosimeter and specific gravity bottles.

2.1. Material development

Both the adsorbents were first washed with distilled water and dried. To oxidize the organic impurities, the adsorbent materials were then dipped overnight in the H_2O_2 solution. In order to remove the moisture contents each material was then kept for about 15 min in an oven at 100 °C. The hard granules of Bottom Ash were further activated at 500 °C for another 15 min. Both the adsorbents were then sieved to mesh sizes 36, 100 and 170 BSS Mesh and stored in separate desiccators.

2.2. Adsorption studies

Batch technique was employed at temperatures 30, 40 and 50 °C. A 25 ml of the dye solutions of varying concentration (1×10^{-5} to 10×10^{-5} M) were taken in different 100 ml conical flasks and desirable pH (pH range 2–10) was adjusted. A suitable amount of the adsorbent of the chosen particle size was added in each volumetric flask and mixture was shaken intermittently till equilibrium was achieved. The solutions were now filtered with Whattman filter paper (number 42) and uptake of dye was analyzed spectrophotmetrically at λ_{max} 502 nm.

2.3. Kinetic studies

For the kinetic study of the adsorption of Methyl Orange over adsorbents, 25 ml of dye solution with specific amount of Bottom Ash and De-Oiled Soya was taken in different 100 ml airtight volumetric flasks and shaken in a water bath at a desired temperature. The uptake capacity of Methyl Orange was studied with different amounts of adsorbents at 30, 40 and 50 °C. These solutions were filtered after a particular time interval and analyzed spectrophotometerically for monitoring the kinetics.

2.4. Column adsorption

In order to establish the practical utility of the waste materials as adsorbents, bulk adsorption of the dye was carried out by filling the adsorbents in glass columns. Glass columns of 30 cm length and 1 cm internal diameter were packed with respective adsorbents of known amounts on a glass wool support. The slurry of weighed amount (1 g of Bottom Ash and 0.125 g of De-Oiled Soya) of each adsorbent was prepared in water and after keeping over night the slurry was fed into the column. The columns were then supported by glass wool and the slurry was fed into the column. To avoid air entrapment in the columns utmost care was maintained as outlined by Fornwalt and Hutchins [31]. Solution of 1×10^{-4} M concentration of Methyl Orange was then percolated through each column at a flow rate to be 0.5 ml/min, which was stopped after about 90% exhaustion of the column.

2.5. Column regeneration

The dye adsorbed in the two columns was then eluted using NaOH solution (pH 11) at a flow rate of 0.5 ml/min in case of both the adsorbents. Total recovery of the dye was achieved by percolating several aliquots of the dilute NaOH (10 ml each) through the column at a flow rate of 0.5 ml/min. After complete recovery of dye the columns were then washed with distilled water.

Table 1
Chemical constituents of the adsorbents

Bottom Ash		De-Oiled Soya	
Constituents	wt.%	Constituents	wt.%
Moisture	15	Moisture	11
SiO_2	45.4	SiO_2	6
Al_2O_3	10.3	Fiber	2
Fe_2O_3	9.7	Ca	0.2
CaO	15.3	P	0.7
MgO	3.1	Profat	48

3. Results and discussion

3.1. Characterization of adsorbents

Chemical and analytical techniques were used for ascertaining the chemical constituents of the adsorbent materials. The chemical constituents of Bottom Ash and De-Oiled Soya are presented in Table 1. The adsorptive nature of the two adsorbents was established by scanning electron microscopic photograph of activated Bottom Ash and De-Oiled Soya. Both the adsorbents were analyzed using infrared spectrophotometeric study. Bottom Ash exhibited a sharp absorption band in the region of 3700–3500 cm^{-1}. The bands at 3467, 2930, 2676, 1502, 1097 and 790 cm^{-1} indicated the presence of laumonite, amber, mulite, azurite, bavenite and kaolinite in Bottom Ash, whereas in case of De-Oiled Soya the bands obtained at 479, 779, 1113, and 3459 cm^{-1} indicated the presence of gorthite (4[FeO·OH]), coesite (SiO_2), corundum (2[α-Al_2O_3]), and laumonite (4[Ca$Al_2Si_4O_{12}$·4H_2O]). Bottom Ash was found to be thermally stable and showed negligible weight loss even at high temperatures as per DTA curves. The *d*-spacing values provided by the X-ray spectrum of the adsorbents reflect the presence of mainly alumina (Al_2O_3), gypsum (CaSO$_4$·2H_2O), beverite [Pb(Cu, Fe, Al)$_3$(SO$_4$)$_2$(OH)$_6$], borax (Na$_2$B$_4$O$_7$·10H_2O) and kaolinite [2($Al_2Si_2O_5$(OH)$_4$)].

3.2. Adsorption studies

3.2.1. Effect of pH

Effect of pH on adsorption of dye has been studied for both the adsorbents over a range of 2–10 and adsorption is found to decrease with increasing pH (Fig. 1). Since both adsorbents show high adsorption at pH 3, all further studies were carried out
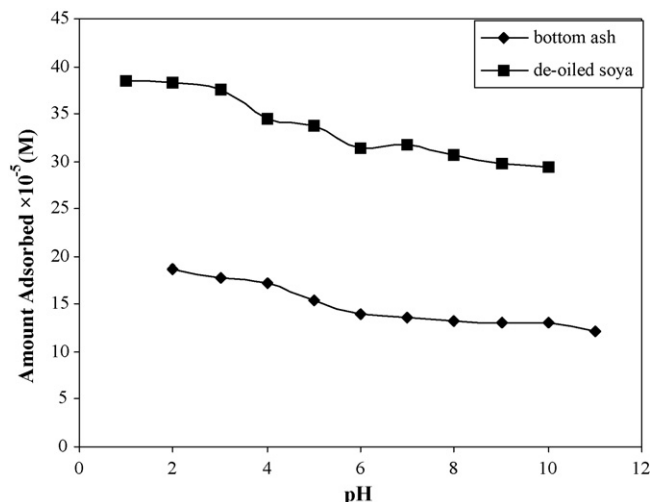

Fig. 1. Effect of pH on uptake of Methyl Orange by Bottom Ash and De-Oiled Soya at 30 °C. Bottom Ash: concentration = 1 × 10^{-4} M, adsorbent dose = 0.1 g, particle size = 100 Mesh. De-Oiled Soya: concentration = 10 × 10^{-5} M, adsorbent dose = 0.05 g, particle size = 36 Mesh.

at this pH. The higher adsorption of the dye at low pH may be due to neutralization of the negative charge at the surface of the adsorbents. However, with increase in pH protonation reduces, which results into retardation of diffusion and adsorption thereby.

3.2.2. Effect of amount of adsorbent

Various amounts ranging from 0.01 to 0.3 g for Bottom Ash and 0.01 to 0.05 g for De-Oiled Soya were taken and adsorption of Methyl Orange was achieved at 30, 40 and 50 °C at a particular concentration and pH. It is observed that in both the cases the adsorption of dye increases with increase in amount of adsorbents (Table 2). Significantly high adsorption of the dye was achieved at 0.1 g of Bottom Ash and 0.05 g of De-Oiled Soya and that is why these weights were chosen for all further studies.

3.2.3. Effect of particle size

Three different particle sizes viz. 36, 100 and 170 BSS Mesh were selected for batch adsorption experiments in case of Bottom Ash and De-Oiled Soya. For both the adsorbents it is found that adsorption increases with increase in mesh size (Table 3). The increase in the adsorption capacity with decrease in the particle size or increase in mesh size is a result of increased

Table 2
Effect of amount of adsorbents on the adsorption of Methyl Orange

Amount of Bottom Ash (g)	Amount adsorbed × 10^{-5} (g)			Amount of De-Oiled Soya (g)	Amount adsorbed × 10^{-5} (g)		
	30 °C	40 °C	50 °C		30 °C	40 °C	50 °C
0.01	11.62	12.77	18.08	0.01	18.00	15.38	6.46
0.05	28.07	34.04	36.41	0.02	24.55	22.67	14.65
0.1	47.05	50.65	53.19	0.03	40.10	35.68	29.95
0.2	64.65	65.87	67.02	0.04	49.92	47.87	44.60
0.3	70.95	71.27	75.28	0.05	51.55	48.93	48.61

Concentration = 1 × 10^{-4} M and pH 3.0.

Table 3
Effect of sieve size of different adsorbents on the rate of adsorption of Methyl Orange over Bottom Ash and De-Oiled Soya

Mesh size	Bottom Ash			De-Oiled Soya		
	Amount adsorbed $\times 10^{-5}$ (g)	k (h^{-1})	$t_{1/2}$ (h)	Amount adsorbed $\times 10^{-5}$ (g)	k (h^{-1})	$t_{1/2}$ (h)
36	17.021	0.065	10.590	38.706	0.031	22.212
100	21.194	0.056	12.309	38.378	0.032	21.963
170	23.240	0.052	13.210	33.468	0.037	18.600

Concentration = 10×10^{-5} M, pH 3.0, temperature = 30 °C, adsorbent dose = 0.1 g (Bottom Ash) and 0.05 g (De-Oiled Soya).

surface area of the adsorbents. Keeping the marginal difference of adsorption amount with respect to mesh size in view, for further studies 36 BSS Mesh size for De-Oiled Soya and 100 BSS Mesh sizes for Bottom Ash were chosen. Rate constants of the process at different temperature and half-life of each process are also presented in Table 3.

3.2.4. Effect of concentration

Various concentrations ranging from 1×10^{-5} to 10×10^{-5} M of Methyl Orange were investigated with fixed amount of adsorbents at temperatures 30, 40 and 50 °C. The study reveals that for both the adsorbents increase in concentration of Methyl Orange increases the extent of adsorption, however adsorption decreases with increase in temperature (Figs. 2 and 3).

3.2.5. Effect of contact time

The studies involving different contact time helps in determining the uptake capacities of the dye at varying time intervals keeping the amount of the adsorbents fixed at different temperatures 30, 40 and 50 °C. It was established that in case of Bottom Ash (0.1 g), 4 h of contact time was found sufficient to acquire equilibrium. On the other hand in case of De-Oiled Soya (0.05 g) equilibrium was noticed in about 150 min. Within the first hour of contact, almost 41.4% adsorption occurred for Bottom Ash (Fig. 4), while De-Oiled Soya adsorbed about 50% of
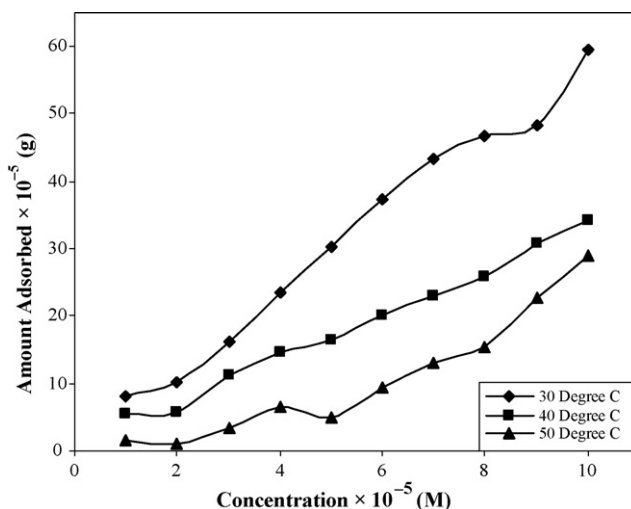

Fig. 3. Effect of concentration for the removal of Methyl Orange by De-Oiled Soya at different temperatures. Adsorbent dose = 0.05 g, particle size = 36 Mesh, pH 3.0.

the dye (Fig. 5). The adsorption rate was found to decrease with increase in time as well as temperature for both the adsorbents. This also confirms the exothermic nature of the adsorption in both the cases. The half-life of each process was calculated and was found 0.786 and 0.982 h for Bottom Ash and De-Oiled Soya, respectively.
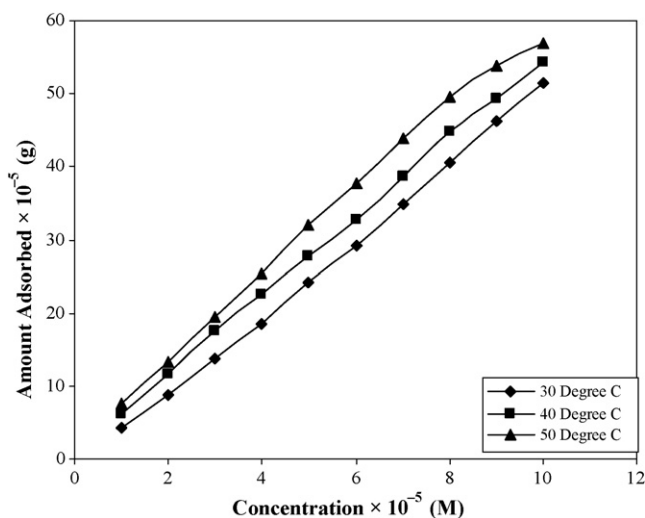

Fig. 2. Effect of concentration for the removal of Methyl Orange by Bottom Ash at different temperatures. Adsorbent dose = 0.1 g, particle size = 100 Mesh, pH 3.0.
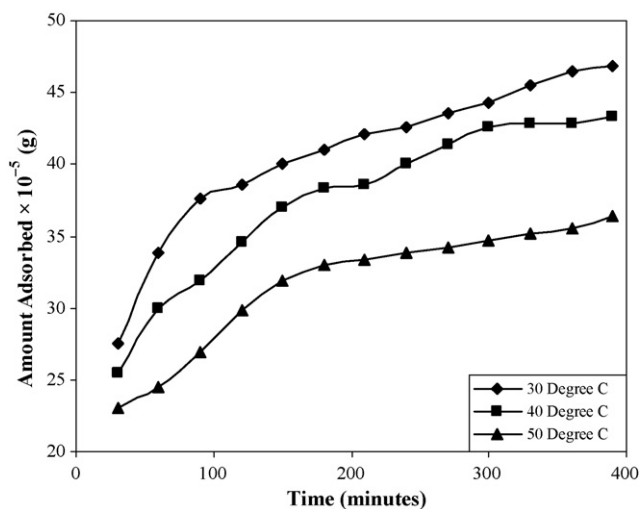

Fig. 4. Effect of contact time for the uptake of Methyl Orange by Bottom Ash at different temperatures and at a concentration of 1×10^{-4} M. Adsorbent dose = 0.1 g, particle size = 100 Mesh, pH 3.0.
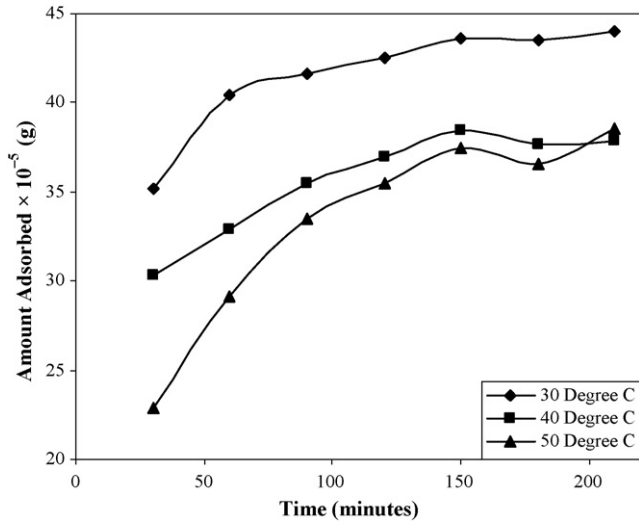
Fig. 5. Effect of contact time for the uptake of Methyl Orange by De-Oiled Soya at different temperatures and at a concentration of 1×10^{-4} M. Adsorbent dose = 0.05 g, particle size = 36 Mesh, pH 3.0.

Fig. 7. Langmuir adsorption isotherms for Methyl Orange–De-Oiled system. Adsorbent dose = 0.05 g, particle size = 36 Mesh, pH 3.0.

3.3. Adsorption isotherms

For both the adsorbents Langmuir and Freundlich isotherms were studied and Langmuir constants were calculated at 30, 40 and 50 °C. The Langmuir isotherm is based on the assumptions that the molecules of the adsorbate are adsorbed at well-defined, energetically equal sites without interacting with each other and each site can hold only one molecule [32].

For the Methyl Orange–Bottom Ash and Methyl Orange–De-Oiled Soya system the plot of $1/q_e$ against $1/C_e$ gives a straight line at each temperature confirming that the adsorption of the dye follows the Langmuir isotherm model [33] (Figs. 6 and 7). On the basis of slopes and intercepts of the straight lines Langmuir constants were calculated and are presented in Table 4.
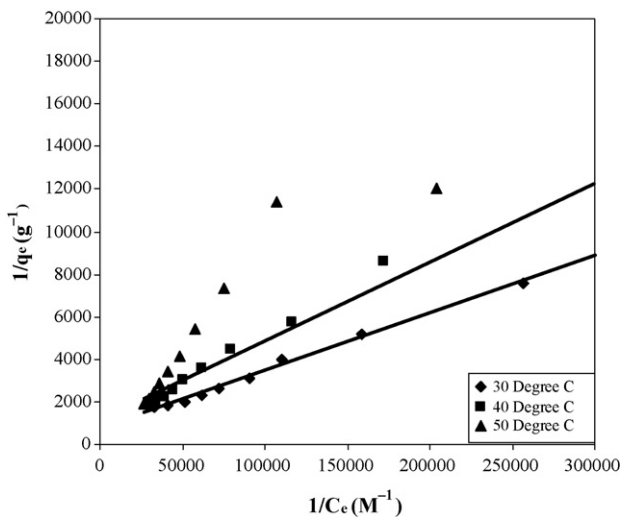
The validity of Freundlich adsorption model [34–36] was established using following relation

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \tag{1}$$

where q_e is the amount adsorbed (g), C_e the equilibrium concentration of the adsorbate and K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. Figs. 8 and 9 clearly reveal that for the adsorbents $\log C_e$ versus $\log q_e$ plots gave straight lines. Freundlich constants derived from these straight lines are presented in Table 4 and clearly indicate that the adsorption capacity decreases with increase in temperature.

Fig. 6. Langmuir adsorption isotherms for Methyl Orange–Bottom Ash system. Adsorbent dose = 0.1 g, particle size = 100 Mesh, pH 3.0.
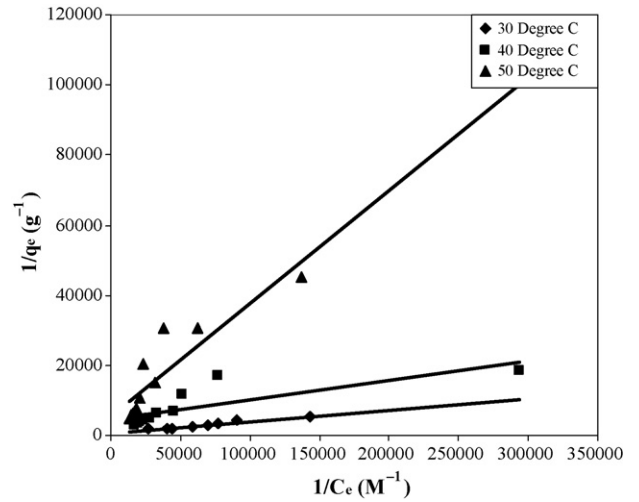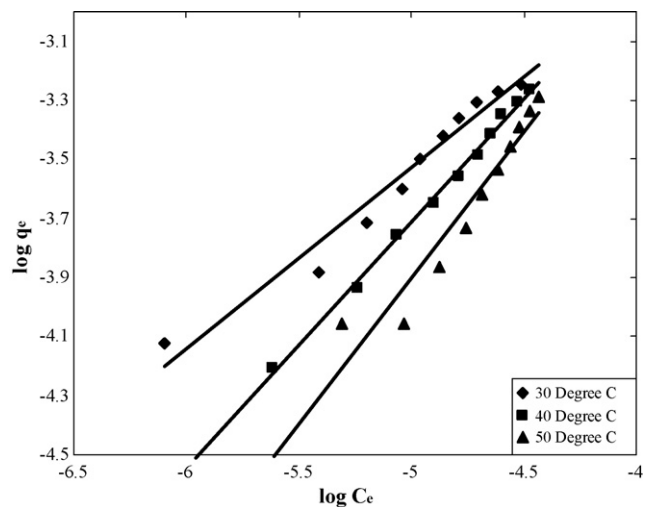

Fig. 8. Freundlich adsorption isotherms for Methyl Orange–Bottom Ash system. Adsorbent dose = 0.1 g, particle size = 100 Mesh, pH 3.0.

Table 4
Freundlich and Langmuir constants for the removal of Methyl Orange through adsorption over different adsorbents

Adsorbent	Freundlich constants					
	n			K_F		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Bottom Ash	1.635	1.197	1.013	0.338	2.907	10.715
De-Oiled Soya	0.906	1.399	1.025	3.162	1.698	1.596

Adsorbent	Langmuir constants					
	$Q_o \times 10^{-4}$			$b \times 10^2$		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Bottom Ash	13.350	8.630	8.550	277.422	313.243	186.306
De-Oiled Soya	13.460	2.170	1.750	229.318	844.670	177.208

Bottom Ash: adsorbent dose = 0.1 g, particle size = 100 Mesh, pH 3.0; De-Oiled Soya: adsorbent dose = 0.05 g, particle size = 36 Mesh, pH 3.0.

3.4. Thermodynamic treatment of adsorption data

Various thermodynamic parameters were also calculated for both adsorbents using following relations [37,38]

$$\Delta G^o = -RT \ln b \qquad (2)$$

$$\Delta H^o = -R \left(\frac{T_2 T_1}{T_2 - T_1} \right) \ln \left(\frac{b_2}{b_1} \right) \qquad (3)$$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \qquad (4)$$

where ΔH^o is the change in enthalpy; ΔS^o the change in entropy; ΔG^o the change in Gibb's free energy; b, b_1 and b_2 are the Langmuir constants at different temperatures. The negative free energy values suggest feasibility of the process in both the cases. The negative value of enthalpy change further confirms the exothermic nature of the process, whereas positive value of entropy change shows increased randomness of the process. The above values have been depicted in Table 5.

In order to calculate the dimensionless separation factor the method suggested by Weber and Chakrabarti is used [39]. The

Table 5
Thermodynamic parameters for the uptake of Methyl Orange

Adsorbent	$-\Delta G^o$ (kJ mol^{-1})			$-\Delta H^o$ (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})
	30 °C	40 °C	50 °C		
Bottom Ash	25.772	26.939	26.405	16.766	30.692
De-Oiled Soya	24.745	27.959	24.110	4.799	58.216

Bottom Ash: adsorbent dose = 0.1 g, particle size = 100 Mesh, pH 3.0; De-Oiled Soya: adsorbent dose = 0.05 g, particle size = 36 Mesh, pH 3.0.

separation factor tells the favorability and the shape of the adsorption isotherms by applying the equation

$$r = \frac{1}{1 + bC_o}$$

where b signifies the Langmuir constant and C_o is the initial concentration. In both the cases, all the r-values obtained are less than unity, confirming that adsorption process is favoured in both the cases. All evaluated r-values are portrayed in Table 6.

3.5. Kinetic studies

Lagergren's first order rate equation [40] was employed to study the specific rate constants for both the systems using following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \qquad (5)$$

where q_e and q_t denote the amount adsorbed at equilibrium and at any time t respectively. The straight lines obtained from the graph of $\log(q_e - q_t)$ versus time suggest involvement of first order
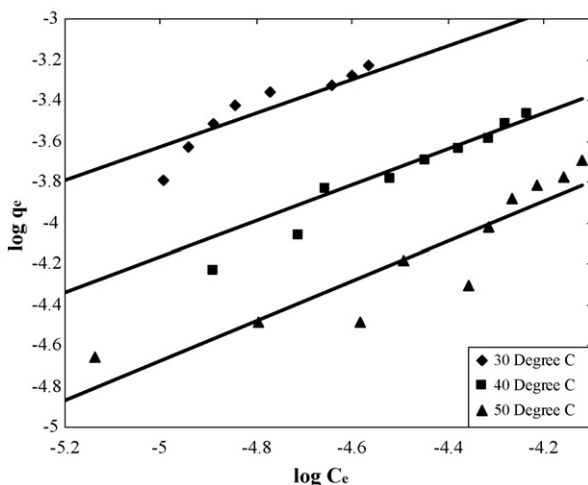

Fig. 9. Freundlich adsorption isotherms for Methyl Orange–De-Oiled Soya system. Adsorbent dose = 0.05 g, particle size = 36 Mesh, pH 3.0.

Table 6
r-Values obtained at different temperatures for Methyl Orange–Bottom Ash and De-Oiled Soya adsorption

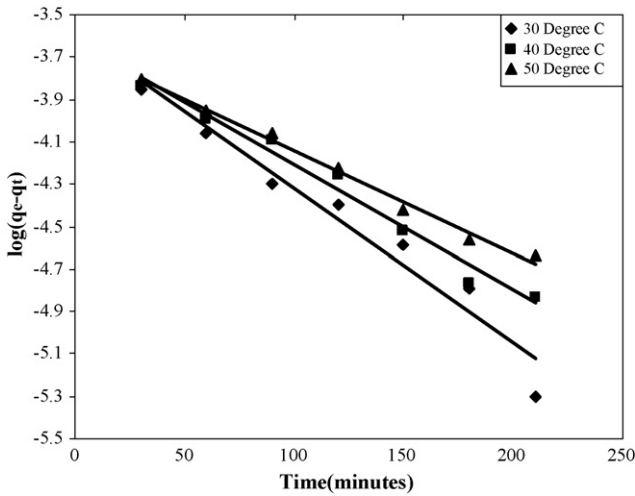| Adsorbent	r-Value		
	30 °C	40 °C	50 °C
Bottom Ash	0.265	0.242	0.349
De-Oiled Soya	0.304	0.106	0.361

Fig. 10. Lagergren's plot of time vs. $\log(q_e - q_t)$ for Methyl Orange–Bottom Ash system at different temperatures.
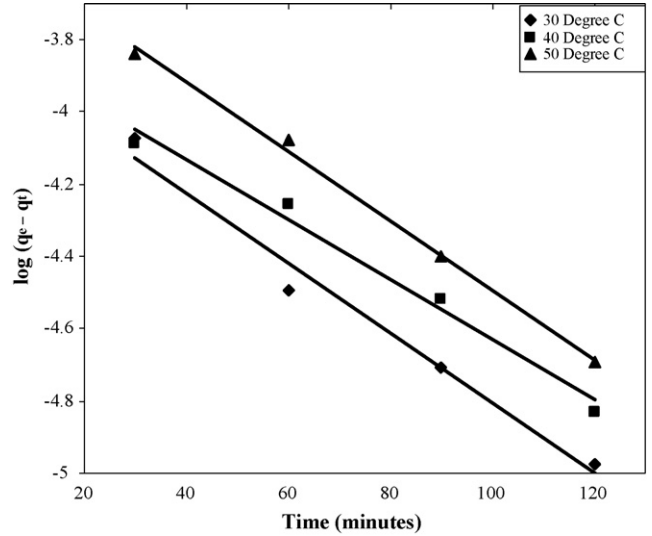

Fig. 11. Lagergren's plot of time vs. $\log(q_e - q_t)$ for Methyl Orange–De-Oiled Soya system at different temperatures.

kinetics (Figs. 10 and 11) in both the cases. Using the values of slopes of these straight lines the values of rate constant (k_{ad}) for both the adsorbents were calculated at different temperatures (Table 7).

One of the essential requirements for the proper interpretation of the experimental data obtained during kinetic studies is to identify the step(s) governing overall rate of removal during the adsorption process. Hence, ingenious mathematical treatment suggested by Boyd et al. [41] and Reichenberg [42] were employed to identify whether the on-going process is a particle diffusion or film diffusion.

In order to establish the actual process involved in the adsorption of Methyl Orange over Bottom Ash and De-Oiled Soya, a quantitative treatment of the sorption dynamics was employed with the help of following expressions:

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

$$F = 1 - \frac{6}{\pi^2} \sum_{t}^{\infty} \left(\frac{1}{n^2}\right) \exp(-n^2 B_t) \qquad (7)$$

$$B = \frac{\pi^2 D_i}{r_o^2} = \text{Time constant} \qquad (8)$$

where F is the fractional attainment of equilibrium at time t; Q_t and Q_∞ the amounts adsorbed after time t and after infinite time, respectively; B the time constant; B_t the time constant after time t; D_i the effective diffusion coefficient of adsorbate in adsorbent phase; r_o the radius of adsorbent particle; n is the Freundlich constant of the adsorbate.

Based on values of F, B_t values were derived from Reichenberg's table and B_t versus time graph was plotted to distinguish between the film diffusion and particle diffusion adsorption rates [42].

Three following steps are thought to be involved during the adsorption of any organic or inorganic substance over the surface of a porous adsorbent:

a. Transport of adsorbate to the surface of the adsorbent (film diffusion).
b. Transport of the adsorbate within the pores of the adsorbent (particle diffusion).
c. Adsorption of adsorbate on the interior surface of the adsorbent.

Out of these three processes the third step is quite rapid, cannot be treated as rate determining step [43]. The rate is governed by particle diffusion when external transport of the ingoing ions is greater than internal transport. Whereas, when external transport is less than internal transport, film diffusion governs the rate. A third possibility also arises when external transport is almost equal to internal transport. This results into formation of a liquid film with a proper concentration gradient around the adsorbent particles and in such a situation transport of ions to the boundary is not possible at a significant rate.

In the present studies, B_t versus time graph exhibit linearity with straight lines passing through the origin in case of adsorption of the dye over Bottom Ash (Fig. 12) at different

Table 7
Rate constant of adsorption (k_{ad}) for the adsorption of Methyl Orange over Bottom Ash and De-Oiled Soya

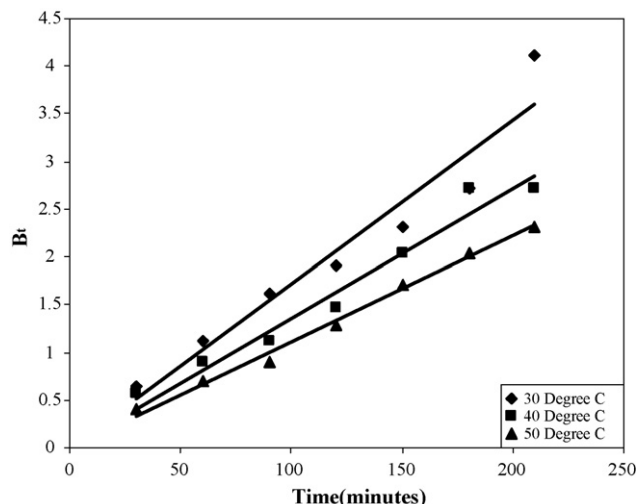| Adsorbent	k_{ad}			β_L		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Bottom Ash	0.017	0.014	0.011	1.066×10^{-7}	9.015×10^{-8}	6.138×10^{-8}
De-Oiled Soya	0.022	0.019	0.022	3.570×10^{-5}	1.587×10^{-5}	1.540×10^{-5}

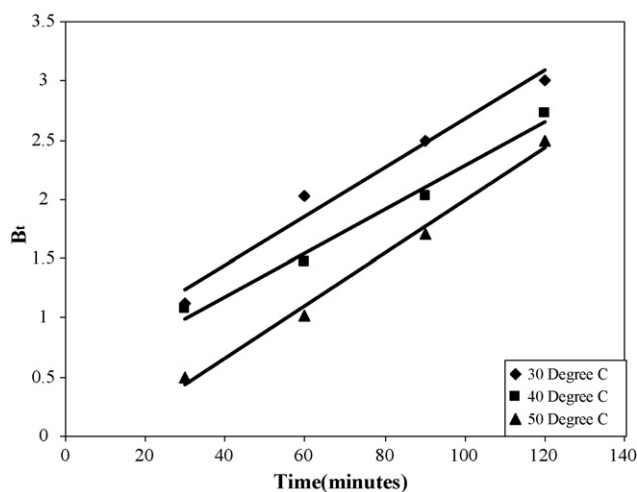Fig. 12. Plot of time vs. B_t for Methyl Orange–Bottom Ash system at different concentrations at 30 °C.

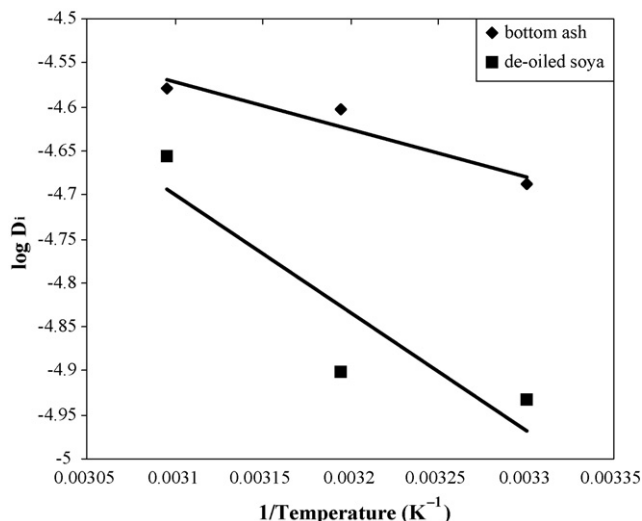Fig. 13. Plot of time vs. B_t for Methyl Orange–De-Oiled Soya system at different concentrations at 30 °C.

Fig. 14. Plot of 1/temperature vs. log D_i for Methyl Orange–Bottom Ash system and Methyl Orange–De-Oiled Soya system.

the mobility of the ions with increase in temperature. The energy of activation (E_a), entropy ($\Delta S^{\#}$) and pre-exponential constant (D_o), values were evaluated using the following relations and shown in Table 8.

$$D_i = D_o \exp \left(\frac{E_a}{RT} \right) \tag{9}$$

$$D_o = \left(\frac{2.72 d^2 kT}{h} \right) \exp \left(\frac{\Delta S^{\#}}{R} \right) \tag{10}$$

where d is the average distance between two successive sites of the adsorbent, k the Boltzmann constant, h the Planks constant, E_a the energy of activation, T the temperature and R is the universal gas constant. The negative values of $\Delta S^{\#}$ obtained for both the systems reflect that no significant change occurs in the internal structure of the adsorbents during the adsorption of the dye.

3.6. Mass transfer study

Following mathematical mass transfer model as given by McKay et al. [44] was employed for studying mass transfer for adsorption of Methyl Orange over Bottom Ash and De-Oiled Soya:

$$\ln \left(\frac{C_t}{C_o} - \frac{1}{1 + mk} \right) = \left(\frac{1 + mk}{mk} \beta_L S_S \right) t + \left(\frac{mk}{1 + mk} \right) \tag{11}$$

temperatures and concentrations suggesting thereby the rate determining process as particle diffusion. However, in case of De-Oiled Soya adsorption, straight lines without passing origin are obtained at different temperatures and concentrations (Fig. 13) the process is interpreted as film diffusion.

The effective diffusion coefficient (D_i) values are calculated from the slopes of B_t versus time graph for both the adsorbents at 30, 40 and 50 °C. It is clear from Fig. 14 plotted between 1/temperature and log D_i indicates that values of D_i also increases with increasing temperature, indicating thereby an increase in

Table 8
Values of effective diffusion coefficient (D_i), pre-exponential constant (D_o), activation energy (E_a) and entropy of activation ($\Delta S^{\#}$) for the diffusion of Methyl Orange adsorbing over Bottom Ash and De-Oiled Soya

Adsorbent	D_i (m^2/min)			D_o (m^2/min)	E_a (J mol^{-1})	$\Delta S^{\#}$ (J K^{-1} mol^{-1})
	30 °C	40 °C	50 °C			
Bottom Ash	1.14×10^{-5}	1.20×10^{-5}	1.31×10^{-5}	1.07×10^{-4}	5659.841	−279.835
De-Oiled Soya	1.021×10^{-4}	8.381×10^{-5}	9.388×10^{-5}	3.29×10^{-4}	3278.201	−270.587

where C_t is the concentration of adsorbate ($mg\,l^{-1}$) after time t and C_o the initial concentration of adsorbate ($mg\,l^{-1}$), k ($l\,g^{-1}$) the constant obtained by multiplying the Langmuir constants Q_o and b, m ($g\,l^{-1}$) and S_S (cm^{-1}) the mass and outer surface area of the adsorbent particles per unit volume of particle free slurry respectively and β_L ($cm\,s^{-1}$) is the mass transfer coefficient are evaluated by using following equations:

$$m = \frac{W}{V} \qquad (12)$$

$$S_S = \frac{6m}{(1 - \varepsilon_P)d_p\rho_P} \qquad (13)$$

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

The $\ln((C_t/C_o) - (1/(1 + mk)))$versus time plots (Figs. 15 and 16) for the Bottom Ash and De-Oiled Soya respectively, give a straight line. The values of β_L are determined from the slopes and intercepts of these graphs for each system and summarized in Table 7. The values of β_L obtained signify that the rate of mass transfer of the Methyl Orange particles on both the adsorbents from bulk to solid phase is rapid. This also reflects good affinity of both the adsorbent materials towards Methyl Orange.

3.7. Column studies

Bulk removal of the adsorbate by column studies proves to be more advantageous over batch studies. Thus, for both the adsorbents, fixed bed column studies were carried out by well-established methods [45,46]. Through the prepared columns 1×10^{-4} M dye solution was passed at the rate of 0.5 ml/min. Breakthrough curves of eluted volume versus concentration of
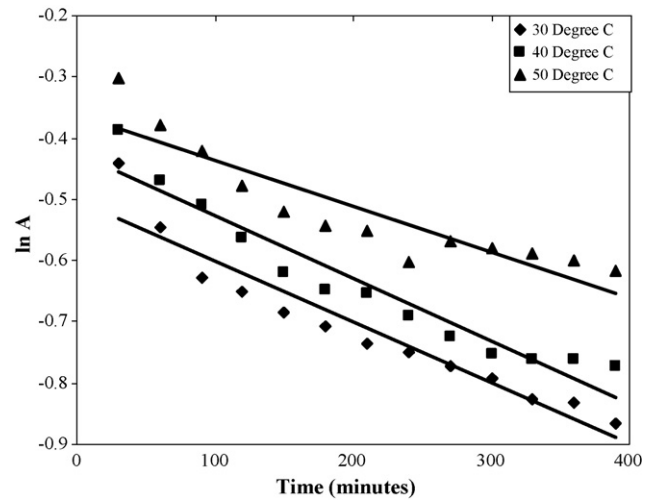

Fig. 15. Plot of time vs. $\ln A$ for the mass transfer of Methyl Orange–Bottom Ash system at different temperatures. Volume of aqueous solution of dye = 25 ml, concentration of adsorbate = 10×10^{-5} M.

the eluted dye for both the systems are plotted and depicted in Fig. 17. It is found that out of 11.45 mg of the dye taken in the solution 3.618 mg adsorbed over 1 g of Bottom Ash, while 4.166 mg of the dye adsorbed over total 0.25 g of De-Oiled Soya out of 15.00 mg of the eluted dye. Breakthrough curves obtained in both the cases are used in calculating parameters like, length of the primary adsorption zone (δ), total time involved for the establishment of primary adsorption zone (t_x), time for the primary adsorption zone to move down its length (t_δ), time for initial formation of primary adsorption zone (t_f), mass rate flow of the adsorbent (F_m) and fractional capacity of the column (f) by using following equations:

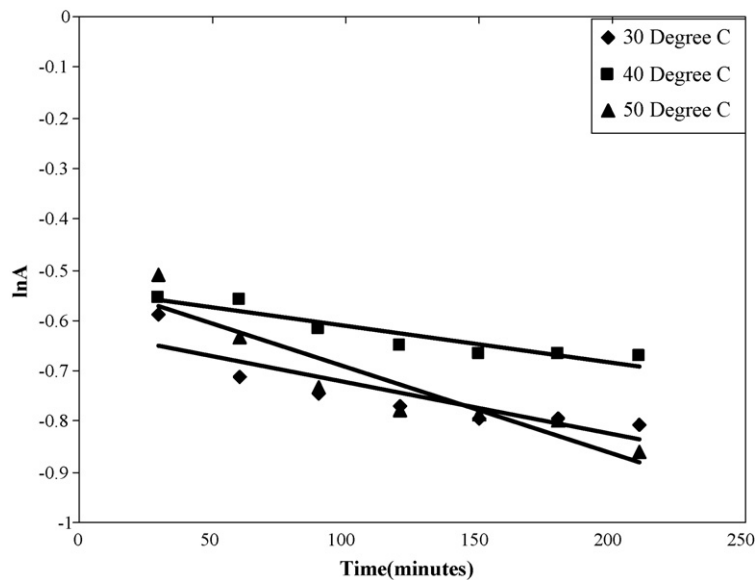$$t_x = \frac{V_x}{F_m} \qquad (14)$$

Fig. 16. Plot of time vs. $\ln A$ for the mass transfer of Methyl Orange–De-Oiled Soya system at different temperatures. Volume of aqueous solution of dye = 25 ml, concentration of adsorbate = 10×10^{-5} M. $A = ((C_t/C_o) - (1/(1 + mk)))$.
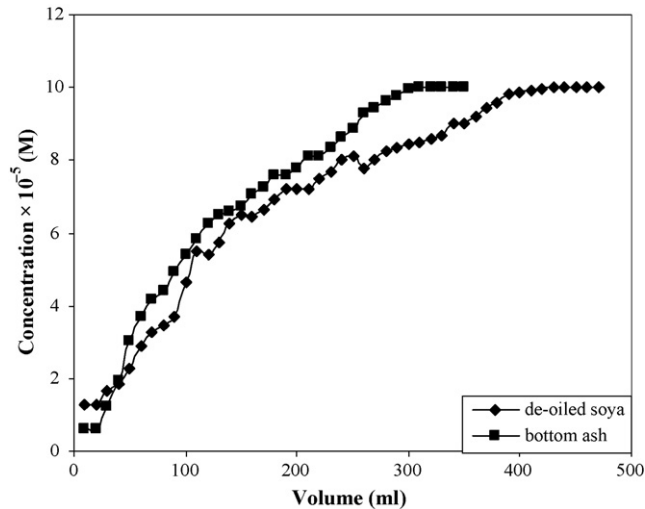
Fig. 17. Breakthrough curve for Methyl Orange–Bottom Ash and Methyl Orange–De-Oiled Soya columns.

Fig. 18. Desorption of Methyl Orange from Bottom Ash and De-Oiled Soya columns.

$$t_\delta = \frac{V_x - V_b}{F_m} \tag{15}$$

$$\frac{\delta}{D} = \frac{t_\delta}{t_x - t_f} = \frac{t_\delta}{t_x + t_\delta(f-1)} = \frac{V_x - V_b}{V_b + f(V_x - V_b)} \tag{16}$$

$$f = 1 - \frac{t_f}{t_\delta} = \frac{M_S}{(V_x - V_b)C_o} \tag{17}$$

$$\text{Percentage saturation} = \frac{D + \delta(f-1)}{D} \times 100 \tag{18}$$

The calculated values of all these parameters are presented in Tables 9 and 10. Table 10 indicates that the values of t_x and t_δ for the Methyl Orange–Bottom Ash adsorption are less than those for the Methyl Orange–De-Oiled Soya system. The data obtained reveals that the time taken for the initial formation of primary adsorption zone (t_f) for both the systems is 0.666 h, whereas, the requisite time for the movement of a zone its own length in the column (t_δ) is between 5.1145 and 319.756 h. For both the systems the fractional capacity f, at breakpoint is calculated around 0.9. The percentage saturation was found to be 99.96% for Bottom Ash column and 99.71% for De-Oiled Soya column. The $V_x - V_b$ values indicate that the additional quantity of adsorbate per unit cross-sectional area that will result
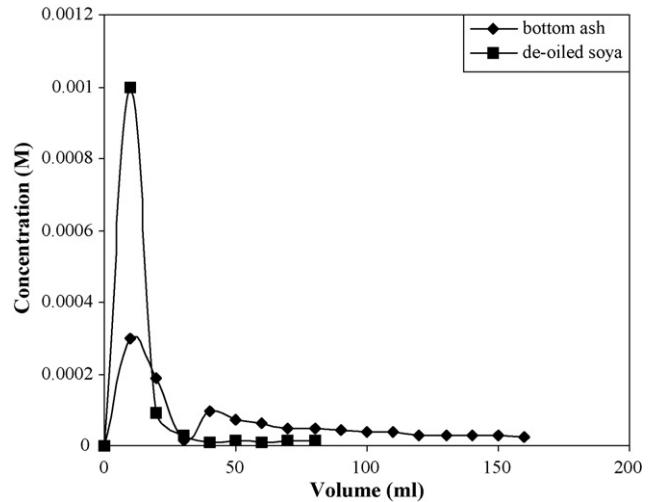
in complete exhaustion of the capacity of adsorbent and are found to be 290.0 and 390.0 ml for Bottom Ash and De-Oiled Soya, respectively.

3.8. Column regeneration and dye recovery

The recovery of the dye and column regeneration was carried out using dilute NaOH (pH 11) through the exhausted column under specified conditions of flow rate, column bed etc. and results obtained are depicted in Fig. 18. In case of Bottom Ash total 160 ml of dilute NaOH was found to be sufficient for desorption of Methyl Orange. For De-Oiled Soya, total about 80 ml of the eluent brought complete desorption of the dye. The total percentage recovery of the dye was almost 98.09 and 93.27% for Bottom Ash and De-Oiled Soya respectively.

The collected volume of the NaOH versus recovered amount of the dye graph exhibits a large collection (45% of the desorbed dye) of the dye was achieved by first 20 ml of the eluent for Bottom Ash column and fourteen more aliquots of 10 ml each were sufficient to recover remaining amount of the dye. Thus, out of adsorbed 3.61×10^{-3} g of the dye, 1.958×10^{-3} g (55%) was removed in first 40 ml and total 160 ml of the solvent could desorb almost 98% (3.548×10^{-3} g) dye. Similarly, during the regeneration of De-Oiled Soya column, initial 60 ml of NaOH

Table 9
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^2)	D (cm)
Bottom Ash	10×10^{-5}	9.98×10^{-5}	0.64×10^{-5}	300	20	280	6.38	1.0
De-Oiled Soya	10×10^{-5}	9.91×10^{-5}	1.29×10^{-5}	470	20	450	0.02	0.75

Table 10
Parameters for fixed bed adsorber

Adsorbent	t_x (min)	t_δ (min)	t_f (min)	f	δ (cm)	Percentage saturation
Bottom Ash	14874.69	13915.04	40	0.997	0.1065	99.96
De-Oiled Soya	20169.22	19185.36	40	0.997	0.714	99.71

desorbed about 90.98% (3.79×10^{-3} g out of 4.16×10^{-3} g of total adsorbed dye) of the Methyl Orange. The remaining dye was obtained by eluting two more aliquots of 10 ml each which resulted in removal of about 93.27% of the dye (3.88×10^{-3} g). Both the columns were then washed with hot water at the flow rate of 0.5 ml min^{-1}.

Loading the dye solution of known concentration and then desorbing the columns several times, gave the breakthrough capacities of the columns. The breakthrough capacities are found about 90, 78, 63 and 58% mg g^{-1} for Bottom Ash column and 85, 72, 59 and 46% mg g^{-1} for De-Oiled Soya column, during first, second, third and fourth cycles, respectively. The drop in the breakthrough capacity of the columns clearly indicates the need of thorough regeneration treatment after each column operation.

4. Conclusion

The fact has been established that Bottom Ash and De-Oiled Soya can be used as potential adsorbents for removal of Methyl Orange from waste waters, the adsorption being dependent on pH, sieve sizes, temperature etc. Adsorption was found to be maximum at pH 3, mesh size 170 and temperature 30 °C. Langmuir and Freundlich models could be successfully applied to show that adsorption is localized to a monolayer and to predict the adsorption capacities of the two adsorbents. The calculated values for thermodynamic parameters such as ΔH^o, ΔS^o and ΔG^o clearly indicate that the ongoing process is exothermic, random and feasible respectively in case of both the adsorbents. The kinetics of the process indicates that the dye removal takes place via particle diffusion for Bottom Ash and via film diffusion in case of De-Oiled Soya. In the column operations, adsorption capacities of the adsorbents are found as 3.618 mg/g for the Bottom Ash and 16.664 mg/g for the De-Oiled Soya, while percentage saturations are found to be 98.61% for Bottom Ash and 99.8% for De-Oiled Soya. The dye can be recovered from these columns using NaOH as an eluent. The percentage recovery is found to be 98.09 and 96.22%, respectively. Thus, a conclusion can be drawn that both Bottom Ash and De-Oiled Soya can act as excellent adsorbers.

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