

Process development for the removal and recovery of hazardous dye erythrosine from wastewater by waste materials—Bottom Ash and De-Oiled Soya as adsorbents

Alok Mittal^{a,*}, Jyoti Mittal^a, Lisha Kurup^a, A.K. Singh^b

^a Department of Applied Chemistry, Maulana Azad National Institute of Technology, Bhopal 462007, India

^b Department of Applied Chemistry, University Institute of Technology, RGPV, Bhopal 462036, India

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Abstract

Erythrosine is a water-soluble xanthene class of dye. It is widely used as colorant in foods, textiles, drugs and cosmetics. It is highly toxic, causes various types of allergies, thyroid activities, carcinogenicity, DNA damage behaviour, neurotoxicity and xenoestrogen nature in the humans and animals. The photochemical and biochemical degradation of the erythrosine is not recommended due to formation of toxic by-products. The present paper is an attempt to remove erythrosine from wastewater using adsorption over Bottom Ash—a power plant waste and De-Oiled Soya—an agricultural waste. Under the batch studies, effect of concentration of dye, temperature, pH of the solution, dosage of adsorbents, sieve size of adsorbents, etc., have been studied for the uptake of the dye over both adsorbents. The adsorption process verifies Langmuir and Freundlich adsorption isotherms in both the cases and based on the data different thermodynamic parameters have been evaluated. Batch studies also include kinetic measurements, rate constant study, mass transfer behaviour and establishment of mechanistic pathway for both the cases. For the bulk removal of the dye column operations have been carried out and breakthrough capacities of the Bottom Ash and De-Oiled Soya columns have been calculated. Attempts have also been made for the recovery of the adsorbed dye from exhausted columns by eluting dilute NaOH and more than 90% of the dye was recovered.

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1. Introduction

Erythrosine is a xanthene class, water-soluble cherry-pink red synthetic coal dye, which is used for dyeing variety of materials, such as wool, silk and nylon. It is one of the widely used colorant in drugs and cosmetics [1,2]. It is also used to color a large variety of food stuffs like, cocktail drinks, tinned cherries, fruits, biscuits, chocolate, dressed crab, luncheon meat, salmon spread, stuffed olives, sweets, bakery, snack foods, chewing gums, jellies, ice cream, etc. [3–5].

It mainly consists of disodium 2-(2,4,5,7-tetraiodo-3-oxidooxanthene-9-yl) benzoate monohydrate and tends to dispose with the industrial wastewater, which leads to severe health threat to the mankind. It is highly toxic and its intake by human

being can cause allergic reactions in eyes, skin irritation, irritation to mucous membrane and upper respiratory tract, severe headaches, nausea, water born diseases like dermatitis, etc., and can also cause atopic diseases [6]. It has been well proved that the dye affects thyroid activities in the humans due the presence of iodine in the molecule and its consumption can also prove fatal, as it is carcinogenic in nature [7,8]. The comet assay on the glandular stomach, colon, liver, kidney, urinary bladder, lung, brain and bone marrow indicates that erythrosine induces DNA damage in the gastrointestinal organs even at a low dose [9]. Researches on the Indian women of lower economic background have also proved that long-term use of erythrosine containing lipsticks may lead to abnormal embryonic development [10,11] in them. Moreover, it is hypothesized as a neurotoxin [12–14] and xenoestrogen [15] in nature.

The toxicity and carcinogenic nature of the erythrosine attracted global attention for the removal of erythrosine from wastewater. Photo-catalytic degradation over TiO₂ particles [16]

* Corresponding author. Tel.: +91 9425025427; fax: +91 755 2670904.
E-mail address: aljmittal@yahoo.co.in (A. Mittal).

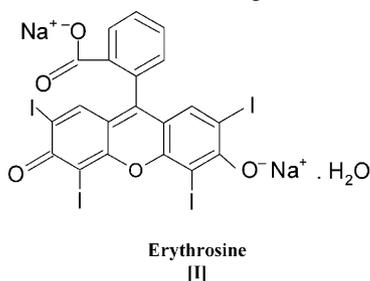
and biochemical degradation [17] have been attempted. Unfortunately, metabolic intermediates after biodegradation have been found more toxic [17]. Removal of erythrosine has also been tried by adsorption technique over activated carbon [18], but the developed method is uneconomical.

Hence, it can be safely judged that despite its high toxicity very limited attempts have been made so far for the removal of erythrosine from the aqueous solutions. This may be either due to high solubility of the dye in water or possibility of generation of toxic intermediates/products during the course of process. Thus, in the present paper attempts have been made to develop an eco-friendly, economic and fast method for the eradication of erythrosine from the wastewater using adsorption over waste materials. One of the major advantages of the adopted method is that it does not produce any toxic by-product during the operations. Moreover, the developed method is easy and versatile because of easy operation and simple design.

For the last few years, our laboratory has exploited cheap adsorbents like Bottom Ash and De-Oiled Soya as efficient and suitable adsorbents for removal and recovery of hazardous dyes [19–22]. Attempts have also been made by other workers to remove hazardous dyes using cheap adsorbents [23–30]. Keeping this in view, these potential adsorbents were now utilized to assess their proficiency for the removal of toxic dye erythrosine. The adsorbents under consideration are ‘Bottom Ash’—a waste product of power generation plants and ‘De-Oiled Soya’—a waste product produced at soyabean oil extracting mills. The Bottom Ash is a coarse, granular, incombustible by-product of coal fired power plants, obtained after combusting coke. It is an undesired collected material, whose disposal has always been a matter of concern to the station authorities, as the dumped ash makes the land infertile [31]. Bottom Ash is not hazardous at all and being a waste material it is negligible in cost. Other adsorbent De-Oiled Soya is the processed out waste material from Soya oil industries, which is obtained after extracting all possible nutrients of soya beans. De-Oiled Soya is being used as animal 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 [32,33].

2. Materials and methods

Erythrosine (disodium 2-(2,4,5,7-tetraiodo-3-oxido-6-oxoxanthene-9-yl) benzoate monohydrate) molecular formula $C_{20}H_6I_4Na_2O_5 \cdot H_2O$, was obtained from M/s Merck and its 0.01 M stock solution was prepared in double distilled water. All other reagents used were 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). The type of coal used by TPS is sub-bituminous and was obtained from M/s South Eastern Coal Field Limited, Chirmiri, Sarguja (India). The other adsorbent, De-Oiled Soya was a kind gift from M/s Surya Agro Oils, Bhopal, India.

The microprocessor based pH meter (model number HI 8424, M/s Henna Instruments, Italy) was used for pH measurements. The IR spectral absorption studies were carried out on infrared spectrometer (HP FT-IR), Quantasorb Model QS-7 surface area analyzer measured the surface area of the adsorbent, X-ray measurements were carried out using Philips X-ray diffractometer and scanning electron microscopy was done using a Philips SEM 501 electron microscope. All absorbance measurements were recorded on UV/vis spectrophotometer model number 117 (M/s Systronics, Ahmedabad, India) over the wavelength range 500–600 nm.

2.1. Material development

For the present research, the adsorbents Bottom Ash and De-Oiled Soya were first washed with doubly distilled water and dried. This dried material was then taken in beaker into which hydrogen peroxide solution was poured with regular stirring and kept undisturbed for 24 h to oxidize the adhering organic material. Afterwards both the adsorbents were kept in an oven at 100 °C to remove the moisture content. Now De-Oiled Soya was sieved to desired particle size, such as 0.30–0.15 mm (50 mesh), 0.15–0.08 mm (100 mesh), ≤ 0.08 mm (170 mesh), etc., whereas Bottom Ash was further activated in a Muffle furnace at 500 °C for 15 min in presence of air and then sieved to different sizes, such as 0.425–0.15 mm (36 mesh), 0.15–0.08 mm (100 mesh) and ≤ 0.08 mm (170 mesh). Final products of both the adsorbents were stored in separate vacuum desiccators until required.

2.2. Adsorption studies

Batch experiments were conducted to observe the effect of pH, temperature, particle size, amount of adsorbent, concentration, contact time, etc., for the adsorption of erythrosine on these adsorbents. Adsorption isotherms were recorded at equilibrium conditions for concentration of dyes over a range 1×10^{-5} to 6×10^{-5} M at a fixed pH (pH range 5–8). The selected concentration range was ascertained after a good deal of examination. For the adsorption studies, in a series of 100 mL volumetric flasks 25 mL of the dye solution of preferred concentration was taken and a known amount of adsorbent of particle size 100 BSS Mesh in case of Bottom Ash and 50 BSS Mesh in case of De-Oiled Soya was added into each flask. The flasks were then mechanically agitated intermittently to achieve equilibrium. When equilibrium is thought to be established, supernatant was carefully filtered through Whattmann filter paper (No. 41) and analyzed spectrophotometrically by measuring the absorbance at λ_{max} of 526 nm.

2.3. Kinetic studies

Kinetic measurements were also carried out through batch technique in airtight 100 mL conical flasks after adding known amount of Bottom Ash and De-Oiled Soya with 25 mL dye solution. The flasks were then kept at water bath maintained at a desired temperature and agitated mechanically. After a preset time interval, the adsorbent was separated by filtration and filtrate thus obtained was analyzed spectrophotometrically to verify equilibrium concentration of the dye. The kinetic studies were also carried out at different adsorbate concentrations.

3. Results and discussion

3.1. Characterization of adsorbent material

The standard analytical methods of chemical analysis [34] were adopted for the characterization of both the activated adsorbents Bottom Ash and De-Oiled Soya. The chemical composition and physicochemical properties obtained are presented in Table 1. Both the adsorbent are acidic in nature [35]. This was confirmed by observing a decline in pH of the deionized water when per gram of each adsorbent was taken separately in 100 mL conical flask and left for 24 h. The scanning electron microscopic photographs show that the particles of Bottom Ash and De-Oiled Soya are porous and can be assumed as spheres. The differential thermal analysis (DTA) curves plotted for activated Bottom Ash exhibited thermal stability of the material and even at high temperature negligible weight loss was accounted. The *d*-spacing values gathered from the X-ray spectrum of the Bottom Ash replicate the presence of mainly alumina (Al₂O₃), gypsum (CaSO₄·2H₂O), beaverite [Pb(Cu,Fe,Al)₃(SO₄)₂(OH)₆], borax (Na₂B₄O₇·10H₂O) and kaolinite [2{Al₂Si₂O₅(OH)₄}. The IR spectral bands obtained at 3467, 2930, 2676, 1502, 1097 and 790 cm⁻¹ indicates the presence of laumonite, amber, mulite, azurite, bavenite and kaolinite in the Bottom Ash. The presence of free hydroxyl groups can be predicted from the sharp adsorption bands in the region of 3700–3500 cm⁻¹. In case of De-Oiled Soya, the presence of gorthite (4[FeO·OH]), corundum (2[α-Al₂O₃]), coesite (SiO₂), laumonite (4[CaAl₂Si₄O₁₂·4H₂O]) was supported by the bands obtained at 479.6, 779.1, 1113.5, 3459 cm⁻¹.

Table 1
Chemical constituents of adsorbents

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

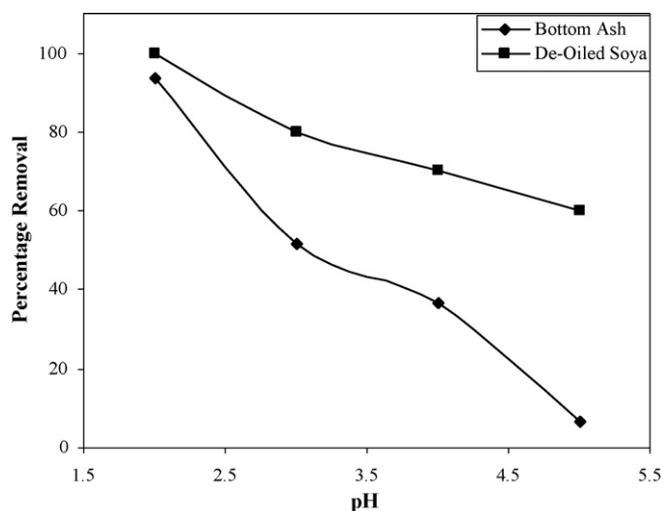


Fig. 1. Effect of pH on uptake of 4×10^{-5} M erythrosine by 0.1 g Bottom Ash (sieve size = 0.15–0.08 mm) and 0.05 g De-Oiled Soya (sieve size = 0.30–0.15 mm) at 30 °C.

3.2. Adsorption studies

To determine the optimum pH range for the removal of the dye, adsorption of both the adsorbents was studied at varying pH range of 2.0–10.0. It was found that in the cases adsorption was appreciable in the pH range between 2 and 5 (Fig. 1). However, at higher pH (≥ 5) adsorption was found to be negligible in case of Bottom Ash, while it decreases to 60% in case of De-Oiled Soya. The nature of the graph clearly depicts that in each system maximum uptake of the dye takes place at around pH 2.0. It was observed that in both cases the uptake of the dye decreases with increase in pH upto 4 and thereafter remains constant. Hence, all the succeeding investigations were performed at pH 2.0 for both the adsorbents.

For both the adsorbents, maximum adsorption of the dye at low pH may be due to increase of protonation by neutralization of negative charge at the surface of the adsorbents. This facilitates the diffusion process and gives more active surface of the adsorbents. The decrease in the adsorption with increase in pH is a result retardation of diffusion, which leads to deprotonation.

Adsorption process was further investigated with different adsorbent doses to optimize the adsorbent dose for the removal of erythrosine from the solutions. The amount of the dye removed by adsorption on Bottom Ash and De-Oiled Soya are summarized in Table 2. From Fig. 2, it is observed that for both the adsorbents the rate of removal of the dye increases with increase in their amount. A significant increase in the adsorption amount

Table 2
Effect of amount of different adsorbents on the rate of uptake of erythrosine

Adsorbent	Amount of adsorbent (g)	Amount adsorbed $\times 10^{-4}$ (g)	<i>t</i> _{1/2} (h)
Bottom Ash	0.05	2.791	14.23
	0.10	6.344	47.86
De-Oiled Soya	0.05	3.080	15.54
	0.10	4.120	21.35

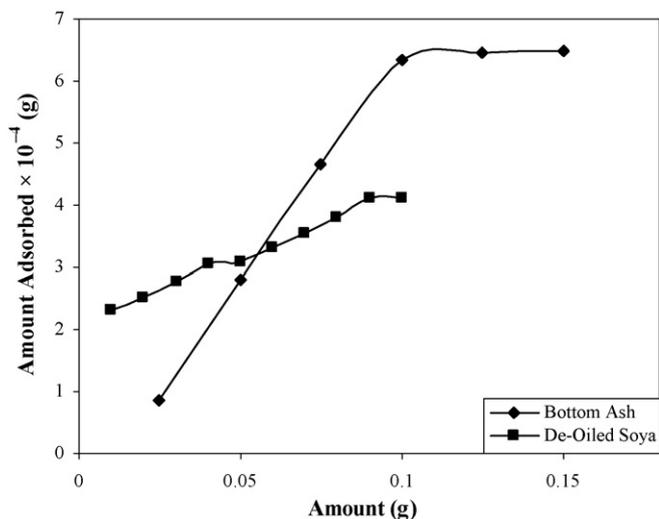


Fig. 2. Effect of amount of adsorbent for the removal of erythrosine (initial concentration = 4×10^{-5} M) using Bottom Ash (sieve size = 0.15–0.08 mm) and De-Oiled Soya (sieve size = 0.30–0.15 mm) at 30 °C and pH 3.

was observed, when adsorption amount is increased from 0.025 to 0.1 g in case of Bottom Ash and 0.01–0.08 g in case of De-Oiled Soya. It is also important to note that any further addition of adsorbent did not cause any significant change in the rate of adsorption. Taking this into consideration, in all subsequent kinetic studies the amount of Bottom Ash and De-Oiled Soya was chosen as 0.10 and 0.05 g, respectively. The half-life of the process was also determined at varying doses for each adsorbent and specified that the half-life increases with increasing amount (Table 2).

The uptake of the dye, erythrosine, separately over Bottom Ash and De-Oiled Soya was investigated at initial concentration ranges from 1×10^{-5} to 6×10^{-5} M at a fixed pH and at different temperatures 30, 40 and 50 °C. Increase in the efficiency of adsorbents with the increase in concentration of the dye in the solution is evident from Fig. 3a and b. Fig. 3a clearly shows that for the Bottom Ash and De-Oiled Soya the uptake is almost 100% at low concentration and about 90% and 39%, respectively, at higher concentration of the dye at 50 °C. These results also signify good efficacy of both the adsorbents towards erythrosine.

The rate of removal of the dye with both the adsorbents at optimum pH and adsorbate concentration was found quite rapid. Fig. 4a and b are illustrating the uptake of dye on Bottom Ash and De-Oiled Soya and depict that the sorption is quite rapid initially, gradually slows down and then reaches to equilibrium. Thus, in the entire temperature range almost 6.4×10^{-4} to 6.8×10^{-4} g and 3.74×10^{-4} to 3.93×10^{-4} g of adsorption of the dye were accomplished over Bottom Ash and De-Oiled Soya, respectively. The plots specify that in both the systems nearly 1 h was sufficient for the attainment of equilibrium by both the adsorbents. Based on above results, the half-lives of both adsorptions were also calculated and found increasing with increase in time.

Furthermore, in the batch adsorption experiments, three different particle sizes, 0.425–0.15 mm (36 mesh), 0.15–0.08 mm

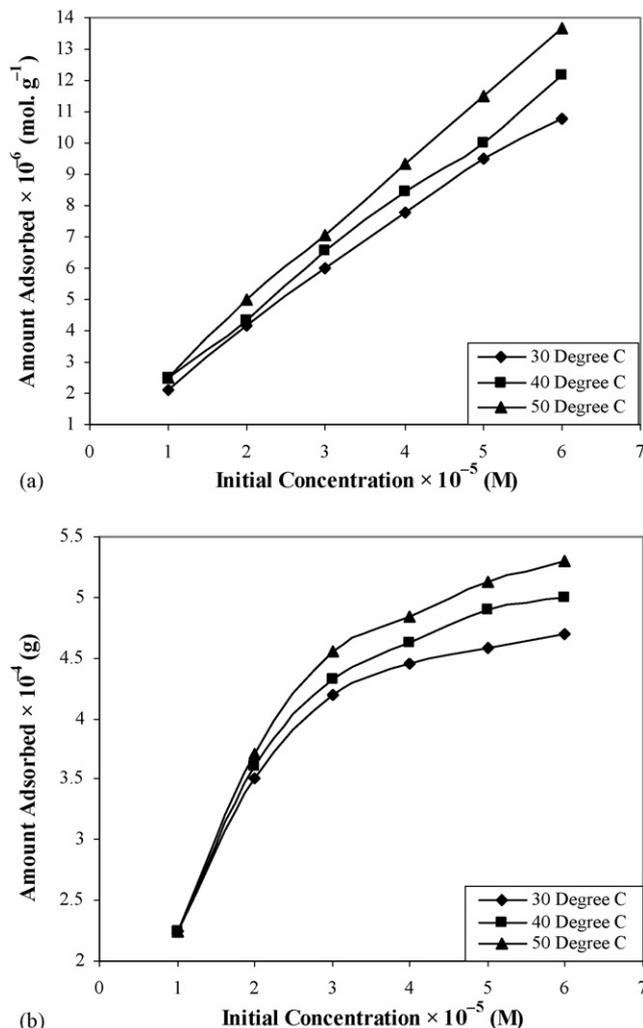
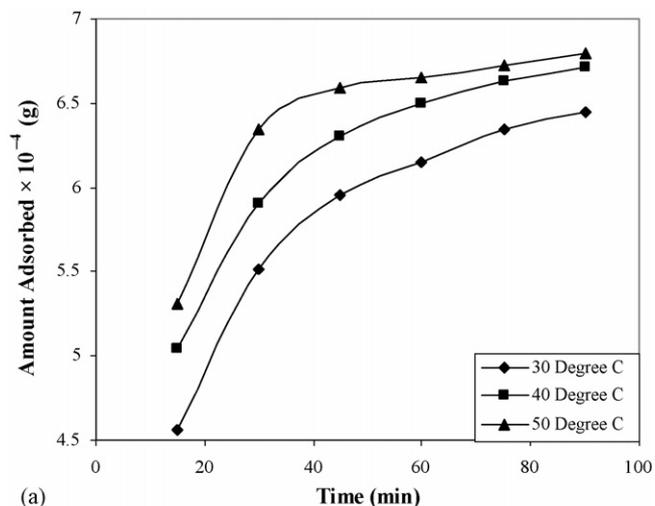


Fig. 3. (a) Effect of concentration for the removal of erythrosine by 0.1 g Bottom Ash (sieve size = 0.15–0.08 mm) at different temperatures and pH 3. (b) Effect of concentration for the removal of erythrosine by 0.05 g De-Oiled Soya (sieve size = 0.30–0.15 mm) at different temperatures and pH 3.

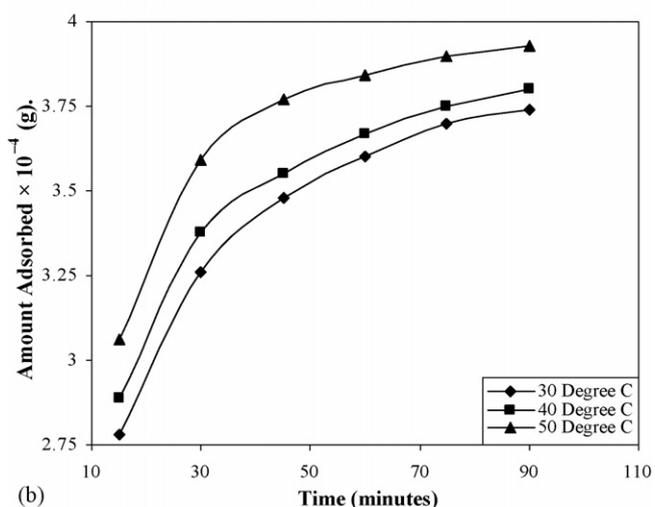
(100 mesh) and ≤ 0.08 mm (170 mesh) in case of Bottom Ash and 0.30–0.15 mm (50 mesh), 0.15–0.08 mm (100 mesh) and ≤ 0.08 mm (170 mesh) in case of De-Oiled Soya have been tried of both the adsorbents and it was observed that in each case the uptake of the dye capacity increases with increasing mesh size (Table 3). However, all further studies were carried out by choosing 0.15–0.08 and 0.30–0.15 mm particle sizes of Bottom Ash and De-Oiled Soya, respectively.

Table 3
Effect of sieve size of different adsorbents on the rate of adsorption of erythrosine

Adsorbent	Particle size (mm)	Amount adsorbed × 10 ⁻⁴ (g)
Bottom Ash	0.15–0.425	4.757
	0.08–0.15	6.344
	≤ 0.08	6.910
De-Oiled Soya	0.15–0.30	3.080
	0.08–0.15	3.819
	≤ 0.08	4.653



(a)



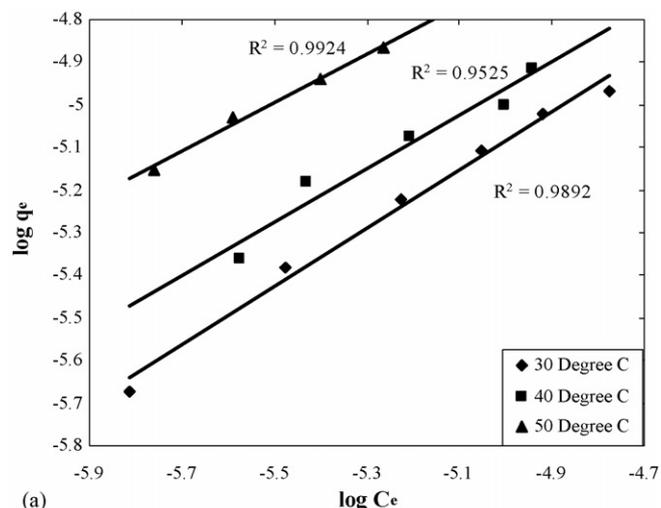
(b)

Fig. 4. (a) Effect of contact time for the uptake of erythrosine (pH 3) by 0.1 g Bottom Ash (sieve size = 0.15–0.08 mm) at different temperatures and at a concentration of 4×10^{-5} M. (b) Effect of contact time for the uptake of erythrosine (pH 3) by 0.05 g De-Oiled Soya (sieve size = 0.30–0.15 mm) at different temperatures and at a concentration of 4×10^{-5} M.

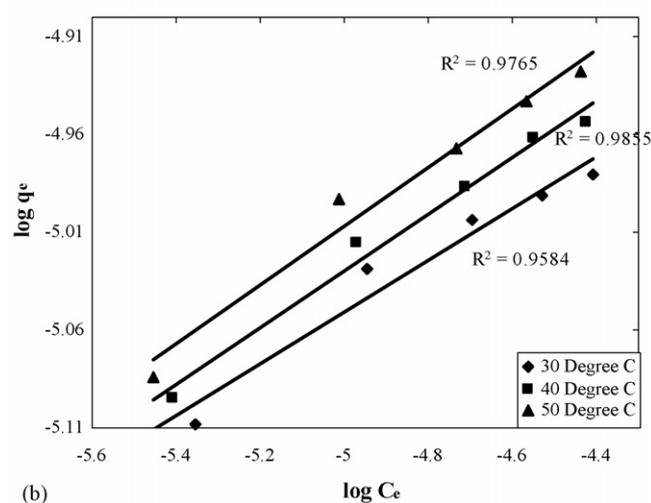
3.3. Adsorption isotherms

The adsorption data obtained at 30, 40 and 50 °C for the erythrosine adsorption over Bottom Ash and De-Oiled Soya were successfully applied on the Freundlich and Langmuir adsorption isotherm models and accordingly thermodynamic parameters were calculated. In order to obtain the equilibrium concentration of adsorbate (C_e) and amount adsorbed at the equilibrium (q_e), linear forms of Langmuir and Freundlich adsorption isotherm equations were employed.

For both the adsorbents, at different temperatures, $\log C_e$ versus $\log q_e$ graphs (Fig. 5a and b) and $1/C_e$ versus $1/q_e$ plots (Fig. 6a and b) gave straight lines and confirm the applicability of Langmuir and Freundlich adsorption models in each case, respectively. The intercept and slope of each straight line were used to evaluate Langmuir and Freundlich constants (Table 4), accordingly. Table 4 indicates that for both the adsorbents, value of Q_0 increases with increase in



(a)



(b)

Fig. 5. (a) Freundlich adsorption isotherm for erythrosine—Bottom Ash system; (b) Freundlich adsorption isotherm for erythrosine—De-Oiled Soya system.

temperature, which confirms an endothermic process in both cases.

The thermodynamic parameters, change in Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) for each system were then assessed from the Langmuir constants. For each system, the negative values of ΔG° establishes the feasibility of the adsorption process. The positive values of enthalpy change (ΔH°) for the processes signifies the endothermic nature and the positive values of entropy change (ΔS°) ponder the excellent affinity of the dye towards adsorbent. The results obtained are represented in Table 5.

To recognize the favourability of the adsorption process the dimensionless separation factor (r) was calculated from the Langmuir isotherm using equation:

$$r = \frac{1}{1 + bC_0} \quad (1)$$

where b signifies the Langmuir constant and C_0 is the initial concentration. At 30, 40 and 50 °C, the separation factor (r) values were found 0.227, 0.216 and 0.092 for Bottom Ash and 0.300, 0.295, 0.290 for De-Oiled Soya, respectively. Less than unity

Table 4
Freundlich and Langmuir constants of erythrosine adsorption over different adsorbents at different temperatures

Adsorbent	Langmuir constants					
	$Q_0 \times 10^{-5}$ (mol/g)			$b \times 10^2$ (L/mol)		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Bottom Ash	1.838	2.327	2.370	850.594	909.909	2460.117
De-Oiled Soya	1.082	1.1399	1.2016	5820.970	5984.175	6119.265

Adsorbent	Freundlich constants					
	n			K_F		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Bottom Ash	1.463	1.596	1.763	0.0215	0.0148	0.0133
De-Oiled Soya	7.513	6.892	6.640	4.12×10^{-5}	4.964×10^{-5}	5.569×10^{-5}

Table 5
Values of thermodynamics parameters for the adsorption of erythrosine on different adsorbents

Adsorbent	$-\Delta G^\circ$ (kJ mol ⁻¹)			ΔH° (kJ mol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)
	30 °C	40 °C	50 °C		
Bottom Ash	28.595	29.714	33.335	44.041	322.275
De-Oiled Soya	33.440	34.616	35.782	2.030	117.067

values of the separation factor (r) indicate highly favourable sorption for both adsorbents.

3.4. Adsorption rate constant study

The adsorption rate constant study was done by considering the following Lagergren's rate equation [36]:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} \times t \quad (2)$$

where q_e and q_t are the amount adsorbed at equilibrium and at time t , respectively. The plot of time versus $\log(q_e - q_t)$ gives straight line at all temperatures for both the systems (Fig. 7a and b) and clearly specify the first order nature of the adsorption process in each case. For each system, the k_{ad} values calculated from the slopes of these straight lines are represented in Table 6.

For wastewater treatment, the rate at which dissolved organic substances are removed from dilute aqueous solutions by solid adsorbents is an extremely significant aspect and the mechanism of the involved process also plays an equally important role. Thus, to identify whether the rate determining step of the enduring process is particle diffusion or film diffusion, the mathematical treatment prescribed by Boyd et al. [37] and Reichenberg [38] was applied.

Table 6
Values of specific rate constant (k_{ad}) and mass transfer coefficient (β_L) obtained for different adsorbents at different temperatures

Adsorbent	k_{ad} (s ⁻¹)			β_L		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Bottom Ash	0.0495	0.0548	0.0675	2.562×10^{-6}	2.059×10^{-6}	1.385×10^{-6}
De-Oiled Soya	0.0488	0.0516	0.0592	5.433×10^{-7}	5.359×10^{-7}	5.239×10^{-7}

3.5. Rate expression and treatment of data

To exactly deduce the experimental findings, sorption data was given a quantitative treatment based on the model proposed by Reichenberg [38] and various parameters were calculated by using the following equations:

$$F = 1 - \frac{6}{\pi^2} \sum_1^{\infty} \left(\frac{1}{n^2} \right) \exp(-n^2 B_t) \quad (3)$$

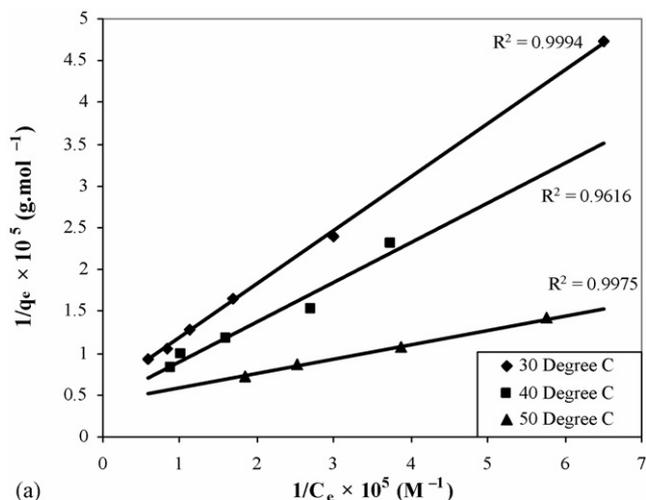
$$B = \frac{\pi^2 D_i}{r_0^2} = \text{time constant} \quad (4)$$

where F is the fractional attainment of equilibrium at time ' t ', D_i the effective diffusion coefficient of adsorbates in adsorbent phase, r the radius of adsorbent particle and n is the Freundlich constant of the adsorbate. The F (fractional attainment) is acquired by applying following equation:

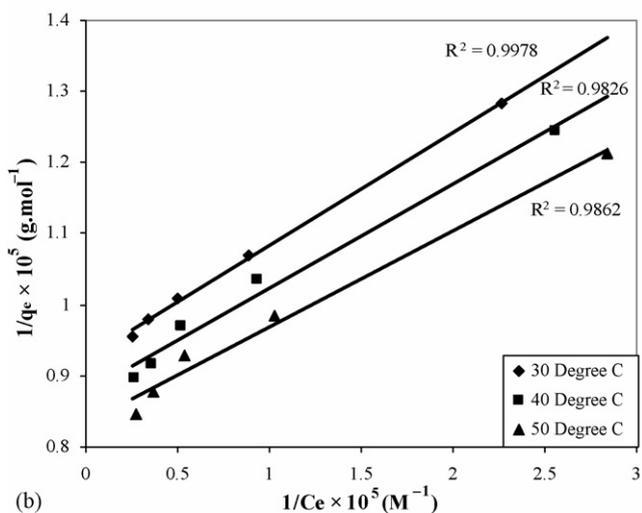
$$F = \frac{Q_t}{Q_\infty} \quad (5)$$

where Q_t and Q_∞ are amounts adsorbed after time t and after infinite time, respectively.

For each calculated value of F , the corresponding value of B_t was derived from Reichenberg's table [38]. From the plots



(a)

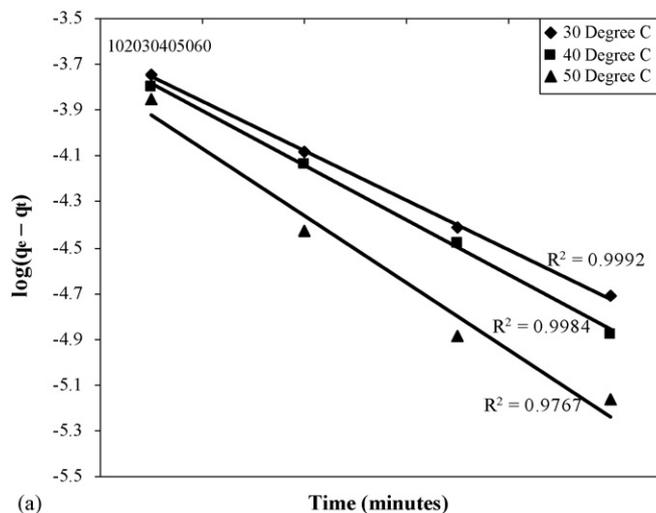


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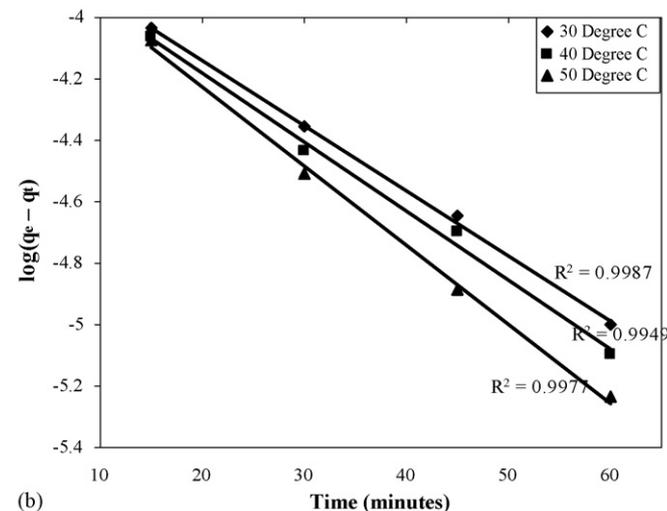
Fig. 6. (a) Langmuir adsorption isotherm for erythrosine—Bottom Ash; (b) Langmuir adsorption isotherm for erythrosine—De-Oiled Soya.

of B_t versus time (Fig. 8a and b), the process was classified as a film diffusion or particle diffusion controlled mechanism. For both the adsorbents at a concentration of 4×10^{-5} M the B_t versus time plots at different temperatures were linear and almost passes through origin, which indicates the ongoing adsorption processes to be governed by particle diffusion mechanism.

From the graphs of time versus B_t , the D_i (effective diffusion coefficient) values for each adsorption process at the three different temperatures 30, 40 and 50 °C were obtained and are represented in Table 7. It is clear from the presented data that the value of D_i increases with increasing temperature. This may be due to the increase in mobility of ingoing ions through the



(a)



(b)

Fig. 7. (a) Lagergren's plot of time vs. $\log(q_e - q_t)$ for erythrosine—Bottom Ash system at different temperatures; (b) Lagergren's plot of time vs. $\log(q_e - q_t)$ for erythrosine—De-Oiled Soya system at different temperatures.

pores of different widths and different electronic fields along the diffusion path. Moreover, as the temperature increases a gradual decline in the retarding forces acting on the diffusing ions takes place which in turn increases the value of D_i . The plot of $\log D_i$ versus $1/T$ shown in Fig. 9 was found to be linear for each system.

From the intercept of Fig. 9 corresponding D_0 values were calculated, which were further used to determine energy of activation (E_a) and change in entropy of activation (ΔS^\ddagger) of the ongoing adsorption processes, using well known Arrhenius

Table 7

Values of effective diffusion coefficient (D_i), pre exponential constant (D_0), activation energy (E_a) and entropy of activation (ΔS^\ddagger) for diffusion of erythrosine in Bottom Ash and De-Oiled Soya

Adsorbent	D_i (m^2/s)			D_0 (m^2/s)	E_a ($J mol^{-1}$)	ΔS^\ddagger ($JK^{-1} Mol^{-1}$)
	30 °C	40 °C	50 °C			
Bottom Ash	2.818×10^{-11}	3.115×10^{-11}	3.879×10^{-11}	4.236×10^{-8}	18652.305	-344.970
De-Oiled Soya	1.066×10^{-10}	1.210×10^{-10}	1.536×10^{-10}	5.429×10^{-9}	9773.487	-362.051

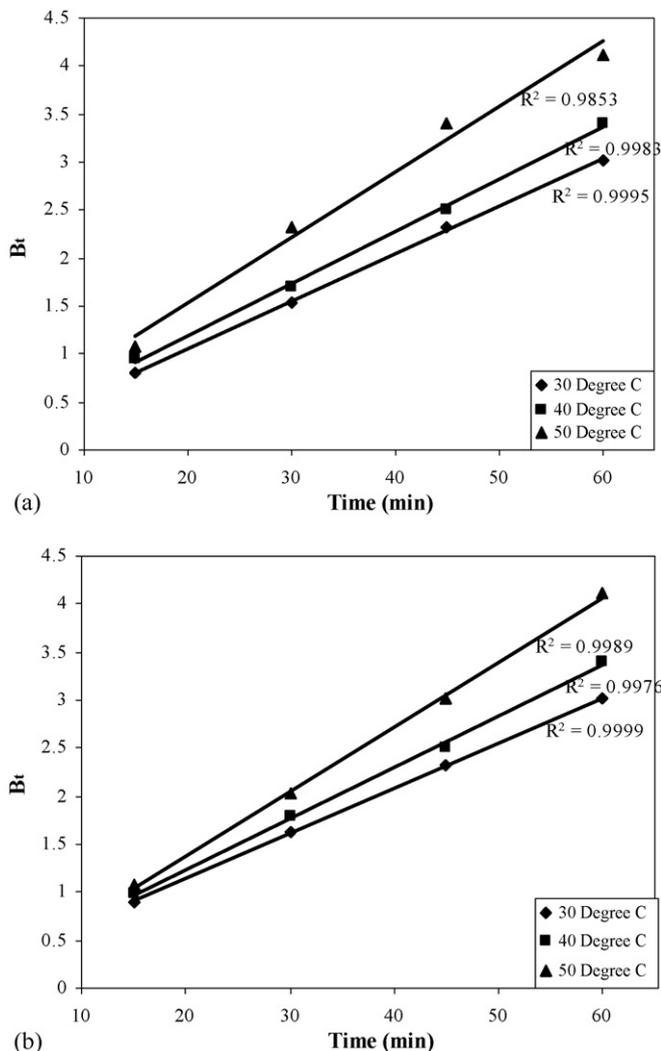


Fig. 8. (a) Plot of time vs. B_t for erythrosine—Bottom Ash system at different temperatures; (b) plot of time vs. B_t for erythrosine—De-Oiled Soya system at different temperatures.

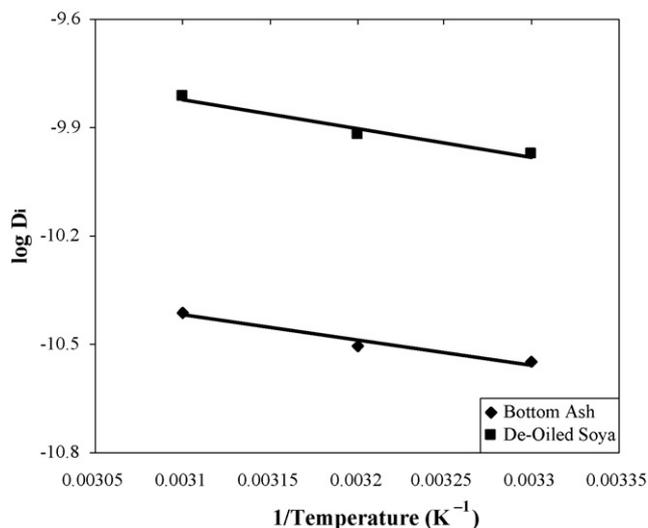


Fig. 9. Plot of $1/\text{temperature}$ vs. $\log D_i$ for erythrosine—Bottom Ash system and erythrosine—De-Oiled soya system.

equation.

$$D_i = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

$$D_0 = \pi \left(\frac{2.72d^2kT}{h}\right) \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (7)$$

The values of ΔS^\ddagger , E_a and pre-exponential constant (D_0) are listed in Table 7. The negative ΔS^\ddagger values indicates that no significant change occur in the internal structure of both the adsorbents throughout the adsorption process.

3.6. Mass transfer study

A mathematical mass transfer model as given by Mckay et al. [39] was employed for studying mass transfer for adsorption erythrosine over Bottom Ash and De-Oiled Soya.

$$\ln\left(\frac{C_t}{C_0} - \frac{1}{1+mk}\right) = \left(\frac{1+mk}{mk}\beta_L S_s\right)t + \left(\frac{mk}{1+mk}\right) \quad (8)$$

where C_t is the concentration of adsorbate (mg L^{-1}) after time t , C_0 the initial concentration of adsorbate (mg L^{-1}), k (L g^{-1}) the constant obtained by multiplying the Langmuir constants Q_0 and b , m (g L^{-1}) and S_s (cm^{-1}) are 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:

$$m = \frac{W}{V} \quad (9)$$

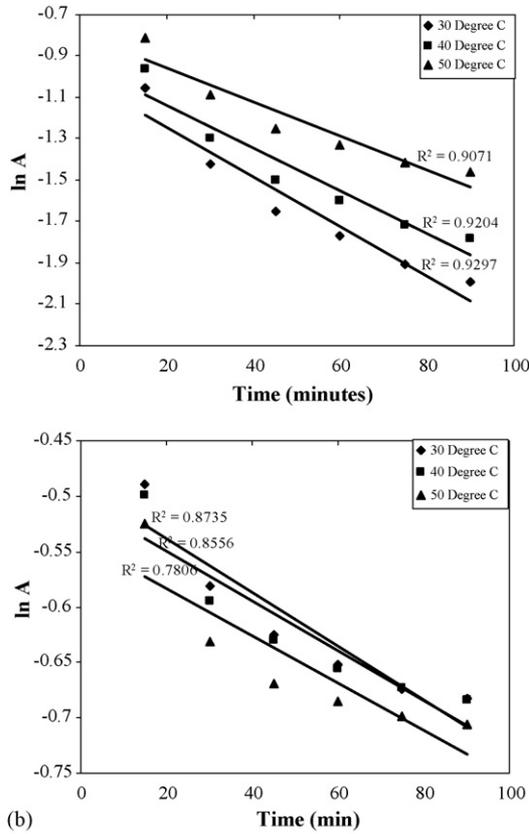
$$S_s = \frac{6m}{(1-\varepsilon_p)d_p\rho_p} \quad (10)$$

where V is the 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 $\ln(C_t/C_0 - 1/1+mk)$ versus time plots shown in Fig. 10a and b for the Bottom Ash and De-Oiled Soya, respectively, gives a straight line. The values of β_L were determined from the slopes and intercepts of these graphs for each system and are summarized in Table 6. The values of β_L obtained signify that the rate of mass transfer of the erythrosine particles on both the adsorbents from bulk to solid phase is rapid. This also reflect good efficacy of both the adsorbent materials towards dye.

3.7. Column studies

Batch studies and adsorption isotherms are generally used as preliminary investigations to obtain operational parameters for the on-going adsorption. However, in order to establish practical utility of the developed method, column-type continuous flow operations are carried out, which have distinct advantage over the batch treatment. Weber [40] proposed a straightforward approach to design a fixed bed adsorber involving such feasible adsorptions processes, where the rate of attainment of equilib-



$$* A = \left[\frac{C_t}{C_o} - \frac{1}{1 + mk} \right]$$

Fig. 10. (a) Plot of time vs. $\ln A^*$ for the mass transfer of erythrosine—Bottom Ash system at different temperatures; (b) plot of time vs. $\ln A^*$ for the mass transfer of erythrosine—De-Oiled Soya system at different temperatures.

riums between the mobile and stationary phases are known and the same has been adopted in the present case.

For both the adsorbents parameters like length of primary adsorption zone (δ), total time involved for the establishment of primary adsorption zone (t_x), time for primary adsorption zone to move down its length (t_δ), time of initial formation of primary adsorption zone (t_f), mass rate flow of the adsorbent (F_m), fractional capacity of the column (f) and percent saturation of column at break point were evaluated (Tables 8 and 9) as per

Table 8
Calculations for fixed bed adsorber columns of Bottom Ash and De-Oiled Soya

Adsorbent	C_0 (mg/mL)	C_x (mg/mL)	C_b (mg/mL)	V_x (mL)	V_b (mL)	$(V_x - V_b)$ (mL)	F_m (mg/cm ²)	D (cm)
Bottom Ash	0.05388	0.05379	0.00413	250	70	180	0.0343	1.0
De-Oiled Soya	0.05388	0.05145	0.00494	280	170	110	0.0343	1.0

Table 9
Parameters for fixed bed adsorbents—Bottom Ash and De-Oiled Soya

Adsorbent	t_x (min)	t_δ (min)	t_f (min)	f	δ (cm)	Percentage saturation (%)
Bottom Ash	72.84.70	5244.99	140	0.9733	0.7341	98.04
De-Oiled Soya	8158.87	3205.28	340	0.8939	0.4099	95.65

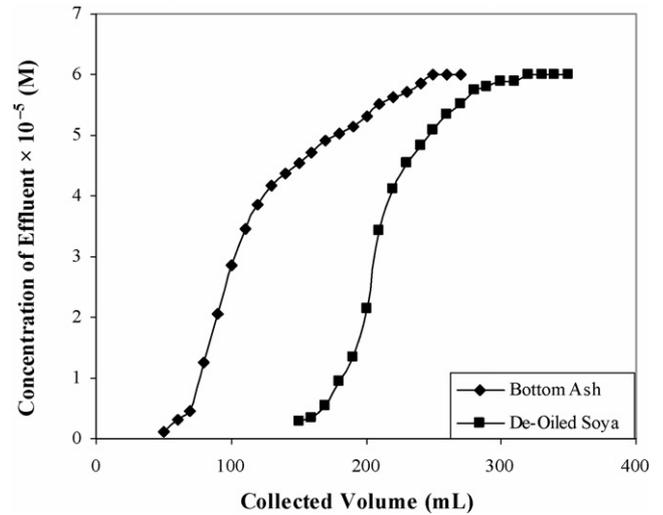


Fig. 11. Breakthrough curve for erythrosine—Bottom Ash and erythrosine—De-Oiled Soya columns.

following equations:

$$t_x = \frac{V_x}{F_m} \tag{11}$$

$$t_\delta = \frac{V_x - V_b}{F_m} \tag{12}$$

$$\frac{\delta}{D} = \frac{t_\delta}{t_x - t_f} = \frac{t_\delta}{t_x + t_\delta(f - 1)} = \frac{V_x - V_b}{V_b + f(V_x - V_b)} \tag{13}$$

$$f = 1 - \frac{t_f}{t_\delta} = \frac{M_s}{(V_x - V_b)C_0} \tag{14}$$

$$\text{percentage saturation} = \frac{D + \delta(f - 1)}{D} \times 100 \tag{15}$$

To determine the breakthrough capacities of each column plot of concentration of collected effluent versus eluted volume (V) was drawn and presented in Fig. 11. The ratio of total area at the points, where the effluent plot joins the effluent and weight of the adsorbent used in the column gave the column capacity. The percentage saturation of the columns was found 98.04% and 95.65%, respectively, for the Bottom Ash and De-Oiled Soya columns. It has been found that the breakthrough capacities of the columns are more than their respective batch capacities. This higher breakthrough capacity may be due to the establishment of

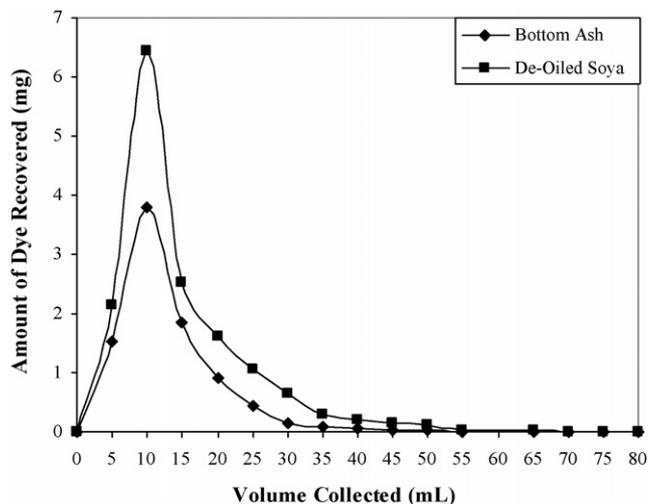


Fig. 12. Regeneration of Bottom Ash and De-Oiled Soya columns.

continuously large concentration gradient at the interface zone in the columns, whereas, in batch procedures the concentration gradient decreases with time.

3.8. Column regeneration and dye recovery

In order to recover the adsorbed erythrosine dye and also to regenerate adsorbents, dilute solution NaOH of pH 12.2 was passed through each exhausted column. In each case, collected volume of NaOH versus amount of the recovered dye was plotted and presented in Fig. 12. It was observed that in each case total 80 mL of dilute NaOH was found adequate to recover about 94% and 96% of the adsorbed dye from the exhausted Bottom Ash and De-Oiled Soya columns, respectively. First two aliquots of 5 mL each removed almost 60% of the total recovered amount from the Bottom Ash Column, while from the De-Oiled Soya column about 56% of collected erythrosine could be recovered. Remaining dye removal could be achieved by 13 more aliquots of 5 mL each. The column was then washed with about 50 mL of hot water in 10 mL fractions at the flow rate 5 mL min^{-1} .

In order to measure the adsorption efficiencies of the columns, columns were reloaded with the dye solutions and breakthrough capacities for Bottom Ash and De-Oiled Soya columns were found to be 86%, 74%, 61% and 49%, and 83%, 71%, 56% and 45%, respectively, during their first, second, third and fourth cycles. The fall in the adsorption capacities of the columns clearly indicates need of regeneration treatment after each column operation.

4. Conclusions

Keeping the obtained results in view, it can be safely concluded that the hazardous water-soluble dye erythrosine can be successfully eradicated from the aqueous solutions by adsorption over Bottom Ash and De-Oiled Soya and both these adsorbents are useful and valuable means for controlling the water pollution due to this dye. The batch adsorption experiments showed that the adsorption of erythrosine over Bottom Ash

and De-Oiled Soya is dependent on pH, particle size, amount of adsorbent, concentration, contact time and temperature. The thermodynamic parameters obtained in both the cases confirm the feasibility of the process at each concentration. Kinetic measurements indicate that for both the adsorbents the adsorption proceeds via film diffusion in the entire concentration range. The column capacity for each process was found to be higher than the batch capacity and the recovery of the dye was achieved by eluting the dilute NaOH through the column and both the adsorbents can be regenerated. From the carried out research, it can also be concluded that both the waste materials can be used as excellent adsorbents and the developed method is quite inexpensive.

References

- [1] F. Ishikawa, S. Shigeoka, M. Nagashima, M. Takahashi, H. Kamimura, Simultaneous determination of eleven dyes and their aluminum lakes in drugs, *J. AOAC Int.* 86 (2) (2003) 215–221.
- [2] C. Desiderio, C. Marra, S. Fanali, Quantitative analysis of synthetic dyes in lipstick by micellar electrokinetic capillary chromatography, *Electrophoresis* 19 (8–9) (1998) 1478–1483.
- [3] Y. Ozsoy, A. Araman, Identification and determination of colorants in chewing gums and jellies, *Acta Pharm. Turcica* 35 (2) (1993) 33–38.
- [4] M. Tripathi, S.K. Khanna, M. Das, A novel method for the determination of synthetic colors in ice cream samples, *J. AOAC Int.* 87 (3) (2004) 657–663.
- [5] S. Virtanen, E. Ali-Mattila, L. Pekka, Determination of synthetic colorants and natural carmine in wines, *J. Int. des Sci. de la Vigne et du Vin.* 33 (3) (1999) 145–147.
- [6] O.K. Uysal, E. Aral, Teratogenic effects and the role in the etiology of atopic diseases of erythrosine (FD and C Red No. 3), *Turk. J. Med. Sci.* 28 (4) (1998) 363–368.
- [7] J.F. Borzelleca, J.B. Hallagan, Lifetime toxicity/carcinogenicity study of FD&C Red No. 3 in mice, *Food Chem. Toxicol.* 25 (1987) 735–737.
- [8] J.F. Borzelleca, J.B. Hallagan, Lifetime toxicity/carcinogenicity study of FD&C Red No. 3 in rats, *Food Chem. Toxicol.* 25 (1987) 723–733.
- [9] Y.F. Sasaki, S. Kawaguchi, A. Kamaya, M. Ohshita, K. Kabasawa, K. Iwama, K. Taniguchi, S. Tsuda, The comet assay with 8 mouse organs: results with 39 currently used food additives, *Mut. Res. Genetic Toxicol. Environ. Mutagenesis* 519 (1–2) (2002) 103–119.
- [10] L. Pereira, B. Ali, K. Mohite, P. Arora, C.V.A. Rao, Study of mutagenic effects of spurious lipsticks chemicals in *Drosophila melanogaster*, *J. Environ. Biol.* 21 (4) (2000) 309–315.
- [11] A.H. Abdel Aziz, S.A. Shouman, A.S. Attia, S.F. Saad, A study on the reproductive toxicity of erythrosine (Red No. 3) in male mice, *Pharmacol. Res.* 35 (1997) 457–462.
- [12] R.B. Mailman, M.H. Lewis, Neurotoxicants and central catecholamine systems, *NeuroToxicology* 8 (1987) 123–140.
- [13] G.J. Augustine Jr., H. Levitan, Neurotransmitter release from a vertebrate neuromuscular synapse affected by a food dye, *Science* 207 (1980) 1489–1490.
- [14] T. Tanaka, Reproductive and neurobehavioral toxicity study of erythrosine (Red 3) administered to mice in the diet, *Food Chem. Toxicol.* 39 (5) (2001) 447–454.
- [15] A.C. Vidaeff, L.E. Sever, In utero exposure to environmental estrogens and male reproductive health: a systematic review of biological and epidemiological evidence, *Reprod. Toxicol.* 20 (2005) 5–20.
- [16] Y. Yang, Y. Guo, C. Hu, C. Jiang, E. Wang, Synergistic effect of Keggin-type $[X^{n+}W_{11}O_{39}]^{(12-n)-}$ and TiO_2 in macroporous hybrid materials $[X^{n+}W_{11}O_{39}]^{(12-n)-}TiO_2$ for the photocatalytic degradation of textile dyes, *J. Mater. Chem.* 13 (7) (2003) 1686–1694.
- [17] Y. Tonogai, M. Iwaida, M. Tati, Biochemical decomposition of coal-tar dyes II. Acute toxicity of coal-tar dyes and their decomposed products, *J. Toxicol. Sci.* 3 (1978) 205–214.
- [18] Z. Hu, M.P. Srinivasan, Mesoporous high-surface-area activated carbon, *Micropor. Mesopor. Mater.* 43 (3) (2001) 267–275.

- [19] A. Mittal, L. Kurup, V.K. Gupta, Use of waste materials—Bottom Ash and De-Oiled Soya, as potential adsorbents for the removal of amaranth from aqueous solutions, *J. Hazard. Mater.* 117 (2005) 171–178.
- [20] A. Mittal, L. Krishnan, V.K. Gupta, Removal and recovery of malachite green from wastewater using an agricultural waste material, De-Oiled Soya, *Sep. Purif. Technol.* 43 (2005) 125–133.
- [21] V.K. Gupta, A. Mittal, L. Krishnan, V. Gajbe, Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using Bottom Ash, *Sep. Purif. Technol.* 40 (2004) 87–96.
- [22] V.K. Gupta, A. Mittal, V. Gajbe, Adsorption and desorption studies of a water soluble dye, quinoline yellow, using waste materials, *J. Colloid Interface Sci.* 284 (2005) 89–98.
- [23] V.K. Gupta, I. Ali, V.K. Saini, T.V. Gerven, B. Van der Bruggen, C. Vandecasteele, Removal of dyes from wastewater using Bottom Ash, *Ind. Eng. Chem. Res.* 44 (11) (2005) 3655–3664.
- [24] V.K. Gupta, I. Ali, V.K. Saini, Suhas, Removal of rhodamine B, fast green and methylene blue from wastewater using red mud—an aluminum industry waste, *Ind. Eng. Chem. Res.* 43 (2004) 1740–1747.
- [25] V.K. Gupta, I. Ali, in: A. Hubbard (Ed.), *Adsorbents for Water Treatment: Low Cost Alternatives to Carbon Encyclopedia of Surface And Colloid Science*, vol. 1, Marcel Dekker, New York, 2002, p. 136.
- [26] A.K. Jain, V.K. Gupta, A. Bhatnagar, Suhas, Utilization of industrial waste products as adsorbents for the removal of dyes, *J. Hazard. Mater.* 101 (2003) 31–42.
- [27] A.K. Jain, V.K. Gupta, A. Bhatnagar, S. Jain, Suhas, A comparative assessment of adsorbents prepared from industrial wastes for the removal of cationic dye, *J. Ind. Chem. Soc.* 80 (2003) 267–270.
- [28] V.K. Gupta, D. Mohan, S. Sharma, M. Sharma, Removal of basic dyes (Rhodamine-B and Methylene blue) from aqueous solutions using bagasse fly ash, *Sep. Sci. Technol.* 35 (2000) 2097–2113.
- [29] V.K. Gupta, I. Ali, Suhas, D. Mohan, Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low cost adsorbents, *J. Colloid Interface Sci.* 265 (2003) 257–264.
- [30] V.K. Gupta, S.K. Srivastava, D. Mohan, Equilibrium uptake, sorption dynamics, process optimization and column operations for the removal and recovery of malachite green from wastewater using activated carbon and activated slag, *Ind. Eng. Chem. Res.* 36 (1997) 2207–2218.
- [31] N.L. Hecht, D.S. Duvall, *Characterization and Utilization of Municipal and Utility Sludges and Ashes: Volume III—Utility Coal Ash*, National Environmental Research Center, U.S. Environmental Protection Agency, 1975.
- [32] L.G. Buttle, A.C. Burrells, J.E. Good, P.D. Williams, P.J. Southgate, C. Burrells, The binding of soybean agglutinin (SBA) to the intestinal epithelium of Atlantic salmon, *Salmo salar* and Rainbow trout, *Oncorhynchus mykiss*, fed high, *Vet. Immunol. Immunopathol.* 80 (2001) 237–244.
- [33] S.V. Rama Rao, A.K. Panda, M.V.L.N. Raju, G. Shyam Sunder, N.K. Prharaj, Requirement of calcium for commercial broilers and white leghorn layers at low dietary phosphorus levels, *Anim. Feed Sci. Technol.* 106 (2003) 199–208.
- [34] A.I. Vogel (Ed.), *Vogel's Textbook of Quantitative Chemical Analysis*, fifth ed., Longman, London, 1989.
- [35] F.L. Slejko, *Adsorption Technology: A Step by Step Approach to Process Evaluation and Applications*, Marcel Dekker, New York, 1985.
- [36] K. Periasamy, C. Namasvayam, Process development for removal and recovery of cadmium from waste water by a low cost adsorbent. adsorption rate and equilibrium studies, *Ind. Eng. Chem. Res.* 33 (1994) 317–320.
- [37] G.E. Boyd, A.W. Adamson, L.S. Meyers, The exchange adsorption of ions from aqueous solution by organic zeolites II. Kinetics, *J. Am. Chem. Soc.* 69 (1947) 2836–2848.
- [38] D. Reichenberg, Properties of ion exchange resins in relation to their structure. III. Kinetics of exchange, *J. Am. Chem. Soc.* 75 (1953) 589–597.
- [39] G. McKay, S.J. Allen, I.F. McConvey, M.S. Ottorburn, Transport processes in sorption of coloured ions by peat particles, *J. Colloid Interface Sci.* 80 (1981) 323–329.
- [40] W.J. Weber Jr (Ed.), *Physicochemical Process for Water quality Control*, Wiley-Interscience, New York, 1972.