



Batch and bulk removal of a triarylmethane dye, Fast Green FCF, from wastewater by adsorption over waste materials

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ABSTRACT

De-Oiled Soya, an agricultural waste material and Bottom Ash a waste of power plants, have been used as adsorbents for the removal and recovery of a triarylmethane dye Fast Green FCF from wastewater. Batch studies have been carried by observing the effects of pH, temperature, concentration of the dye, amount of adsorbents, sieve size of adsorbent, contact time, etc. Graphical correlation of various adsorption isotherm models like, Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich have been carried out for both the adsorbents. The adsorption over both the materials has been found endothermic and feasible in nature. Various thermodynamic parameters, such as, Gibb's free energy, entropy and enthalpy of the on-going adsorption process have been calculated. The kinetic studies suggest the process following pseudo first order kinetics and involvement of particle diffusion mechanism. The bulk removal of the dye has been carried out by passing the dye solution through columns of Bottom Ash and De-Oiled Soya and saturation factor of each column has been calculated. Attempts have also been made to recover the dye by eluting dilute NaOH through the columns.

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1. Introduction

Use of different types of dyes in industries producing textile, paper, rubber, plastic, leather, cosmetics, pharmaceutical and food stuff, is well known [1]. The effluents of these industries dispose a large amount of dye contents, which on mixing with water bodies cause severe problems such as increasing the chemical oxygen demand (COD) and reducing light penetration and visibility, thereby pose adverse effects on the marine life [2]. The presence of these dyestuffs in water bodies also makes water unfit for drinking purpose due to highly toxic effects of different types of dyes on human being.

Various physical methods like, coagulation and flocculation [3,4], oxidation or ozonation [5,6], membrane separation [7], ultra chemical filtration [8], chemical treatments [9], activated carbon adsorption [10], etc. have been used for the dye removal but they are either quite expensive or cannot be applied to large volumes of water [11]. Thus in recent time, alternative methods for the removal of dyes from wastewaters with the use of various low cost adsorbents is in high demand. Some low cost adsorbents such as bagasse fly ash [12], wool [13], fertilizer waste [14], shale oil ash [15], rice husk [16], fruit stones [17], red mud [18], etc. have been used by various workers. The biggest advantage of the use of waste materi-

als as adsorbents is their low cost, versatility and easy operations [19]. In recent years Gupta et al. [20–29] have also contributed some important and useful research publications on the dye removal by waste materials.

Fast Green FCF (Fig. 1) is a sea green triarylmethane food dye (C.I. No. 42053), which is also known as Food Green 3, FD and C Green No. 3, Green 1724 and Solid Green FCF. With absorption maximum ranging from 622 to 626 nm, Fast Green FCF possesses a brilliant colour, which is less likely to fade [30]. It is widely used as a staining agent like quantitative stain for histones at alkaline pH after acid extraction of DNA, as a protein stain in electrophoresis and recommended as a replacement of Light Green SF Yellowish in Masson's trichome (a staining protocol used in histology) [31].

Toxicological data reveal that Fast Green FCF is highly toxic [32]. It is an allergen to the humans and may cause eye and skin irritation and irritation in the upper respiratory tract. It also acts as a presynaptic locus by inhibiting the release of neurotransmitters in the human/animal nervous system [33]. It is carcinogenic and can produce sarcomas at the site of repeated subcutaneous injection [34,35]. For long time Fast Green FCF was used for colouring the foodstuffs, however looking in view of its toxicity results European Union and many other countries have prohibited its edible use [36].

Present paper is an attempt to utilize two waste materials – Bottom Ash and De-Oiled Soya, for the removal of Fast Green FCF from wastewater. The adsorbent 'Bottom Ash' is a waste product of power generation plants and 'De-Oiled Soya' is a waste product produced at soyabean oil extracting mills. Bottom Ash is a dark

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Chemical Structure of Fast Green FCF

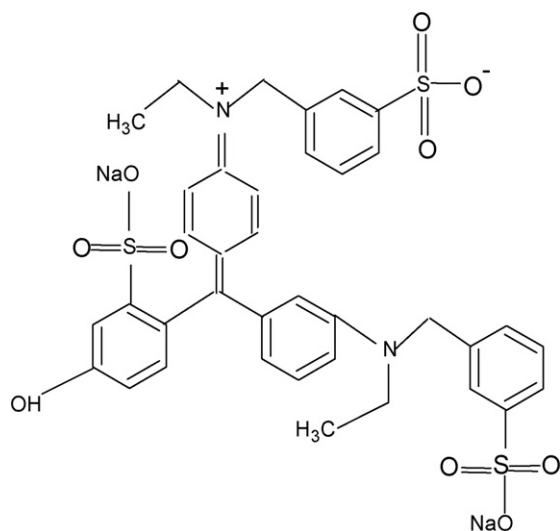


Fig. 1. Chemical structure of Fast Green FCF.

coloured, coarse, granular, incombustible material obtained as a by-product of coal fired power plants after combusting the coke. Its disposal has always been a matter of concern to the plant authorities, as the dumped ash makes agricultural land barren. Bottom Ash is completely non-toxic and possesses extremely good adsorbing capacity in aqueous medium [37,38]. Other adsorbent De-Oiled Soya is pale yellow, flaky material obtained after extracting all possible nutrients of Soya beans. It is a waste material, which is unfit for the animal feed due to presence of hexane [39]. Dry De-Oiled Soya is porous and can also be used as a potential adsorbent for the removal of toxic dyes [38,40].

2. Materials and method

Fast Green FCF (4,4'-bis-(*N*-(ethyl-3-sulphobenzyl)-amino-2-sulpho-4-hydroxy-fuchsonium, disodium salt), molecular formula $C_{37}H_{34}N_2O_{10}S_3Na_2$ and molecular weight 808.85 was obtained from M/s Merck. A stock solution was prepared in double distilled water.

Bottom Ash was obtained from thermal power station (TPS) of M/s Bharat Heavy Electrical Limited (B.H.E.L.), Bhopal (India) and De-Oiled Soya was obtained from Sanwaria Agro Oils Ltd. Bhopal. The pH measurements were done using a microprocessor based pH meter model HI 8424 (M/s Henna Instruments, Italy) and absorption studies were carried out on UV-Vis spectrophotometer model number 117 (M/s Systronics, Ahmedabad, India). The chemical analysis of the adsorbent materials was achieved by conventional methods. Quantasorb Model QS-7 surface area analyzer was used to measure the surface area of the adsorbents granules. Mercury porosimeter and specific gravity bottles were used to determine the porosity and density of the adsorbent materials, respectively. All X-ray measurements were carried out using Philips X-ray diffractometer employing Ni filtered Cu K radiations and Philips SEM 501 electron microscope was used for the scanning electron microscopic analysis. IR spectra were recorded over HP FTIR spectrophotometer.

2.1. Material development

In the first stage, both the adsorbents, Bottom Ash and De-Oiled Soya were washed with distilled water and dried. The organic impu-

rities present were then oxidized after dipping the materials in H_2O_2 solution (30%, v/v) for 24 h. For the removal of moisture contents both the adsorbents were kept in an oven at $100^\circ C$ for 15 min. Further activation of Bottom Ash was made in a furnace at $500^\circ C$ for 15 min. This removes all possible volatile matter trapped in the voids of Bottom Ash. Finally the adsorbents were sieved to various mesh sizes viz. 36, 100 and 170 BSS mesh and stored separately in desiccators.

2.2. Adsorption studies

Batch studies were performed taking 25 mL of the dye solution of known concentration in 100 mL volumetric flask at 30, 40 and $50^\circ C$ and definite pH. Desired mesh sizes for the adsorbent materials were selected (particle size 100 BSS mesh for Bottom Ash and 36 BSS mesh for De-Oiled Soya) and studies were carried out by changing the adsorbent dosage, concentration of adsorbate, pH of solution, etc. After 24 h these solutions were filtered with Whatman filter paper (No. 41) and the amount of the dye uptake was analyzed spectrophotometrically at λ_{max} 622 nm.

2.3. Kinetic studies

For the kinetic measurements 25 mL of the dye solutions were taken in a series of 100 mL volumetric flasks and suitable amount (0.10 g) of the adsorbent materials was added to each at 30, 40 and $50^\circ C$. Solutions were then shaken intermittently, filtered after a particular time interval and finally the amount of dye uptake was analyzed spectrophotometrically in each case.

2.4. Column studies

Glass columns of 30 cm length and 1 cm internal diameter were used for carrying out column studies. Slurries of both the adsorbents were separately made in water and kept overnight. The slurries were then fed into two separate columns over a support of glass wool. Dye solution of 5×10^{-5} M concentration of Fast Green FCF was then flown into the columns at a flow rate of 0.5 mL/min in both the cases till a colourless solution is obtained.

The dye adsorbed in the two columns, was then eluted with NaOH (pH 9.5), maintaining the flow rate to be 0.5 mL/min. Aliquots (10 mL each) of eluted solutions were collected in test tubes and amount of dye in each aliquot was analyzed spectrophotometrically at λ_{max} 622 nm. At zero absorbance of the aliquot regeneration operation was stopped and columns were washed with hot distilled water.

3. Results and discussion

3.1. Characterization of adsorbents

Chemical analysis of the Bottom Ash and De-Oiled Soya was carried out by using conventional chemical methods and available analytical techniques. The results of the chemical constituents present in the two adsorbents are given elsewhere [37,38]. Surface texture and porosity of the activated material of two adsorbents are clearly revealed by the Scanning electron microscopic photographs. Based on these photomicrographs, particles of the Bottom Ash can be approximated as spheres. Based on these photomicrographs, particles of the Bottom Ash and De-Oiled Soya can be approximated as spheres. DTA plots of the activated Bottom Ash exhibit its thermal stability and even at high temperatures negligible weight loss was accounted. The *d*-spacing values provided by X-ray spectrum of the adsorbent reflect the presence of mainly alumina (Al_2O_3), gypsum ($CaSO_4 \cdot 2H_2O$), Beaverite [$Pb(Cu,Fe,Al)_3(SO_4)_2(OH)_6$], borax

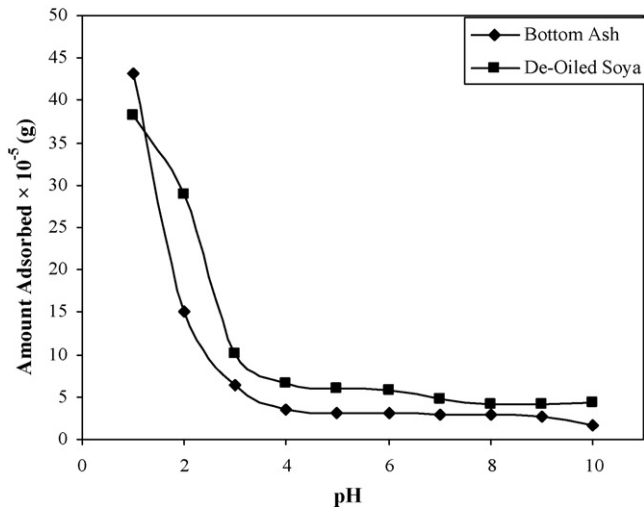


Fig. 2. Effect of pH on the uptake of dye by Bottom Ash and De-Oiled Soya at 30 °C [Bottom Ash: concentration of dye = 5×10^{-5} M, adsorbent dose = 0.05 g, particle size = 100 BSS mesh] [De-Oiled Soya: concentration of dye = 5×10^{-5} M, adsorbent dose = 0.05 g, particle size = 36 BSS mesh].

($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and kaolinite [$2\{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\}$]. In case of De-Oiled Soya, its IR spectrum exhibits bands at 479.6, 779.1, 1113.5, 3459.4 cm^{-1} indicating thereby the presence of gorthite ($4[\text{FeO} \cdot \text{OH}]$), Corundum ($2[\alpha\text{-Al}_2\text{O}_3]$), Coesite (SiO_2), Laumontite ($4[\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}]$).

3.2. Adsorption studies

3.2.1. Effect of pH

The effect of pH on the adsorption of the dye was studied in the pH range of 1.0–10.0 for Bottom Ash and De-Oiled Soya. With the increase in pH, adsorption was found to decrease till pH 4 in each case (Fig. 2) and after pH 4, no significant difference in the amount of dye adsorbed was observed on proceeding further till pH 10.

The decrease in adsorption by increasing pH can be explained on the basis of protonation and deprotonation. On the addition of acid, protonation of the anionic dye takes place, which allows considerable affinity towards the negatively charged adsorbents. On increasing the pH, deprotonation of the dye takes place, which thereby decreases the amount adsorbed. pH 2 has been chosen for the studies on account of the fact that the amount adsorbed in this case is maximum.

3.2.2. Effect of amount of adsorbents

In order to study the variation in adsorption on the basis of amount of the adsorbent materials, various amounts (0.1–0.3 g) of Bottom Ash and De-Oiled Soya were taken and studies were made at 30, 40 and 50 °C, 5×10^{-5} M dye concentration and pH 2. In both the cases, at all the three temperatures, the uptake capacity of the dye increases with increase in the amount of adsorbent (Figs. 3 and 4).

3.2.3. Effect of particle size

For batch adsorption experiments, three different particle sizes viz. 36, 100 and 170 BSS mesh were selected for both the adsorbents and difference in the amount adsorbed was noticed with the increase in mesh size. Table 1 presents effect of sieve size of adsorbents on the adsorption at 30 °C. For both the adsorbents, adsorption was found to increase with the increase in the mesh sizes. This is due to increase in the surface area of the adsorbents and accessibility of the adsorbent pores towards the dye.

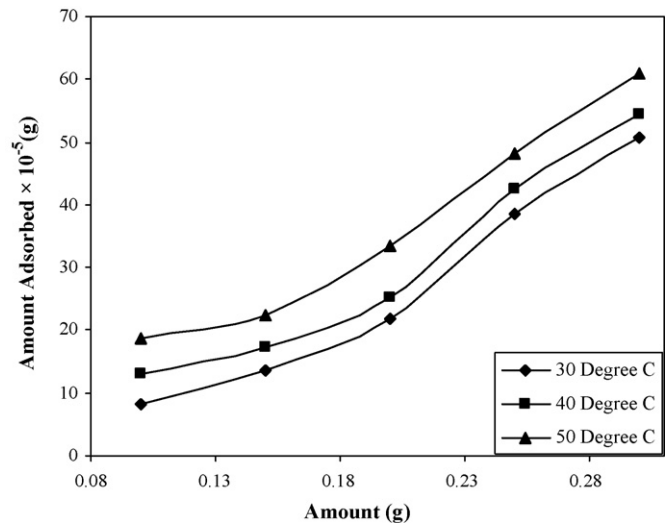


Fig. 3. Effect of amount of adsorbent for the removal of Fast Green FCF using Bottom Ash [Bottom Ash: concentration = 5×10^{-5} M, particle size = 100 BSS mesh, pH 2.0].

3.2.4. Effect of concentration

For the study of effect of concentration 5×10^{-6} – 5×10^{-5} M aqueous solutions of Fast Green FCF were investigated for the dye removal with fixed amount of adsorbent dose at different temperatures (30, 40 and 50 °C). Experiments reflect that increase in concentration of Fast Green FCF and temperature increases the extent of adsorption in case of Bottom Ash and De-Oiled Soya (Figs. 5 and 6).

3.2.5. Effect of contact time

With the increase in time and temperature the adsorption rate increases for both the adsorbents – Bottom Ash and De-Oiled Soya, respectively. The percentage adsorption of the dye during the first 4 h of contact was almost 36% for Bottom Ash and 48% for De-Oiled Soya. For both the cases, half-lives of the processes were also calculated and found as 0.045 and 0.062 h, respectively. These results also confirm the endothermic nature of the adsorption in both the cases.

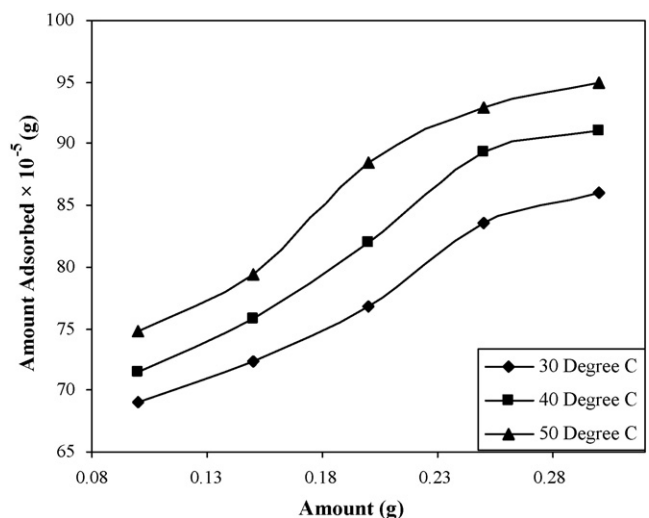


Fig. 4. Effect of amount of adsorbent for the removal of Fast Green FCF using De-Oiled Soya [De-Oiled Soya: concentration = 5×10^{-5} M, particle size = 36 BSS mesh, pH 2.0].

Table 1
Effect of sieve sizes of different adsorbents on the rate of adsorption of Fast Green FCF over Bottom Ash and De-Oiled Soya

Mesh size	Bottom Ash			De-Oiled Soya		
	Amount adsorbed × 10 ⁻⁵ (g)	k (h ⁻¹)	t _{1/2} (h)	Amount adsorbed × 10 ⁻⁵ (g)	k (h ⁻¹)	t _{1/2} (h)
36	16.20	0.007	95.37	25.00	0.012	58.34
100	20.20	0.009	74.52	28.30	0.014	50.62
170	36.40	0.019	37.26	42.40	0.023	30.53

Concentration = 5 × 10⁻⁵ M, pH 2.0, temperature = 30 °C, adsorbent dose = 0.1 g Bottom Ash and 0.1 g De-Oiled Soya.

3.3. Adsorption isotherms

Present investigation mainly deals with the isotherm models, namely Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich (D–R) adsorption isotherms for both the adsorbents. From the studies of Langmuir and Freundlich isotherms, their constants were calculated at 30, 40 and 50 °C.

The Langmuir isotherm theory assumes that sorption is localized in a monolayer and no interaction between the adsorbate molecules takes place. According to the theory, once a dye molecule occupies a site, no further adsorption takes place at that site. Therefore no further adsorption can take place once a saturation value is reached [41]. Straight lines obtained for 1/C_e versus 1/q_e plots (Figs. 7 and 8) reveal that the adsorption of Fast Green FCF over

Bottom Ash and De-Oiled Soya follow Langmuir isotherm model at each temperature. These plots proved helpful in calculating Langmuir constants (Table 2). Using Langmuir adsorption data, various thermodynamic parameters of the adsorption systems such as change in Gibbs's free energy (ΔG°), change in entropy (ΔS°) and change in enthalpy (ΔH°), were calculated from the following relations:

$$\Delta G^\circ = -RT \ln b \tag{1}$$

$$\Delta H^\circ = -R \left(\frac{T_2 T_1}{T_2 - T_1} \right) \times \ln \left(\frac{b_2}{b_1} \right) \tag{2}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{3}$$

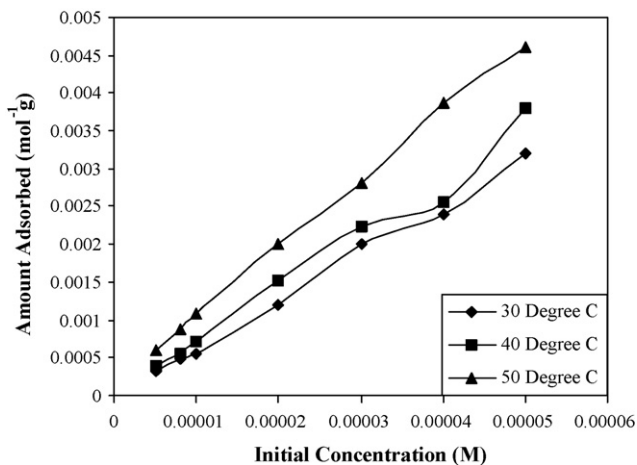


Fig. 5. Effect of concentration for the removal of Fast Green FCF by Bottom Ash at different temperatures [adsorbent dose = 0.1 g, particle size = 100 BSS mesh, pH 2.0].

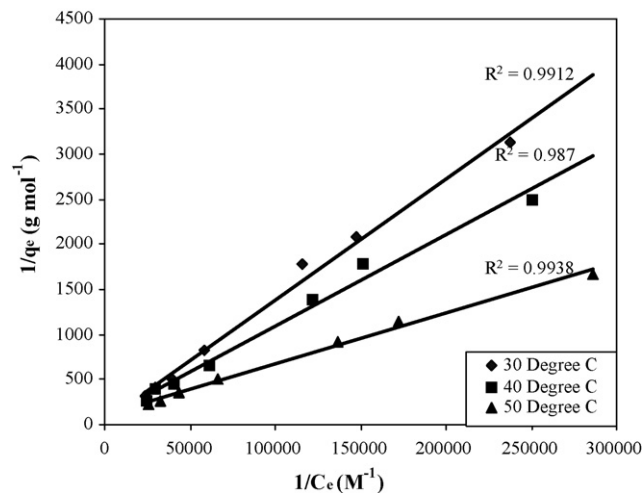


Fig. 7. Langmuir adsorption isotherm for Fast Green FCF–Bottom Ash [adsorbent dose = 0.1 g, particle size = 100 BSS mesh, pH 2.0].

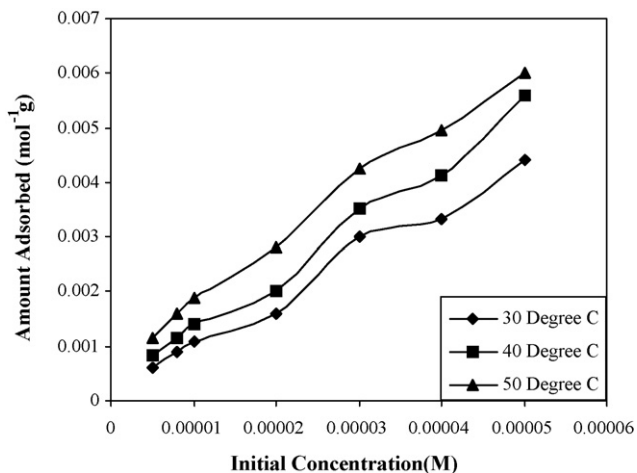


Fig. 6. Effect of concentration for the removal of Fast Green FCF by De-Oiled Soya at different temperatures [adsorbent dose = 0.1 g, particle size = 36, pH 2.0].

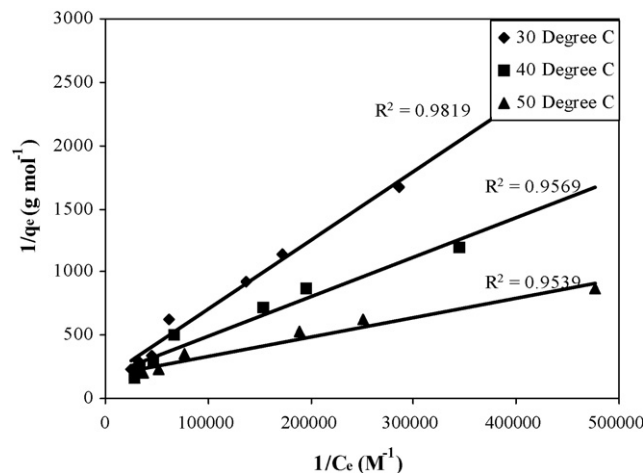


Fig. 8. Langmuir adsorption isotherm for Fast Green FCF–De-Oiled Soya [adsorbent dose = 0.1 g, particle size = 36 BSS mesh, pH 2.0].

Table 2
Freundlich and Langmuir constants for removal of Fast Green FCF

Adsorbent	Freundlich constants					
	<i>n</i>			<i>K_F</i>		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Bottom Ash	0.97	1.03	1.16	7.00×10^{-5}	1.00×10^{-4}	2.00×10^{-4}
De-Oiled Soya	1.00	1.00	2.00	2.00×10^{-4}	4.00×10^{-4}	7.00×10^{-4}
Adsorbent	Langmuir constants					
	<i>Q₀</i> × 10 ³ (mol/g)			<i>b</i> × 10 ³ (L mol ⁻¹)		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Bottom Ash	25.05	14.13	9.39	2.97	6.93	19.01
De-Oiled Soya	6.57	5.63	5.50	27.63	57.25	121.03

Bottom Ash: adsorbent dose = 0.1 g, particle size = 100 mesh, pH 2.0. De-Oiled Soya: adsorbent dose = 0.1 g, particle size = 36 mesh, pH 2.0.

where *b*, *b*₁ and *b*₂ are the Langmuir constants at 30, 40 and 50 °C respectively, which are obtained from slopes and intercepts of Langmuir isotherm plots. Positive values of entropy change and enthalpy show increased randomness and endothermic nature of the process respectively, whereas the negative values of free energy suggest feasibility of the process. The above values have been depicted in Table 3.

Dimensionless separation factor 'r' was calculated using the method suggested by Weber and Chakrabarti [42], as per the following equation

$$r = \frac{1}{1 + bC_0} \quad (4)$$

In the above equation, *C*₀ the initial concentration and *b* signifies the Langmuir constant. The separation factor tells the favourability and the shape of the adsorption isotherms. The values of 'r' have been found 0.98, 0.96 and 0.91 for Bottom Ash and 0.87, 0.77 and 0.62 for De-Oiled Soya at 30, 40 and 50 °C, respectively. In both the cases the *r*-values obtained are less than unity, indicating thereby favourable adsorption process in both the cases.

The data obtained data for the adsorption of Fast Green FCF over the two adsorbents at 30, 40 and 50 °C were also correlated with Freundlich adsorption isotherm model [43], by using following mathematical expression:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (5)$$

*C*_e here denotes the equilibrium concentration (M) of the adsorbate and *q*_e, the amount adsorbed (g mol⁻¹) and *K_F* and *n* are the Freundlich constants related to the adsorption capacity and adsorption intensity respectively. The plots of log *q*_e versus log *C*_e were also found linear for both the adsorbents at all the three temperatures (Figs. 9 and 10) and verify the involvement of Freundlich isotherm model.

The Tempkin isotherm model [44,45] assumes effect of some indirect interactions amongst adsorbate particles and suggests a linear decrease in the heat of adsorption of all the molecules in

Table 3
Thermodynamic parameters for the uptake of Fast Green FCF

Adsorbent	−Δ <i>G</i> ⁰ (kJ/mol)			Δ <i>H</i> ⁰ (kJ/mol)	Δ <i>S</i> ⁰ (J K ⁻¹ mol ⁻¹)
	30 °C	40 °C	50 °C		
Bottom Ash	20.15	23.01	26.45	74.70	312.35
De-Oiled Soya	25.76	28.50	31.42	79.56	345.22

Bottom Ash: adsorbent dose = 0.1 g, particle size = 100 mesh, pH 2.0. De-Oiled Soya: adsorbent dose = 0.1 g, particle size = 36 mesh, pH 2.0.

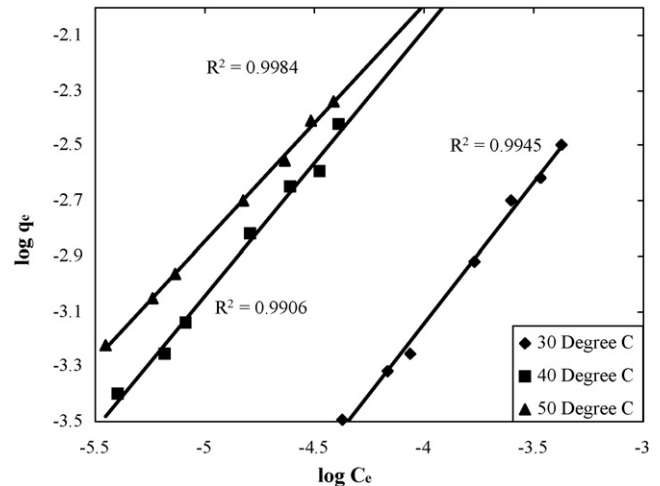


Fig. 9. Freundlich adsorption isotherm for Fast Green FCF–Bottom Ash system [adsorbent dose = 0.1 g, particle size = 100 BSS mesh, pH 2.0].

the layer, due to these interactions. Tempkin isotherm expression is given as:

$$q_e = k_1 \ln k_2 + k_1 \ln C_e \quad (6)$$

In the above equation *q*_e denotes amount of the adsorbate adsorbed per unit mass of the adsorbent in mol/g, *C*_e is the final concentration in mol L⁻¹, *k*₁ is Tempkin isotherm energy constant in L mol⁻¹ and *k*₂ is Tempkin isotherm constant. At 30, 40 and 50 °C, straight lines are obtained from the ln *C*_e versus *q*_e graphs (Figs. 11 and 12) for both the adsorbents, indicating thereby verification of Tempkin model. The values obtained for the Tempkin isotherm constants are presented in Tables 4 and 5.

The isotherm model suggested by Dubinin and Radushkevich [46,47] has been used to describe the liquid phase adsorption and on the basis of Dubinin–Radushkevich equation adsorption energy can be estimated. Assuming that the adsorption in micropores is limited to a monolayer and the Dubinin–Radushkevich equation can be written as:

$$\ln C_{ads} = \ln X_m - \beta \epsilon^2 \quad (7)$$

*C*_{ads} in the above expression is the amount of the dye adsorbed per unit weight of the adsorbent in mg g⁻¹, *X*_m denotes the maximum sorption capacity obtained from the intercept in μmol/g, β is

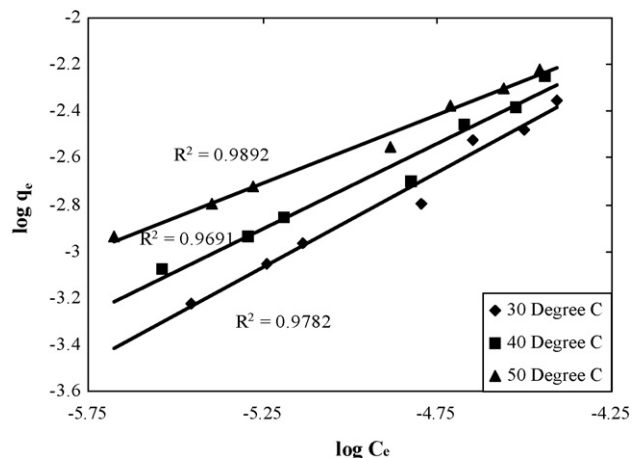


Fig. 10. Freundlich adsorption isotherm for Fast Green FCF–De-Oiled Soya system [adsorbent dose = 0.1 g, particle size = 36 BSS mesh, pH 2.0].

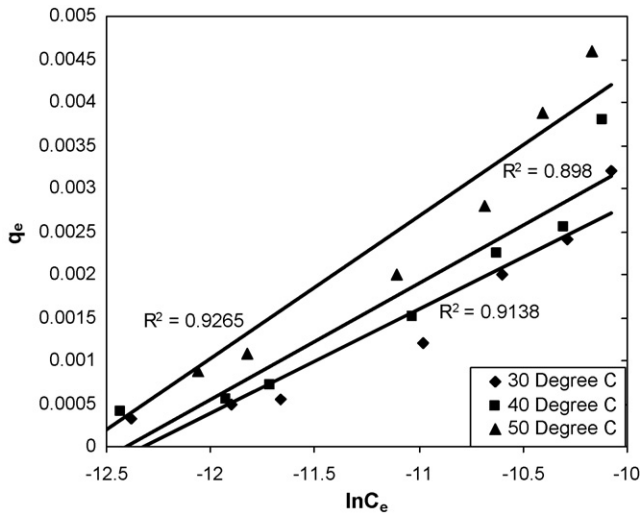


Fig. 11. Temkin isotherm for Fast Green FCF–Bottom Ash system at different temperatures.

obtained from the slope of the straight-line plot of $\ln C_{ads}$ versus ϵ^2 in mol^2/J^2 and ϵ is the Polanyi potential, which is calculated as:

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (8)$$

Here, R is the universal gas constant in $\text{kJ}/(\text{mol K})$, T is the temperature in Kelvin and C_e is the equilibrium concentration of adsorbate in units of gram per gram. With the help of this isotherm the mean sorption energy E is calculated using the relation given below, the magnitude of which is useful for estimating the type of adsorption reaction.

$$E = (-2K)^{-1/2} \quad (9)$$

Figs. 13 and 14 clearly verify the applicability of Dubinin–Radushkevich isotherm model in both the cases. The straight lines obtained were useful in calculating the D–R isotherm constants, which are given in Tables 4 and 5, respectively for the Bottom Ash and De-Oiled Soya adsorptions. Values of E have been found between 8 and 16 kJ/mol for both the adsorbents. This indicates involvement of chemisorption at all the temperatures [48,49].

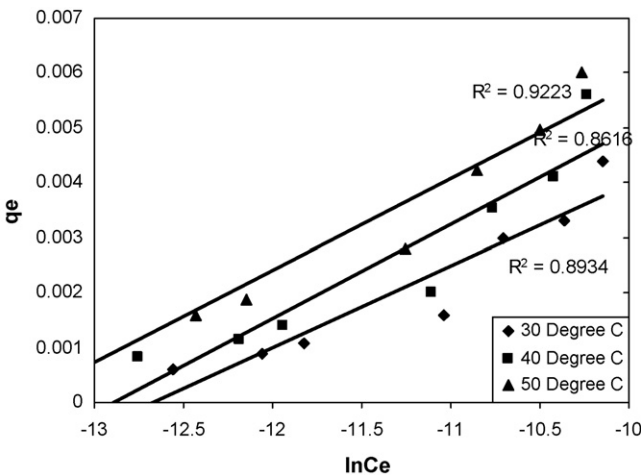


Fig. 12. Temkin isotherm for Fast Green FCF–De-Oiled Soya system at different temperatures.

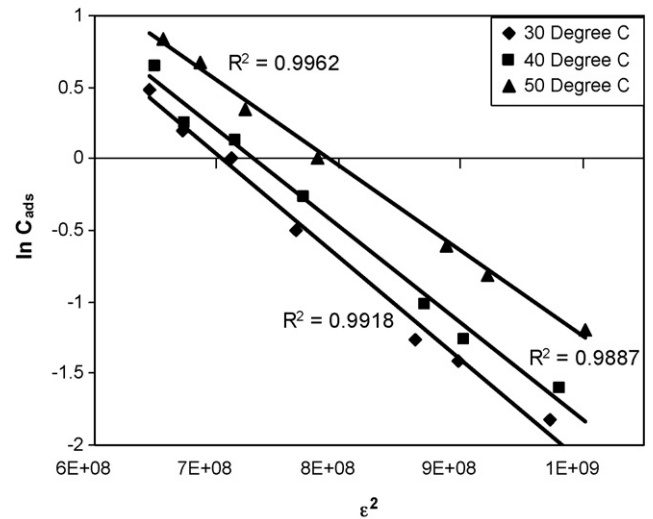


Fig. 13. D–R isotherm for Fast Green FCF–Bottom Ash system at different temperatures.

3.4. Kinetic measurements

3.4.1. Rate constant study

In order to determine the kinetics of the process, the adsorption data was applied to pseudo first order (Eq. (10)) and pseudo second order (Eq. (11)) rate equations [50,51].

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} \times t \quad (10)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (11)$$

Here, q_e and q_t denote the amount adsorbed at equilibrium and at any time 't', respectively.

To verify Lagergren's pseudo first order kinetics, graphs between time versus $\log(q_e - q_t)$ were plotted for the Bottom Ash and De-Oiled Soya adsorptions. The values of specific rate constants (k_{ad}) for both the adsorbent materials were calculated from the slopes of straight lines obtained at 30, 40 and 50 °C and found as 0.007, 0.010 and 0.012 min^{-1} for Bottom Ash and 0.011, 0.015 and 0.016 min^{-1} for De-Oiled Soya, respectively.

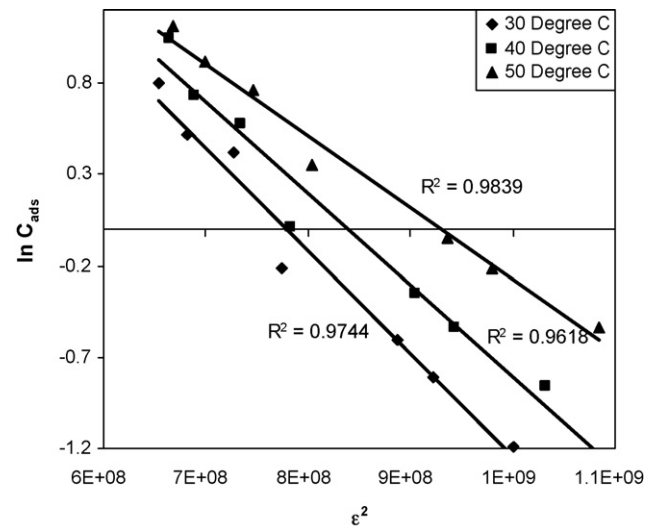


Fig. 14. D–R isotherm for Fast Green FCF–De-Oiled Soya system at different temperatures.

Table 4
Tempkin and D–R constants for Fast Green FCF–Bottom Ash system

Temperature	Tempkin constants			D–R constants	
	k_1 (L mol ⁻¹)	k_2	β (mol ² /J ²)	X_m (μmol/g)	E (kJ/mol)
30 °C	0.0012	2.47×10^5	-7.00×10^{-9}	154.92	8.45
40 °C	0.0013	4.10×10^5	-7.00×10^{-9}	138.73	8.65
50 °C	0.0016	4.42×10^5	-6.00×10^{-9}	111.62	9.13

Table 5
Tempkin and D–R constants for Fast Green FCF–De-Oiled Soya system

Temperature	Tempkin constants			D–R constants	
	k_1 (L mol ⁻¹)	k_2	β (mol ² /J ²)	X_m (μmol/g)	E (kJ/mol)
30 °C	0.0015	2.97×10^5	-6.00×10^{-9}	80.44	9.13
40 °C	0.0017	4.69×10^5	-5.00×10^{-9}	66.31	10.00
50 °C	0.0017	5.60×10^5	-4.00×10^{-9}	38.86	11.18

3.4.2. Distinction of operational mechanism

In order to identify the step that governs the overall rate of removal in the adsorption process mathematical treatments suggested by Boyd et al. [52] and Reichenberg [53] were used. The expressions given below were used to calculate the fractional attainment F , of equilibrium at time t :

$$F = \frac{Q_t}{Q_\infty} \quad (12)$$

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

$$F = 1 - \frac{6}{\pi^2} \sum_1^\infty \left(\frac{1}{n^2} \right) \exp(-n^2 B_t) \quad (13)$$

$$B = \frac{\pi^2 D_i}{r_0^2} = \text{time constant} \quad (14)$$

Here, D_i is the effective diffusion coefficient of adsorbate in adsorbent phase, n is Freundlich constant of the adsorbate and r_0 is the radius of adsorbent particles.

After obtaining the F values B_t values were retrieved from the Reichenberg's table and with the help of B_t graphs, a distinction between film diffusion and particle diffusion adsorption rates was made. For both the adsorbent materials at 30, 40 and 50 °C, time versus B_t graphs do not give straight lines (Figs. 15 and 16) suggest-

ing thereby involvement of film diffusion mechanism in both the cases.

3.5. Mass transfer study

Mass transfer for the adsorption of Fast Green FCF over Bottom Ash and De-Oiled Soya was studied using following mathematical mass transfer model of McKay et al. [54]:

$$\ln \left(\frac{C_t}{C_0} - \frac{1}{1 + mk} \right) = \left(\frac{1 + mk}{mk} \beta_L S_S \right) t + \left(\frac{mk}{1 + mk} \right) \quad (17)$$

In the above equation C_t is the concentration of adsorbate (M) after time t (min), C_0 is initial concentration of adsorbate (M) and k ($L g^{-1}$) is a constant, which is obtained as a product of 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. The constants m and S_S are calculated by using following equations:

$$m = \frac{W}{V} \quad (18)$$

$$S_S = \frac{6m}{(1 - \varepsilon_p) d_p \rho_p} \quad (19)$$

W is weight of adsorbent (g), V is volume of particle free adsorbate solution (L), ε_p is the porosity of the adsorbent particle,

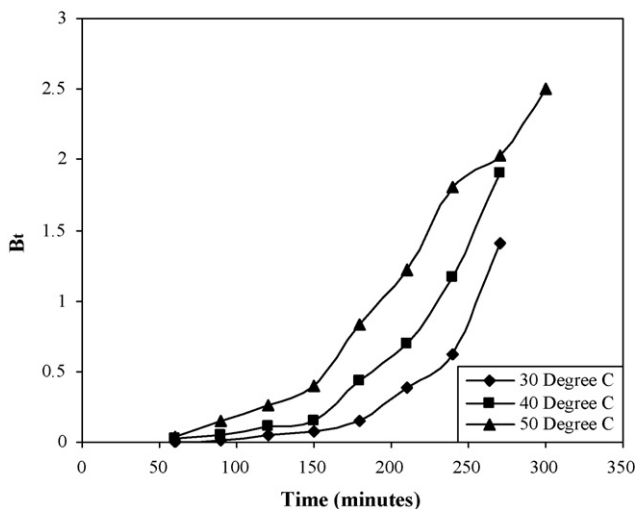


Fig. 15. Plot of time versus B_t for Fast Green FCF–Bottom Ash system at different temperatures.

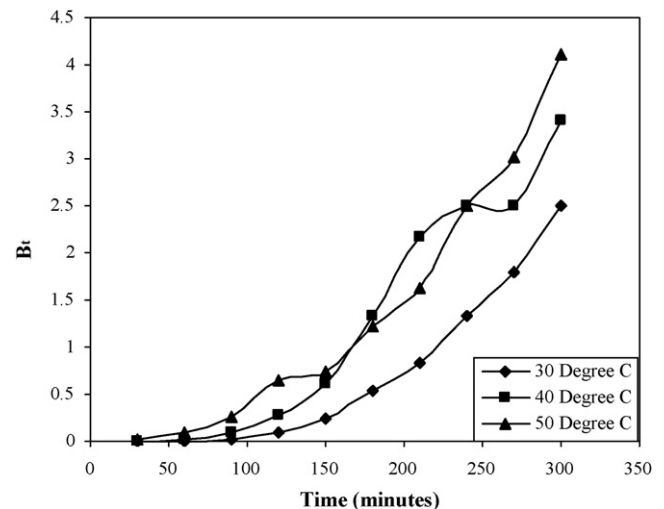


Fig. 16. Plot of time versus B_t for Fast Green FCF–De-Oiled Soya system at different temperatures.

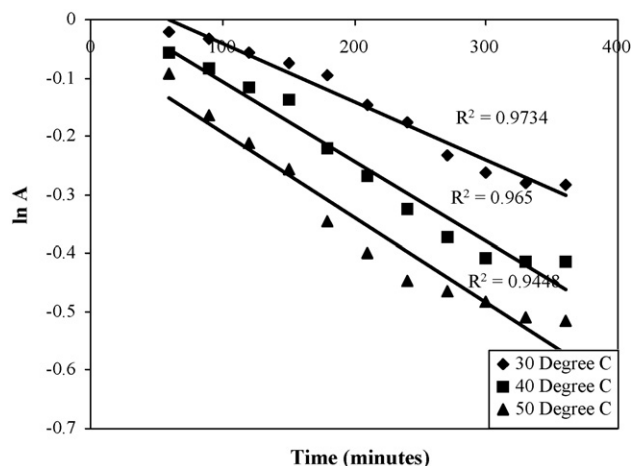


Fig. 17. Plot of time versus $\ln A^*$ for the mass transfer of Fast Green FCF–Bottom Ash system at different temperatures [volume of aqueous solution of dye = 25 mL, concentration of adsorbate = 5×10^{-5} M].

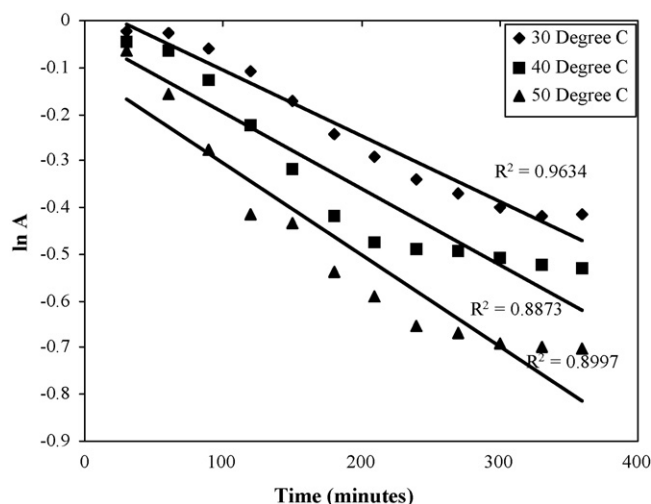


Fig. 18. Plot of time versus $\ln A^*$ for the mass transfer of Fast Green FCF–De-Oiled Soya system at different temperatures [volume of aqueous solution of dye = 25 mL, concentration of adsorbate = 5×10^{-5} M]. $A^* = ((C_t/C_0) - (1/1 + mk))$.

d_p is particle diameter (cm) and ρ_p is density of adsorbent ($g\text{ cm}^{-3}$).

For the mass transfer studies time versus $\ln((C_t/C_0) - (1/1 + mk))$ plots (Figs. 17 and 18) for adsorption of the dye over Bottom Ash and De-Oiled Soya give straight lines. The slopes and intercepts of these graphs furnish β_L values for both the adsorbents. The values of β_L lies between 6.56×10^{-9} and 9.65×10^{-9} for Bottom Ash and 1.09×10^{-8} and 4.77×10^{-8} for De-Oiled Soya at different temperatures. The values of β_L obtained are indicative of the fact that the rate of mass transfer of the Fast Green FCF particles on both the adsorbents from bulk to solid phase is rapid and both the adsorbent materials show a considerable affinity towards the dye.

Table 6
Fixed bed adsorber calculations

Adsorbent	C_0 (M)	C_x (M)	C_b (M)	V_x (mL)	V_b (mL)	$(V_x - V_b)$ (mL)	F_m (mg/cm ² /min)	D (cm)
Bottom Ash	5.00×10^{-5}	3.65×10^{-5}	6.00×10^{-6}	50	10	40	0.02	0.75
De-Oiled Soya	5.00×10^{-5}	4.12×10^{-5}	9.40×10^{-6}	260	80	180	0.02	0.70

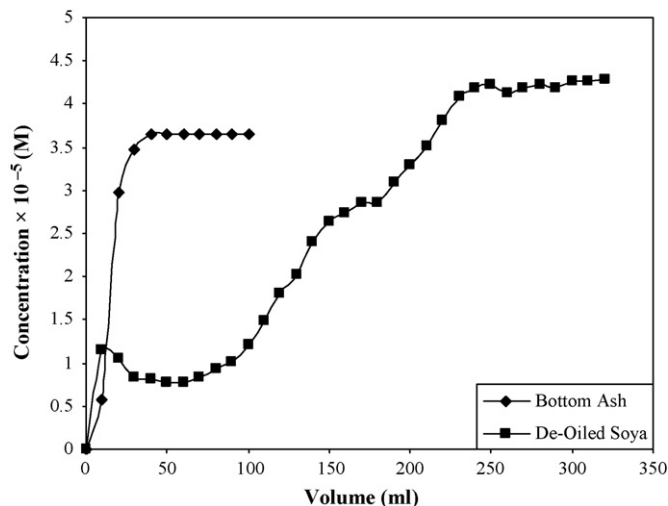


Fig. 19. Breakthrough curve for Fast Green FCF–Bottom Ash and Fast Green FCF–De-Oiled Soya columns.

3.5.1. Column studies

3.5.1.1. Dye removal and column exhaustion. In addition to the batch studies appreciable absorptive capacity of the two adsorbents was further reflected by fixed bed column studies [55]. A dye solution of concentration 5×10^{-5} M was passed through the columns at the rate of 0.5 mL/min. Fig. 19 shows the breakthrough curves for both the adsorbents.

The parameters such as 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), were calculated in the column studies using the equations below:

$$t_x = \frac{V_x}{F_m} \tag{20}$$

$$t_\delta = \frac{V_x - V_b}{F_m} \tag{21}$$

$$\frac{\delta}{D} = \frac{t_\delta}{t_x - t_f} = \frac{t_\delta}{t_x + t_\delta(f - 1)} = \frac{V_x - V_b}{V_b + f(V_x - V_b)} \tag{22}$$

$$f = 1 - \frac{t_f}{t_\delta} = \frac{M_s}{(V_x - V_b)C_0} \tag{23}$$

$$\text{Percentage saturation} = \frac{D + \delta(f - 1)}{D} \times 100 \tag{24}$$

The values calculated for all these parameters are shown in Tables 6 and 7.

Table 7
Parameters for fixed bed adsorber

Adsorbent	t_x (min)	t_δ (min)	t_f (min)	f	δ (cm)
Bottom Ash	1962.50	1570.00	20	0.98	0.60
De-Oiled Soya	10104.00	6995.05	160	0.97	0.50

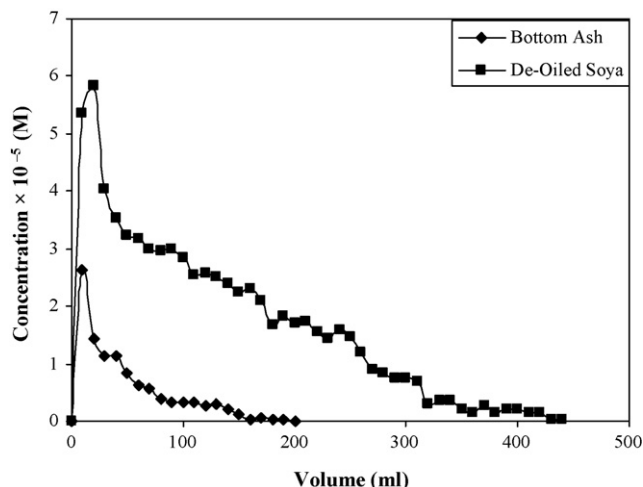


Fig. 20. Desorption of Fast Green FCF from Bottom Ash and De-Oiled Soya columns.

In case of Bottom Ash 1.36 mg was adsorbed over 0.5 g of Bottom Ash out of 4 mg dye in the solution and 6.13 mg was adsorbed over 0.25 g of De-Oiled Soya out of 13.32 mg of the dye in the solution. The values for total time involved for the establishment of primary adsorption zone (t_x), for the Fast Green FCF–Bottom Ash and Fast Green FCF–De-Oiled Soya system were 32.70 and 168.39 min respectively whereas the time for the primary adsorption zone to move down its length (t_s), were 26.16 and 116.58 h respectively. On comparing the two, it has been noted that the values for Fast Green FCF–Bottom Ash system are comparatively lesser than Fast Green FCF–De-Oiled Soya system. The time for initial formation of primary adsorption zone (t_f) was calculated to be 0.33 h for Bottom Ash and 2.66 h for De-Oiled Soya. On the other hand the fractional capacity f values at breakpoint were 0.987 and 0.977 respectively. In Bottom Ash column, the percentage saturation of the column was found to be 98.94 and 98.38% in case for De-Oiled Soya.

3.5.2. Column regeneration and dye recovery

In order to recover the adsorbed dye, NaOH solution of pH 9.5 was eluted through the exhausted columns of both the adsorbents at a flow rate of 0.5 mL/min. For complete desorption of Fast Green FCF in case of Bottom Ash, 200 mL of NaOH was required and for De-Oiled Soya, about 440 mL of the eluent brought complete desorption of the dye. The percentage recovery of the dye for Bottom Ash and De-Oiled Soya was almost 64.09 and 98.02% respectively.

The collected volume of the NaOH (pH 9.5) versus recovered amount of the dye graph in case of Bottom Ash column exhibits a collection of 52.14% of the adsorbed dye in first 80 mL of the eluent and twelve more aliquots of 10 mL each were required to recover remaining amount of the dye (Fig. 20). Hence out of adsorbed 1.36×10^{-3} g of the dye, 7.11×10^{-4} g was removed in first 80 mL and total 200 mL of the eluent could desorb almost 64.10% (8.75×10^{-4} g) dye. On the other hand initial 150 mL of NaOH desorbed about 64.84% (3.97×10^{-3} g out of 6.13×10^{-3} g of total adsorbed dye) of the Fast Green FCF in case of De-Oiled Soya column regeneration (Fig. 20). The remaining dye was obtained by eluting twenty-nine more aliquots of 10 mL each, which resulted in removal of about 98.03% of the dye (6.01×10^{-3} g).

4. Conclusion

Studies clearly reveal that Bottom Ash and De-Oiled Soya can be effectively used for the removal of Fast Green FCF from wastew-

aters. The adsorption over both the materials follows Langmuir, Freundlich, Tempkin and D–R adsorption isotherm models. The adsorption process of Fast Green FCF over both the adsorbents has been found endothermic, spontaneous and feasible and monolayer chemisorption has been found to be operative. Values of thermodynamic parameters – Gibb's free energy, entropy and enthalpy for both the adsorbents have been found comparable. For Bottom Ash and De-Oiled Soya respectively, the mean Gibb's free energies are around 23 and 28 kJ/mol, enthalpies are 74.70 and 79.56 kJ/mol, while entropies are 312.35 and 345.22 J K⁻¹ mol⁻¹. The adsorption of the dye over both the materials follows pseudo first order kinetics with k_{ad} values ranging from 0.007 to 0.016 min⁻¹ through film diffusion mechanism. On the basis of mass transfer studies it is also concluded that transportation of the dye towards adsorbent materials is rapid and both the adsorbents exhibit good affinity towards the dye. Bulk removal of the dye is carried out through column operations and percentage saturation of Bottom Ash and De-Oiled Soya columns are found 98.94 and 98.38%, respectively. The dye recovery is made by eluting NaOH of pH 9.5 through both the exhausted columns and about 64 and 98% of the dye is recovered from Bottom Ash and De-Oiled Soya columns, respectively.

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