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# Use of waste materials—Bottom Ash and De-Oiled Soya, as potential adsorbents for the removal of Amaranth from aqueous solutions

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# Abstract

Bottom Ash, a power plant waste material and De-Oiled Soya, an agriculture waste product were successfully utilized in removing trisodium 2-hydroxy-1-(4-sulphonato-1-naphthylazo)naphthalene-3,6-disulphonate—a water-soluble hazardous azo dye (Amaranth). The paper incorporates thermodynamic and kinetic studies for the adsorption of the dye on these two waste materials as adsorbents. Characterization of each adsorbent was carried out by I.R. and D.T.A. curves. Batch adsorption studies were made by measuring effects of pH, adsorbate concentration, sieve size, adsorbent dosage, contact time, temperature etc. Specific rate constants for the processes were calculated by kinetic measurements and a first order adsorption kinetics was observed in each case. Langmuir and Freundlich adsorption isotherms were applied to calculate thermodynamic parameters. The adsorption on Bottom Ash takes place via film diffusion process at lower concentrations, while in the case of De-Oiled Soya process only particle diffusion takes place in the entire concentration range.

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## 1. Introduction

Removal of hazardous industrial effluents is one of the growing needs of the present time. Various techniques like, coagulation, adsorption, chemical oxidation and froth floatation etc. have been used for the removal of organics as well as inorganics from wastewaters. Amongst these, adsorption is considered to be most potential one due to its high efficiency and ability to separate wide range of chemical compounds [1,2]. Over the years, waste materials from industrial and agricultural products, such as blast furnace slag, rubber tyres, sawdust, rice straw, coconut husk, peat moss etc. have been exploited as possible alternative to activated carbon to remove hazardous chemicals [3]. Leaving away these commonly used adsorbents we have been trying to utilize some waste materials to remove hazardous dyes [4].

Trisodium 2-hydroxy-1-(4-sulphonato-1-naphthylazo) naphthalene-3,6-disulphonate (Amaranth) is a widely used hazardous dye. This is used for colouring textiles, paper, phenol-formaldehye resins, wood and leather. Before its legal prohibition to use as colouring agent for food and beverages, it was also employed as food additive in jams, jellies, ketchup and cake decoration. Though its carcinogenic nature is still debatable but it has now been well proved that higher concentration of this dye can adversely affect human/animal health and can cause tumour, allergic and respiratory problems [5–7]. There are also some evidences, which suggest that it may also cause birth defects [8]. It is a water-soluble dye with high solubility and thus difficult to remove by common chemical treatments. Keeping these in view, it is considered necessary to attempt and provide an easy, feasible and reliable method for its removal and the use of adsorption technique was exploited.

The 'Bottom Ash' is a waste material obtained by thermal power generation plants after combusting coke. It is

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an undesired collected material, which is transported and dumped near the surrounding land. Its disposal has always been a matter of concern to the station authorities, as the dumped ash is considered highly unsuitable for the agricultural utilization. Though it has been used as a potential adsorbent for the removal of metals [9,10] in previous years, however, its capability to adsorb organic substances [11] is not much exploited so far.

The De-Oiled Soya is the processed out waste material from Soya industries, which is obtained after extracting all possible nutrients of Soya beans. India is one of the leading producers of the Soya bean crop and captivatingly many Soya Oil industries near Bhopal, India. Thus, use of De-Oiled Soya, as an adsorbent is a thoughtful attempt for its valuable, necessitous and needy utilization for the mankind, which also fits best in the agro industrial scenario.

In our earlier work [3], we reported the adsorption of Malachite Green from wastewaters using Bottom Ash. Present paper is devoted to evaluate the effectiveness of activated Bottom Ash and De-Oiled Soya as adsorbents for the removal of trisodium 2-hydroxy-1-(4-sulphonato-1-naphthylazo)naphthalene-3,6-disulphonate (Amaranth). This paper incorporates a comprehensive and detailed comparison of adsorption kinetics and equilibrium uptake of Amaranth using these adsorbents.

## 2. Materials and methods

Trisodium 2-hydroxy-1-(4-sulphonato-1-naphthylazo) naphthalene-3,6-disulphonate (Amaranth) (molecular formula  $C_{20}H_{11}N_2O_{10}S_3Na_3$ ), was obtained from M/s Merck and its stock solution (1 mM) was prepared in doubly distilled water. All other reagents used were of A.R. grade.



The Bottom Ash was procured from thermal power station (TPS) of M/s Bharat Heavy Electrical Limited (B.H.E.L), Bhopal (India). The sub-bituminous coal used by TPS was obtained from M/s South Eastern Coal Field Limited, Chirmiri, Sarguja (India). The De-Oiled Soya was a free gift from M/s Surya Agro Oils, Bhopal, India.

The chemical analysis of the Bottom Ash was achieved by conventional methods as reported by Vogel [12]. The pH of each solution was measured by using microprocessor based pH meter; model number HI 8424 (M/s Henna Instruments, Italy) and absorbance measurements were carried out on UV/vis spectrophotometer model number 117 (M/s Systronics, Ahmedabad, India) over the wavelength range 200–500 nm.

#### 2.1. Material development

Adsorbents, Bottom Ash and De-Oiled Soya were first washed with doubly distilled water and dried. The dried material was then treated with hydrogen peroxide for 24 h to oxidize the adhering organic material and for the removal of moisture; the product obtained was kept in an oven at 100 °C for 12 h. Now De-Oiled Soya was sieved to desired particle size, while Bottom Ash was further activated in furnace at 500 °C for 15 min in presence of air and then sieved to obtain different particle sizes. Finally the products were stored in a vacuum desiccator until used.

## 2.2. Adsorption studies

Adsorption studies with both the adsorbents were carried out by batch technique at 30, 40 and 50 °C temperatures. A series of 100 mL graduated conical flasks containing 25 mL of adsorbate solutions of varying concentrations were employed at a desired pH. These were agitated intermittently to achieve equilibration. The concentration of the dye in the solution after equilibrium adsorption was determined spectrophotmetrically by measuring the absorbance at  $\lambda_{max}$  of 520 nm. The wavelength was recorded before and after the adsorption and no shift in the peak was observed. For kinetic studies, 25 mL solution of Amaranth of known concentration and a known amount of adsorbent were taken in an airtight 100-mL conical flask. Keeping the flask in a water bath, maintained at desired temperature, mixture was mechanically agitated. After a definite interval of time, the solution of the flasks was filtered and filtrate of each was analysed for the uptake of dye. The kinetic studies were also performed at different adsorbate concentrations.

# 3. Results and discussion

#### 3.1. Characterization of adsorbents

The chemical analysis of the adsorbents is given in Table 1 differential thermal analysis (DTA) curves plotted for the activated Bottom Ash exhibited its thermal

Table 1		
Chemical	constituents	of adsorbents

Bottom Ash		De-Oiled Soya	
Constituents	Percentage by weight	Constituents	Percentage by weight
Moisture	15.0	Moisture	11
SiO <sub>2</sub>	45.4	Fibre	6
$Al_2O_3$	10.3	SiO <sub>2</sub>	2
Fe <sub>s</sub> O <sub>3</sub>	9.7	Ca	0.2
CaO	15.3	Р	0.7
MgO	3.1	Profat	48
Na <sub>2</sub> O	1.0	Proteins	29
		Amino acids	3

stability and negligible weight loss was accounted, even at high temperatures. d-Spacing values provided by Xray spectrum of the adsorbent reflected the presence of mainly alumina (Al<sub>2</sub>O<sub>3</sub>), gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), beaverite [Pb(Cu,Fe,Al)<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>], borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O) and kaolinite [2{Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>}]. Scanning electron microscopic photographs of the activated Bottom Ash and De-Oiled Soya revealed their surface texture and porosity and based on these photomicrographs, particles of the Bottom Ash were approximated as spheres.

The IR spectrum of activated Bottom Ash exhibited sharp adsorption bands in the region  $3700-3500 \text{ cm}^{-1}$  indicating thereby the presence of free hydroxyl group. The bands at 3467, 2930, 2676, 1502, 1097 and 790 cm<sup>-1</sup> showed the presence of laumonite, amber, mulite, azurite, bavenite and kaolinite. In case of De-Oiled Soya, the bands obtained at 479, 779, 1113, 3459 represented gorthite (4[FeO·OH]), corundum (2[ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>]), coesite (SiO<sub>2</sub>), laumonite (4[CaAl<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>·4H<sub>2</sub>O]).

#### 3.2. Adsorption studies

The adsorption behaviour of the dye on Bottom Ash and De-Oiled Soya was studied over a wide range of pH (2–7), as depicted in Fig. 1. From the figure it is clear that in both the adsorbents the maximum uptake of Amaranth takes place at a pH 2.0. Hence, all subsequent studies were performed at pH 2.0.

The adsorption of Amaranth was also recorded at adsorbate concentrations ranging from  $3 \times 10^{-5}$  to  $1 \times 10^{-4}$  M, at a pH of 2.0 and at different temperatures (30, 40 and 50 °C). Fig. 2 shows that the adsorption of Amaranth on both the adsorbents increases with an increase in temper-

ature, indicating thereby the process to be endothermic in nature in both cases. The removal of Amaranth in both cases is fast at lower concentrations and at higher concentrations, the uptake changes from 100 to 52.05% for Bottom Ash and 100 to 92.38% in case of De-Oiled Soya at  $50 \,^{\circ}$ C.

Sorption data of Amaranth by Bottom Ash and De-Oiled Soya have been correlated with Langmuir (Eq. (1)) and Freundlich (Eq. (2)) models:

$$\frac{1}{q_{\rm e}} = \frac{1}{Q_{\rm o}} + \frac{1}{bQ_{\rm o}} \times \frac{1}{C} \tag{1}$$

$$\log q_{\rm e} = \log K_{\rm f} + \frac{1}{n} \log C \tag{2}$$

where C is measured molar concentration in solution at equilibrium,  $Q_0$  is number of moles of solute adsorbed per unit weight of adsorbent,  $q_e$  is the number of moles of solute adsorbed per unit weight at concentration C and b,  $K_f$  and n are constants.

The values of Langmuir (Fig. 3) and Freundlich (Fig. 4) constants obtained from the plots are listed in the Table 2. The data indicates that the value of  $K_f$  is almost similar for both the systems at all temperatures. In both cases, values of  $Q_0$  obtained from the intercepts of Langmuir plots (i.e. maximum uptake) increases with increase in temperature. This also indicates the processes to be endothermic in nature. However, the  $Q_0$  values appeared to be slightly higher for Amaranth–De-Oiled Soya system, indicating thereby better adsorption ability of De-Oiled Soya. It is pertinent to mention that the Langmuir model is slightly better fitted then the Fraundlich model in the present studies and indicates the formation of the monolayers of the dye on the adsorbent.



Fig. 1. Effect of pH on percentage removal of Amaranth by Bottom Ash and De-Oiled Soya (a) Bottom Ash: amount, 0.1 g/25 mL; sieve size, 0.08–0.15 mm; concentration,  $8 \times 10^{-5}$  M. (b) De-Oiled Soya: amount, 0.05 g/25 mL; sieve size,  $\leq 0.3$ ; concentration,  $9 \times 10^{-5}$  M.



Effect of Concentration on Adsorption of Amaranth over Bottom Ash & De-Oiled Soya at Different Temperatures

Fig. 2. Effect of concentration on adsorption of Amaranth over Bottom Ash & De-Oiled Soya at different temperatures (a) Bottom Ash: amount, 0.1 g/25 mL; sieve size, 0.08-0.15 mm pH 2; (b) De-Oiled Soya: amount, 0.05 g/25 mL; sieve size,  $\leq 0.3 \text{ mm}$ , pH 2.



Fig. 3. Langmuir adsorption isotherms for Amaranth adsorption at different temperatures. (a) Bottom Ash adsorption, (b) De-Oiled Soya adsorption.



Fig. 4. Freundlich adsorption isotherms for Amaranth at different temperatures. (a) Bottom Ash adsorption, (b) De-Oiled Soya adsorption.

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1	7	5

Adsorbent	Langmuir constants						
	$\overline{Q_{ m o} \times 10^{-3}}$ (m	$\overline{Q_{ m o} \times 10^{-3}} \; ({ m mol/g})$			$b \times 10^3 (L/mol)$		
	30°C	40 °C	50 °C	30 °C	40 °C	50 ° C	
BA	1.965	2.053	2.123	13.768	14.252	14.564	
DOS	2.304	2.336	2.786	153.356	228.877	237.748	
	Freundlich constants						
	n			$K_{\rm f}$ (L/g)			
BA	0.1520	0.1452	0.1397	0.9999	0.9999	0.9999	
DOS	0.1423	0.1650	0.1368	0.9999	1.0000	1.0000	
	<i>r</i> -values						
BA	0.908	0.467	0.462				
DOS	0.068	0.046	0.045				

Table 2 Freundlich & Langmuir constants and *r*-values of Amaranth adsorption over Bottom Ash (BA) & De-Oiled Soya (DOS) at different temperatures

To confirm the favourability of adsorption process, method suggested by Weber and Chakraborti [13] was employed and separation factor 'r' [14], a dimensionless constant, was calculated by following equation:

$$r = \frac{1}{1 + bC_0} \tag{3}$$

where values *b* and  $C_o$  were obtained from Langmuir isotherm. The linear, favourable or irreversible nature of isotherm is dependent on the obtained value of *r* as unity, between 0 and 1, and zero, respectively. Table 2 clearly exhibits that the values of *r* are less then 1 at all temperatures for both the adsorbents, indicating thereby a highly favourable adsorption in both the cases (r < 1).

Thermodynamic data of each system was calculated from the concern Langmuir isotherms (Table 3) using following equations:

$$\Delta G^{\circ} = -RT \ln b \tag{4}$$

$$\Delta H^{\circ} = -R\left(\frac{T_2T_1}{T_2 - T_1}\right)\ln\left(\frac{b_2}{b_1}\right)$$
(5)

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} \tag{6}$$

where b,  $b_1$ ,  $b_2$  are the equilibrium constants at different temperatures and obtained from the slopes of adsorption isotherms at different concentrations.

In each case, the feasibility and spontaneous nature of adsorption process is well confirmed from the negative values of  $\Delta G^{\circ}$ . It is also observed that in each case,  $\Delta G^{\circ}$  value decreases with the increasing temperature, indicating thereby

greater adsorption at higher temperature. The positive values of enthalpy change  $(\Delta H^{\circ})$  further suggest the endothermic nature, while positive  $\Delta S^{\circ}$  values reflect the affinity of the adsorbent materials towards Amaranth.

## 3.3. Kinetic studies

Attempts were also made to innovate more effective designing and modelling of the adsorption process on these cheap and easily available adsorbents. For this purpose, kinetics of the adsorption process was carefully monitored by recording effects of some major parameters like contact time, amount and particle size of adsorbent and concentration of adsorbate solution on the uptake of Amaranth on Bottom Ash and De-Oiled Soya.

Preliminary investigations suggest that the uptake of Amaranth within first hour was almost in the range 0.75-5.27% and 42.75-47.39% over the Bottom Ash and De-Oiled Soya, respectively, at each temperature (Fig. 5). In case of Bottom Ash equilibrium was established within 9-10 h, whereas, in case of De-Oiled Soya 6-7 h were found sufficient for attaining the equilibrium. Further, kinetics of the process at different temperatures (30, 40 and  $50 \,^{\circ}$ C) exhibits an increase in adsorption with the increasing temperature (Fig. 5). The half-life of each process was also calculated and was found to decrease with increase in temperature. These results once again confirm endothermic nature of the on-going process in both cases.

The effect of amount of adsorbent on the rate of removal of Amaranth was also studied and results obtained are presented in Table 4. It was found that with the increasing dosage of

Table 3

Values of thermodynamics parameters for the adsorption of Amaranth on different adsorbents

Adsorbent	$-\Delta G^\circ$ (kJ mol <sup>-</sup>	<sup>-1</sup> )		$\Delta H^{\circ}$ (kJ mol <sup>-1</sup> )	$\Delta S^{\circ} (\mathrm{J}\mathrm{K}^{-1} \mathrm{mol}^{-1})$
	30 °C	40 °C	50 °C		
Bottom Ash	23.976	24.857	25.709	2.277	86.658
De-Oiled Soya	30.080	32.115	33.243	121.844	490.917



Effect of Contact Time for Adsorption of Amaranth at different Temperatures (a) Bottom Ash adsorption (b) De-Oiled Soya adsorption

Fig. 5. Effect of contact time for adsorption of Amaranth at different temperatures (a) amount of Bottom Ash, 0.1 g/25 mL; sieve size, 0.08-0.15 mm; concentration of dye,  $8 \times 10^{-5} \text{ M}$ ; (b) Amount of De-Oiled Soya, 0.05 g/25 mL; sieve size,  $\leq 0.3$ ; concentration of dye,  $9 \times 10^{-5} \text{ M}$ .

 Table 4

 Effect of amount of different adsorbents on the uptake of Amaranth

Adsorbent	Amount of adsorbent (g per 25 mL)	Adsorbed amount of Amaranth $\times 10^{-4}$ (g)	<i>t</i> <sub>1/2</sub> (h)
Bottom Ash	0.1	7.86	15.81
	0.2	9.05	12.03
De-Oiled Soya	0.1	12.88	5.63
	0.2	13.45	3.64

adsorbent the rate of removal of adsorbate also increases. It is important to note that there is a substantial increase in adsorption when amount of adsorbents is increased by two times of the undertaken amount (Table 5); however a further introduction of the adsorbents amount did not change the rate significantly. Keeping this in view, in all subsequent kinetic studies the amount of Bottom Ash and De-Oiled Soya was taken as 0.1 g and 0.05 g, respectively. The half-life ( $t_{1/2}$ ) of the process was also calculated at different doses of each adsorbent and it was found that the half-life decreases with increasing amount of adsorbent at a constant temperature (Table 5). This very well confirms the dependence of rate of adsorption on the amount of adsorbent and also specifies the advantage of

Table 5 Effect of sieve size of different adsorbents on the uptake of Amaranth

Adsorbent	Particle size (mm)	Adsorbed Amount of Amaranth $\times 10^{-4}$ (g)	<i>t</i> <sub>1/2</sub> (h)
Bottom Ash (0.1 g per 25 mL)	0.15–0.3	2.416	74.53
	0.08-0.15	7.86	15.81
	$\leq 0.08$	8.16	14.78
De-Oiled Soya (0.05 g per 25 mL)	0.425–0.6	9.15	14.87
	0.3-0.425	12.60	6.35
	$\leq 0.3$	13.39	3.94

powdered adsorbent over granular form from a kinetic viewpoint.

#### 3.3.1. Adsorption rate constant study

To determine the specific rate constant of adsorption processes of Amaranth–Bottom Ash and Amaranth–De-Oiled Soya systems, Lagergren's first order rate expression was applied [15] by using following equation:

$$\log(q_{\rm e} - q_{\rm t}) = \log q_{\rm e} - \frac{k_{\rm ads}}{2.303} \times t \tag{7}$$

where  $q_e$  and  $q_t$  are the amount adsorbed at equilibrium and time *t*, respectively. The plots between  $\log(q_e-q_t)$  and *t* were found to be linear for both the systems (Fig. 6), which clearly confirm the first order nature of the processes in each case. The values of the rate constant,  $k_{ads}$ , for each system was also calculated from the respective Lagergren's plots and are listed in Table 6.

#### 3.3.2. Rate expression and treatment of data

Table 6

For the proper interpretation of experimental data, it is essential to identify the steps in the adsorption process, which govern the overall removal rate in each case. To identify, whether the on-going process is particle diffusion or film diffusion, the kinetic data has been treated by ingenious mathematical treatment suggested by Boyd et al. [16] and Reichenberg [17].

During the adsorption of an organic/inorganic compound by a porous adsorbent, there are three possible consecutive

Values of specific rate constant  $(k_{ads})$  obtained for different adsorbents at different temperatures

Adsorbent	$k_{\rm ads}$ (h <sup>-1</sup> )			
	30 °C	40 °C	50 °C	
Bottom Ash	0.285	0.321	0.351	
De-Oiled Soya	0.239	0.255	0.272	





Fig. 6. Time vs.  $log(q_e - q_t)$  plot for the adsorption of Amaranth at different temperature.

steps involved, viz. film diffusion, particle diffusion and adsorption of adsorbate on the interior surface of the adsorbent. Out of these processes the third one is quite rapid, hence cannot be considered as rate-limiting step [18]. Remaining two steps give rise to following three distinct cases; Case I, when external transport > internal transport, where rate is governed by particle diffusion, Case II, when external transport < internal transport and the rate for these processes is governed by film diffusion and a Case III, when external transport  $\approx$  internal transport, meaning thereby the transport of ions to the boundary may not be possible at a significant rate, hence formation of a liquid film surrounding the adsorbent particles takes place with a proper concentration gradient. To investigate the actual process involved in the present adsorption, a quantitative treatment of the sorption dynamics was employed with the help of following expressions:

$$F = 1 - \frac{6}{\pi^2} \sum_{l=1}^{\infty} \left(\frac{1}{n^2}\right) \exp(-n^2 B_l)$$
(8)

where F is the fractional attainment of equilibrium at time 't' and is obtained by using Eq. (7) and n is Freundlich constant of the adsorbate.

$$F = \frac{Q_t}{Q_\infty}$$

where  $Q_t$  and  $Q_{\infty}$  are amounts adsorbed after time *t* and after infinite time, respectively.

$$B = \frac{\pi^2 D_i}{(r_{\alpha}^2)}$$
 = time constant

where  $D_i$  is the effective diffusion coefficient of adsorbate in the adsorbent phase and  $r_0$  is the radius of adsorbent particles assumed to be spherical.

For every observed value of F, corresponding values of  $B_t$ was derived from Reichenberg's table [17]. The plot of  $B_t$  versus time clearly distinguishes between the film diffusion and the particle diffusion controlled rates of adsorption. In case of Bottom Ash, at low concentrations ( $< 5 \times 10^{-5}$  M) the linearity deviates, while at higher concentrations (>5  $\times$  10<sup>-5</sup> M) the linearity is maintained and straight lines passing through origin are obtained. This suggests involvement of film diffusion at low concentrations and particle diffusion mechanisms at higher concentrations, as the rate-controlling steps. The  $B_t$  versus time plot for Amaranth–De-Oiled Soya system at lower concentrations ( $<5 \times 10^{-5}$  M) were non-linear confirming the film diffusion to be rate-determining mechanism. However, at higher concentrations ( $\geq 5 \times 10^{-5}$  M), the obtained  $B_t$  versus time plots were found linear and passing through the origin, thus the process seems to be particle diffusion controlled in this region, while during the later stages, the film diffusion mechanism also becomes operative, because of deviation of the plot from linearity.

Table 7

Values of effective diffusion coefficient ( $D_i$ ), pre exponential constant ( $D_o$ ), activation energy ( $E_a$ ) and entropy of activation ( $\Delta S^{\#}$ ) for diffusion of Amaranth in Bottom Ash (0.08–0.15 mm) and De-Oiled Soya ( $\leq 0.3 \text{ mm}$ )

Adsorbent	$D_i (\mathrm{m^2/s})$	$D_i$ (m <sup>2</sup> /s)			$E_{\rm a}$ (J mol <sup>-1</sup> )	$\Delta S^{\#} (\mathrm{JK}^{-1} \mathrm{mol}^{-1})$
	30 °C	40 °C	50 °C			
Bottom Ash	$1.25  imes 10^{-10}$	$1.37  imes 10^{-10}$	$1.57 \times 10^{-10}$	$5.750  imes 10^{-10}$	9676.23	-55.274
De-Oiled Soya	$4.99\times10^{-10}$	$5.32\times10^{-10}$	$5.76\times10^{-10}$	$5.244\times10^{-10}$	5936.50	-56.039

The  $D_i$  values for Amaranth–Bottom Ash and Amaranth– De-Oiled Soya systems were also calculated at different temperatures and are listed in the Table 7. It is observed that in each case the  $D_i$  value increases with increasing temperature. This is due to fact that with the rise in temperature the mobility of ions increases, which decreases the retarding force acting on the diffusing ions. The energy of activation  $E_a$ , entropy of activation  $\Delta S^{\#}$  and pre-exponential constant ( $D_o$ ) analogous to the Arrhenius frequency factor are evaluated using Eqs. (9) and (10):

$$D_i = D_0 \, \exp\left(-\frac{E_a}{RT}\right) \tag{9}$$

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

here 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  $E_a$ ,  $D_o$  and  $\Delta S^{\#}$  for the diffusion of Amaranth in Bottom Ash, and De-Oiled Soya are also listed in Table 7. The value of activation energy ( $E_a$ ) was found highest in case of Amaranth-De-Oiled Soya system, indicating thereby high amount of adsorption in this case. The negative values of  $\Delta S^{\#}$  obtained for each system reflect that no significant change occurs in the internal structure of the adsorbents during the adsorption of Amaranth.

#### 4. Conclusions

Waste materials 'Bottom Ash' and 'De-Oiled Soya' were efficiently utilized as adsorbents for the removal of hazardous dye like Amaranth. Batch adsorption studies indicate that in both the cases, almost 100% of the adsorption could be achieved at lower concentrations of the dye, while at higher concentrations it is slightly lower. Kinetics of the processes clearly exhibit that in case of Bottom Ash the adsorption takes place via film diffusion process at lower concentrations and particle diffusion process at higher concentrations, while in the case of De-Oiled Soya process seems to be only particle diffusion controlled through out the entire concentration range. Thermodynamic parameters obtained in both the cases confirm the feasibility of the processes at each concentration. Results clearly indicate that both materials can act as excellent absorbers and are quite economic than commercially available adsorbents.

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