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Process development for the batch and bulk removal and recovery of a hazardous, water-soluble azo dye (Metanil Yellow) by adsorption over waste materials (Bottom Ash and De-Oiled Soya)

Alok Mittal[a], V.K. Gupta[b,*], Arti Malviya[a], Jyoti Mittal[a]

[a] *Department of Applied Chemistry, Maulana Azad National Institute of Technology, Bhopal 462007,MP, India*
[b] *Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India*

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Abstract

Bottom Ash and De-Oiled Soya have been used as adsorbents for the removal of a hazardous azo dye—Metanil Yellow from its aqueous solutions. Adsorption of Metanil Yellow on these adsorbents has been studied as function of time, temperature, concentration and pH. Batch adsorption studies, kinetic studies and column operations enabled extraction of lethal dye from wastewaters. Adsorption equilibrium data confirms both Langmuir and Freundlich isotherm models and monolayer coverage of dye over adsorbents. Kinetic data have been employed to calculate specific rate constants, indicating thereby involvement of first order kinetics in the on-going adsorption and activation energy was determined as 0.813 and 1.060 kJ mol^{-1} for Bottom Ash and De-Oiled Soya, respectively. For both adsorbents, the adsorption process has been found governing by film diffusion, over the entire concentration range. Column operations have also been performed for the bulk removal of the dye and also to examine the practical utilization of fixed bed adsorption technique in elimination of dangerous effluent. Saturation factors for Bottom Ash and De-Oiled Soya columns have been calculated as 99.15 and 99.38%, respectively. Attempts have also been made to regenerate the dye from the exhausted columns using aqueous sodium hydroxide as eluent.

Keywords: Metanil Yellow; Bottom Ash; De-Oiled Soya; Adsorption; Kinetics

1. Introduction

Removal of toxic industrial, water-soluble non-biodegradable waste, particularly organic dyes, is of great concern. Removal of colored waste from aqueous effluents is of significant environmental, technical and commercial importance and that is why various physico-chemical techniques like, coagulation, adsorption, chemical oxidation and froth floatation, etc., have been used for the removal of organics as well as inorganics from wastewaters. Using sophisticated instruments, electrochemical processes like electro coagulation [1], electrochemical degradation [2], electrochemical oxidation [3] and photoelectrocatalytic methods [4,5] the task to eradicate toxic pollutants from water have also been accomplished. Amongst all these techniques adsorption is considered one of the most efficient one, due to its easy methodology and operations. The most commonly used adsorbent is activated carbon, which is considered as an expensive sorbent, making wastewater treatment a cost-challenging step. In past one decade, low cost adsorbents like, Chaff [6], Soymeal hull [7], Palm kernel fibre [8], Pinus pinaster bark [9], Sugar beet pulp [10], etc., have emerged as potential alternative resources for removing water-soluble toxic materials from contaminated water. In recent past, our laboratories have also developed some waste materials like Bottom Ash, De-Oiled Soya, Hen Feathers, etc., [11–15] as effective and efficient adsorbents.

Present studies explore the feasibility of using Bottom Ash and De-Oiled Soya as adsorbents for the removal of a hazardous coloring agent, Metanil Yellow from wastewaters. Metanil Yellow is highly water-soluble and belongs to azo group of the dyes. Although Metanil Yellow is a non-permitted color, but still it is widely used as a colorant in sweet meat, ice creams, soft drinks and beverages. Due to its orange-yellow color, the dye is also extensively used for coating turmeric. It is widely

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* Corresponding author. Tel.: +91 1332 285801; fax: +91 1332 273560.
E-mail address: vinodfcy@iitr.ernet.in (V.K. Gupta).

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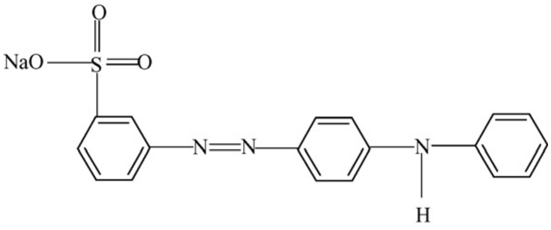
used in leather, paper and textile industries [16] and also as a stain and colorant for the wool [17,18]. It is also used as coloring material for lacquers and cosmetic products. The dye is highly suitable for the preparation of colored water-fast inks [19] and can also be employed for determining trace amounts of Mo(VI) [20]. Apart from all these, Metanil Yellow can act as an indicator for the determination of H^+ ion concentration in the pH range of 1.2–2.3 [21].

Toxicity data reveals that oral feeding or intraperitoneal and intratesticular administration of Metanil Yellow in animals produces testicular lesions due to which seminiferous tubules suffer damage and rate of spermatogenesis is decreased. On oral consumption, it causes toxic methaemoglobinaemia [22] and cyanosis [23] in humans, while skin contact results into allergic dermatitis [24]. Metanil Yellow also has tumour-producing effects and can also create intestinal [25] and enzymic [26] disorders in human body. Though it is not mutagenic but can alter the expression of genes [27]. Thus, keeping the hazardous effects of the dye in view, attempts have been made by various workers to remove Metanil Yellow from wastewater [28–32]. Present work is also an attempt to formulate an easy, reliable and feasible method for its removal from the wastewaters.

Two adsorbent materials—Bottom Ash and De-Oiled Soya chosen for the present studies are purely waste materials. Bottom Ash is obtained from thermal coal-fired power generation plants and appears as granules of dark gray black color. Its disposal in the surrounding lands is always a problem to the concerned authorities because it makes the agricultural land barren and unfit for cultivation [33,34]. The adsorbent, De-Oiled Soya is obtained from Soyabean oil extracting mills as a by-product after extracting all possible nutrients of Soyabean. Captivatingly, our state Madhya Pradesh is one of the leading producers of the Soyabean crop and a large number of Soyabean oil extracting plants are surrounding our city. It is a porous and dry flaky material with brownish white color. About a decade back it was used as animal and fish feed but nowadays it is a banned edible substance due to toxicity as well as bitter taste. The toxicity of De-Oiled Soya is due to use of more than 170 ppm of hexane as solvent during oil extraction [35–37], while bitterness is due to the formation of anti-metabolites, like lipoxygenase and trypsin, during the oil extraction [38,39].

2. Materials and methods

Metanil Yellow ($C_{18}H_{14}N_3NaO_3S$) having IUPAC name 3-(4-anilinophenylazo) benzene sulphonic acid sodium salt (other common names are C.I Acid Yellow 36, Tropaeoline G and Acid Leather Yellow R) was procured from M/s Merck. Other chemicals used were A.R grade reagents. All solutions were prepared in double distilled water. Bottom Ash was obtained from the thermal power plant (TPP) of M/s Bharat Heavy Electricals Limited, Bhopal and De-Oiled Soya was a kind gift from M/s Sanwaria Agro Oils Limited, Bhopal. The coal used by TPP, BHEL, Bhopal was obtained from M/s South Eastern Coal Field Limited, Chirmiri, Sarguja (India).



Metanil Yellow
(I)

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 of 300–600 nm. Philips SEM 501 Electron microscope was employed for scanning electron microscopy and Philips X-ray diffractophotometer was used for X-ray measurements. Quantasorb model QS-7 surface area analyzer, mercury porosimeter and specific gravity bottles were employed for determining pore properties of the adsorbents.

2.1. Material development

The adsorbents Bottom Ash and De-Oiled Soya were first washed with double distilled water and dried. The materials thus obtained were then treated with hydrogen peroxide for 24 h to remove the adhering organic impurities and moisture. De-Oiled Soya was sieved to desired particle size, while Bottom Ash was further activated in a furnace at 500 °C and then sieved. Finally both the adsorbents were stored separately in vacuum desiccators until required.

2.2. Adsorption studies

Adsorption studies of adsorbents Bottom Ash and De-Oiled Soya were performed at 30, 40 and 50 °C. For every adsorption study, a series of 100 mL graduated volumetric flasks containing equal volume of adsorbate solutions at different concentrations were employed at desired pH. An appropriate amount of adsorbent of a particular particle size was added into each flask and was periodically agitated. The solution was then filtered using Whattman filter paper (No. 41) and the uptake of the dye was monitored spectrophotometrically by measuring absorbance at λ_{max} 495 nm. Batch technique was employed to investigate rate and equilibrium data. For kinetic study, 25 mL of solution of Metanil Yellow of known concentration and a known amount of adsorbent was taken in an airtight 100 mL conical flask. The flask containing mixture was kept in a water bath at a desired temperature and was agitated mechanically. After a definite interval of time, the solution of flask was filtered and filterate of each was evaluated spectrophotometrically for uptake of the dye.

2.3. Column studies

Practical utilization of adsorbents was assessed by column operations. Two glass columns of length 30 cm and internal diameter 1 cm were filled separately with known amount of Bottom Ash and De-Oiled Soya of mesh size 100 (0.15–0.08 mm) and 36 BSS mesh (0.425–0.15 mm), respectively, on a glass wool support. An appropriate amount of adsorbent was weighed and its slurry was prepared in water. To minimize air entrapment in the column [40] the slurry was then fed slowly into the column. Each column was then loaded with an adsorbate solution of known concentration, which was percolated through the column at the flow rate of 0.5 mL/min. The column is operated till the effluent concentration matches the concentration of the loaded dye. Elution with a suitable solvent was done through the exhausted column, for regeneration and recovery of adsorbent. For Metanil Yellow desorption, NaOH solution of pH 13 was eluted through each column.

3. Results and discussion

3.1. Characterization of adsorbents

Characteristics of adsorbents were determined by conventional chemical as well as analytical techniques. The chemical constituents of Bottom Ash and De-Oiled Soya are presented in Table 1. Scanning electron microscopic photograph of activated Bottom Ash and De-Oiled Soya revealed the surface and pore properties of the adsorbents along with its adsorptive nature. Both the adsorbents were analyzed using infrared spectrophotometeric study. Bottom Ash exhibited a sharp absorption band in the region of 3700–3500 cm^{-1}. The bands at 3467, 2930, 2676, 1502, 1097 and 790 cm^{-1} indicated the presence of laumonite, amber, mulite, azurite, bavenite and kaolinite [$2(Al_2Si_2O_5(OH)_4)$] in Bottom Ash, whereas in case of De-Oiled Soya the bands were obtained at 479, 779, 1113, and 3459 cm^{-1} which indicated the presence of gorthite (4[FeO·OH]), coesite (SiO_2), corundum (2[α-Al_2O_3]), and laumonite (4[$CaAl_2Si_4O_{12}\cdot 4H_2O$]), respectively. DTA curves indicated that Bottom Ash was thermally stable and showed negligible weight loss even at high temperatures. The presence of mainly alumina (Al_2O_3), gypsum ($CaSO_4\cdot 2H_2O$), beverite [$Pb(CuFeAl)_3(SO_4)_2(OH)_6$], borax ($Na_2B_4O_7\cdot 10H_2O$) and kaolinite [$2(Al_2Si_2O_5(OH)_4)$] was confirmed by the *d*-spacing values provided by the X-ray spectrum of the adsorbents.

Table 1
Chemical constituents of the adsorbents

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

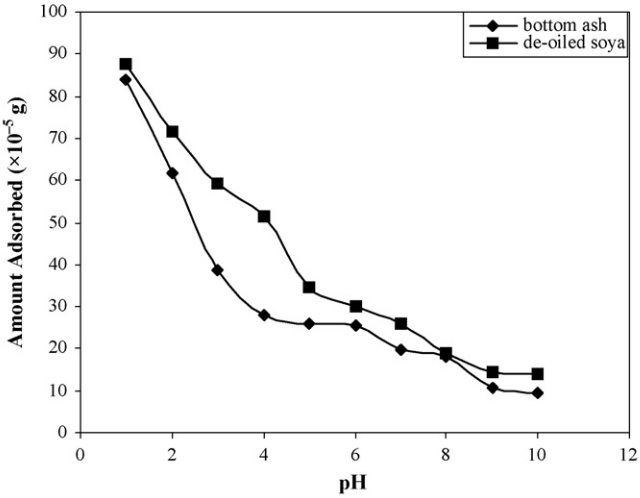


Fig. 1. Effect of pH on uptake of Metanil Yellow by Bottom Ash and De-Oiled Soya at 30 °C. Bottom Ash: concentration = 10 × 10^{-5} M, adsorbent dose = 0.05 g, particle size = 100 BSS mesh. De-Oiled Soya: concentration = 10 × 10^{-5} M, adsorbent dose = 0.05 g, particle size = 36 BSS mesh.

3.2. Adsorption studies

3.2.1. Effect of pH

A wide range of pH from 1 to 10 was selected to determine the adsorption behavior of the dye. The study clearly indicates that the extent of adsorption of the dye is affected significantly with pH due to its impact on both surface binding site of the adsorbent and the ionization process of the dye molecule. The result depicted in Fig. 1 suggest that in both the cases adsorption decreases with increase in pH. Since both adsorbents show high adsorption at low pH, all subsequent studies were carried out at pH 2 as an optimum value.

Higher adsorption of the dye at low pH may be due to increased protonation by neutralization of the negative charge at the surface of the adsorbents. This facilitates the diffusion process and provides more active sites of the adsorbent. However, with increase in pH, protonation reduces, which retards diffusion and adsorption thereby.

3.2.2. Effect of particle size

For the batch adsorption studies three sizes of the adsorbents −36, 100 and 170 BSS mesh, were selected for each adsorbent. A series of 25 mL of 10 × 10^{-5} M solution was added with 0.1 g of Bottom Ash and 0.05 g of De-Oiled Soya of known particle size each in 100 mL volumetric flask and it is kept for shaking for optimum time. The sample is then filtered and analyzed for different particle sizes of adsorbents from 36 to 100 BSS mesh [0.425–0.15 mm (36 mesh); 0.15–0.08 mm (100 mesh); ≤0.08 mm (170 mesh)]. It is found that with increase in mesh size adsorption increases. This can be attributed to the fact that the smaller adsorbent particles have a greater ratio of surface area to volume, making them more accessible to diffusion from solution. For further studies, 36 BSS mesh size (0.425–0.15 mm) for De-Oiled Soya and 100 BSS mesh size (0.15–0.08 mm) for Bottom Ash were chosen based on the adsorption capacity and availability of the adsorbent. Rate constants and half-life

Table 2
Effect of sieve size of different adsorbents on the rate of adsorption of Metanil Yellow over Bottom Ash and De-Oiled Soya

Mesh size (mm)	Bottom Ash			De-Oiled Soya		
	Amount adsorbed ($\times 10^{-5}$ g)	$t_{1/2}$ (h)	k (h^{-1})	Amount adsorbed ($\times 10^{-5}$ g)	$t_{1/2}$ (h)	k (h^{-1})
36 (0.425–0.15)	10.88	7.72	0.090	23.92	12.17	0.057
100 (0.15–0.08)	13.69	8.64	0.080	27.86	13.70	0.051
170 ($\leq$0.08)	18.76	10.33	0.067	29.64	14.43	0.048

Concentration = 10 × 10^{-5} M, pH 2.0, temperature = 30 °C, adsorbent dose = 0.05 g (Bottom Ash) and 0.05 g (De-Oiled Soya).

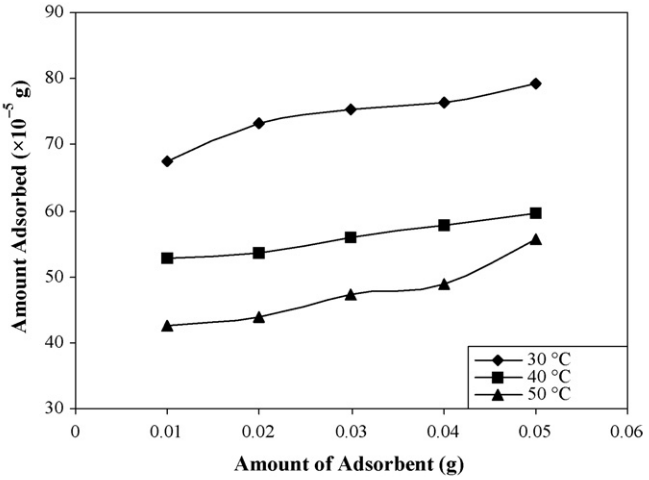


Fig. 2. Effect of amount of adsorbent for the removal of Metanil Yellow using Bottom Ash at different temperatures, concentration = 10 × 10^{-5} M, particle size = 100 BSS mesh, pH 2.0.

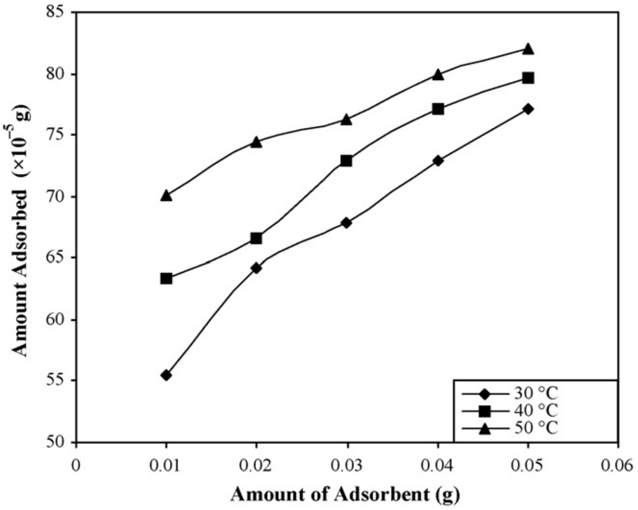


Fig. 3. Effect of amount of adsorbent for the removal of Metanil Yellow using De-Oiled Soya at different temperatures, concentration = 10 × 10^{-5} M, particle size = 36 BSS mesh, pH 2.0.

of each process were also calculated and are presented in Table 2.

3.2.3. *Effect of adsorbent dose*

The effect of adsorbent dosage on the removal of Metanil Yellow was investigated at 10 × 10^{-5} M dye concentration. A range of 0.01–0.05 g of both the adsorbents were mixed with 25 mL of the dye solution and the effect was studied at fixed pH, temperature and adsorbate concentration. The results displayed in Figs. 2 and 3 and values of amount adsorbed obtained in Table 3 shows that an increase in the adsorbents quantity causes increase in the adsorption. Such a trend is mainly due to increase in sorptive surface area and availability of more adsorption sites. The uptake of the dye decreases with increase in the temperature for Metanil Yellow–Bottom Ash system, while adsorption increases as temperature is raised from 30 to 50 °C for Metanil Yellow–De-Oiled Soya system.

3.2.4. *Effect of concentration of adsorbate*

The adsorption process for Metanil Yellow–Bottom Ash and Metanil Yellow–De-Oiled Soya was investigated at concentration ranging from 1 × 10^{-5} M to 10 × 10^{-5} M at a fixed pH and at different temperatures (30, 40 and 50 °C). The extent of adsorption of Metanil Yellow on both the adsorbents was found to increase linearly with increase in the concentration of the adsorbate as evident from Table 4. Percentage adsorption at higher concentration was nearly 61.00 and 34.70% at 30 °C and 50 °C, respectively for Bottom Ash, while 41.83 and 62.65% at 30 °C and 50 °C, respectively for De-Oiled Soya, which suggest

Table 3
Effect of amount of adsorbents on the adsorption of Metanil Yellow

Amount of Bottom Ash (g)	Amount adsorbed ($\times 10^{-5}$ g)			Amount of De-Oiled Soya (g)	Amount adsorbed ($\times 10^{-5}$ g)		
	30 °C	40 °C	50 °C		30 °C	40 °C	50 °C
0.01	67.44	52.72	42.49	0.01	55.53	63.41	70.06
0.02	73.26	53.60	43.80	0.02	64.16	66.60	74.48
0.03	75.42	55.90	47.18	0.03	67.82	72.98	76.35
0.04	76.45	57.87	48.87	0.04	72.98	77.10	79.92
0.05	79.35	59.57	55.72	0.05	77.20	79.64	82.08

Concentration = 10 × 10^{-5} M and pH 2.0.

Table 4
Effect of concentration of Metanil Yellow on the adsorption over Bottom Ash and De-Oiled Soya

Concentration of the dye ($\times10^{-5}$ M)	Amount adsorbed (Bottom Ash) ($\times10^{-5}$ g)			Concentration of the dye ($\times10^{-5}$ M)	Amount adsorbed (De-Oiled Soya) ($\times10^{-5}$ g)		
	30 °C	40 °C	50 °C		30 °C	40 °C	50 °C
1	9.00	6.84	8.63	1	8.47	8.72	9.07
2	7.50	5.34	3.75	2	1.22	4.69	7.50
3	13.13	10.79	6.84	3	9.73	9.73	9.75
4	18.10	14.07	8.25	4	7.03	13.13	18.29
5	23.73	16.88	10.70	5	11.25	16.88	23.17
6	29.64	23.45	16.90	6	15.00	22.32	30.11
7	37.24	29.45	22.51	7	18.76	28.51	36.96
8	45.21	35.08	22.51	8	27.01	37.43	45.68
9	52.72	40.80	28.14	9	34.33	43.71	54.03
10	61.91	47.65	34.70	10	41.83	51.02	62.66

Adsorbent dose = 0.05 g (Bottom Ash) and 0.05 g (De-Oiled Soya).

possibility of exothermic process for Metanil Yellow–Bottom Ash system and endothermic process for Metanil Yellow–De-Oiled Soya system.

3.2.5. *Effect of contact time*

In order to innovate more effective modeling of the adsorption process, kinetics of the process was monitored. Adsorption experiments were carried out for different contact time with a fixed adsorbent dose (0.04, 0.05 and 0.06 g) at pH 2 and at different temperatures (30, 40 and 50 °C). Primary investigation suggests that the uptake of Metanil Yellow is almost 44% over both the adsorbents, within first hour of contact at 30 °C. About 50% of the adsorption gets over in about 4 h for Bottom Ash and 1.50 h for De-Oiled Soya. The saturation in the adsorption was achieved at about 5.50 h and 4 h for Bottom Ash and De-Oiled Soya, respectively (Figs. 4 and 5).

3.3. *Adsorption isotherms*

The adsorption of Metanil Yellow onto two adsorbents was studied for three temperatures, viz. 30, 40 and 50 °C at different times with intermittent shaking and initial dye concentration 10×10^{-5} M. The experimental equilibrium adsorption data were compared with Freundlich and Langmuir isotherm models.

3.3.1. *The Freundlich adsorption isotherm model*

The Freundlich model assumes a heterogeneous adsorption surface having unequally available sites with different energies of adsorption [41]. The validity of Freundlich adsorption model was established using following relation:

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

where q_e is the amount adsorbed (mol/g) and C_e is the equilibrium concentration of the adsorbate (M). K_F and n are the Freundlich constants incorporating all the factors affecting the adsorption process like adsorption capacity and adsorption intensity, respectively. Figs. 6 and 7 clearly reveal that for the adsorbents $\log C_e$ versus $\log q_e$ plots are linear. Freundlich constants were derived from the slopes and intercepts of $\log C_e$ versus $\log q_e$ and are presented in Table 5. The

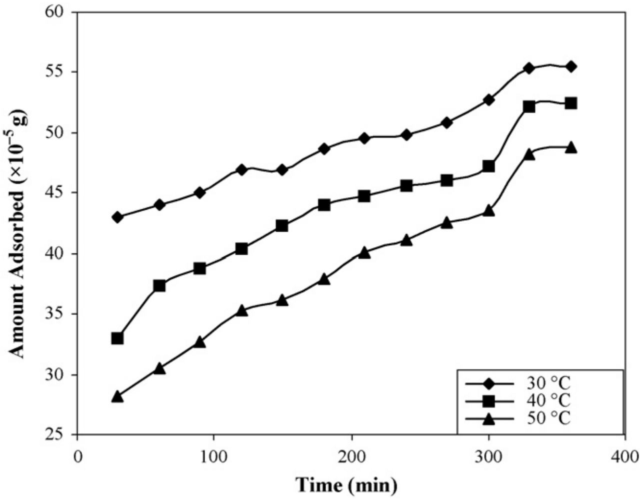


Fig. 4. Effect of contact time for the uptake of Metanil Yellow by Bottom Ash at different temperatures and at a concentration of 10×10^{-5} M, adsorbent dose = 0.05 g, particle size = 100 BSS mesh, pH 2.0.

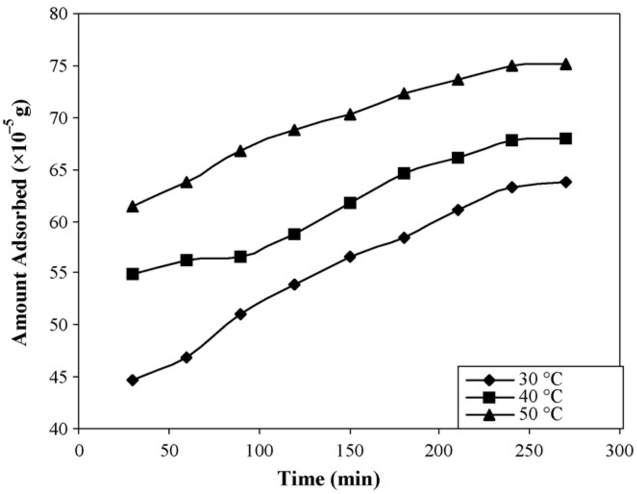


Fig. 5. Effect of contact time for the uptake of Metanil Yellow by De-Oiled Soya at different temperatures and at a concentration of 10×10^{-5} M, adsorbent dose = 0.05 g, particle size = 36 BSS mesh, pH 2.0.

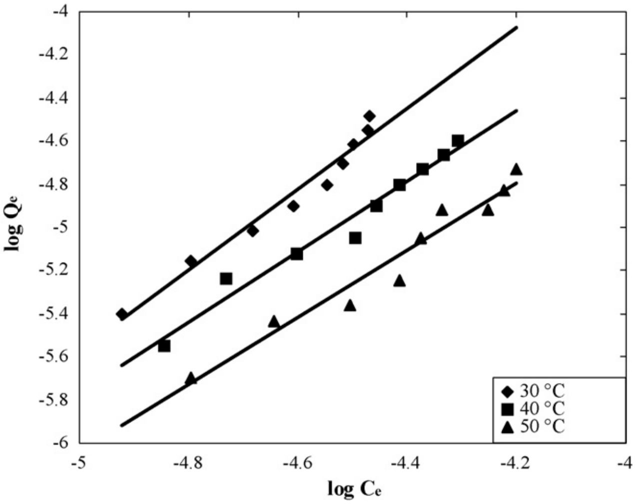


Fig. 6. Freundlich adsorption isotherm for Metanil Yellow–Bottom Ash system at different temperatures, adsorbent dose = 0.05 g, particle size = 36 BSS mesh, pH 2.0.

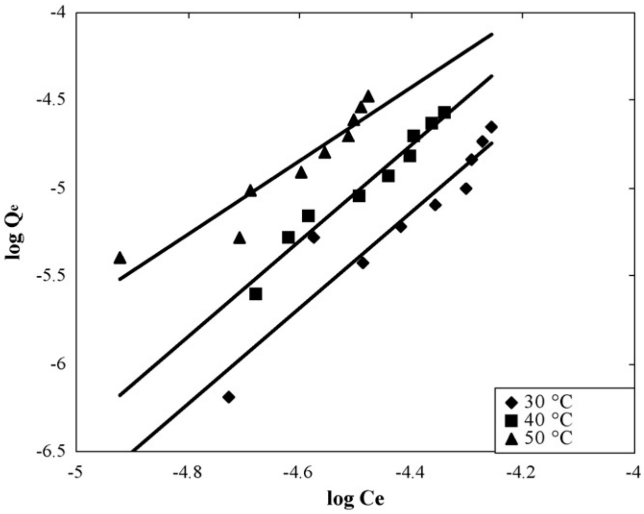


Fig. 7. Freundlich adsorption isotherm for Metanil Yellow–De-Oiled Soya system at different temperatures adsorbent dose = 0.05 g, particle size = 36 BSS mesh, pH 2.0.

results clearly indicate that the adsorption capacity decreases with increase in temperature for Bottom Ash, while the adsorption increases with increase in temperature for De-Oiled Soya.

3.3.2. The Langmuir adsorption isotherm model

Langmuir sorption model is based on the physical hypothesis that there is no interaction between adsorbed molecules and the adsorption energy is distributed homogenously over the entire coverage surface. Also there is no transmigration of the adsorbate in the plane of the surface of the adsorbent [42,43]. The experimental values of Langmuir constants were evaluated using well-known linear form of Langmuir's adsorption isotherm equation [44,45]:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \tag{2}$$

where q_e is the amount of Metanil Yellow adsorbed (mol/g), C_e the equilibrium molar concentration of the dye and Q_0 and b are the Langmuir constants related to the maximum adsorption capacity and energy of adsorption, respectively. For both the systems under investigation, the plot of $1/q_e$ against $1/C_e$ gives a straight line at each temperature, thereby confirming that the Langmuir isotherm is followed in the adsorption process (Figs. 8 and 9). The values of calculated parameters for Langmuir are presented in Table 5.

3.3.3. Calculation for thermodynamic parameters

Various thermodynamic parameters [46–48] were also calculated for both adsorbents using following relations:

$$\Delta G^\circ = -RT \ln b \tag{3}$$

$$\Delta H^\circ = -R\left[\frac{T_2T_1}{T_2 - T_1}\right] \ln \left[\frac{b_2}{b_1}\right] \tag{4}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{5}$$

where ΔH° is the change in enthalpy, ΔS° the change in entropy, ΔG° the change in Gibb's free energy and b, b_1 and b_2 are the Langmuir constants at different temperatures. The negative free

Table 5
Freundlich and Langmuir constants for removal of Metanil Yellow

Adsorbent	Freundlich constants					
	n			K_F		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Bottom Ash	0.535	0.610	0.639	5919.704	263.0873	59.7723
De-Oiled Soya	0.365	0.386	0.474	8.44×10^6	1.62×10^7	7.13×10^4

Adsorbent	Langmuir constants					
	Q_0			$b\ (\times 10^4)$		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Bottom Ash	1.27×10^{-5}	1.22×10^{-5}	1.09×10^{-5}	2.053	1.440	0.995
De-Oiled Soya	9.76×10^{-6}	1.07×10^{-5}	6.54×10^{-6}	1.077	1.5186	2.529

Bottom Ash: adsorbent dose = 0.05 g, particle size = 100 BSS mesh, pH 2.0; De-Oiled Soya: adsorbent dose = 0.05 g, particle size = 36 BSS mesh, pH 2.0.

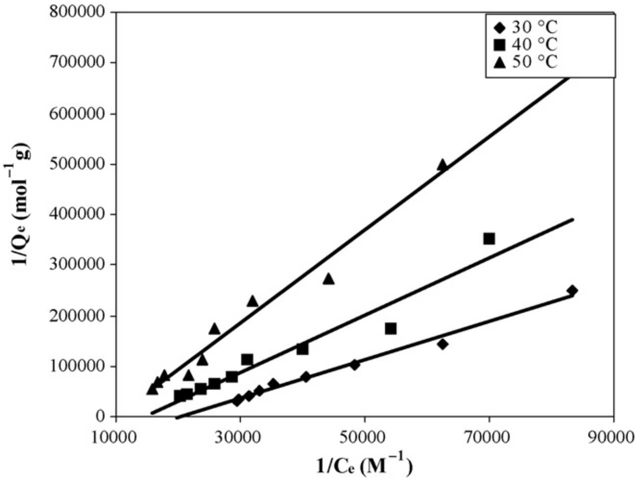


Fig. 8. Langmuir adsorption isotherm for Metanil Yellow–Bottom Ash system at different temperatures adsorbent dose = 0.05 g, particle size = 100 BSS mesh, pH 2.0.

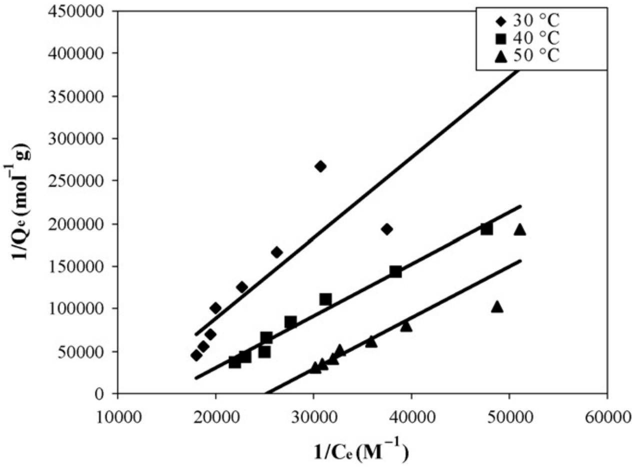


Fig. 9. Langmuir adsorption isotherm for Metanil Yellow–De-Oiled Soya system at different temperatures, adsorbent dose = 0.05 g, particle size = 100 BSS mesh, pH 2.0.

energy values suggest feasibility of the process in both the cases. The negative value of ΔH° further confirms the exothermic nature of the process for Metanil Yellow–Bottom Ash system, while positive value of ΔH° indicates endothermic nature for Metanil Yellow–De-Oiled Soya system. The positive value of entropy change (ΔS°) shows increased randomness of the process. All obtained values for the thermodynamic parameters have been depicted in Table 6.

Table 7
r–Values obtained at different temperatures for Metanil Yellow–Bottom Ash and Metanil Yellow–De-Oiled Soya adsorption

Adsorbent	r–Value		
	30 °C	40 °C	50 °C
Bottom Ash	0.327	0.409	0.501
De-Oiled Soya	0.481	0.397	0.283

3.3.4. Calculation for separation factor

In order to ascertain the favorability and the shape of the adsorption isotherms, the dimensionless separation factor is calculated by applying the equation:

$$r = \frac{1}{1 + bC_0} \tag{6}$$

as recommended by Weber and Chakrabarti [49], where, b denotes the Langmuir constant and C_0 is the initial concentration. In each case the r-value was found between 0 and 1 and confirms the favorability of the process. The increase in the r values for Bottom Ash indicate that low temperature favors the adsorption process, whereas, the decline in the r values for Metanil Yellow–De-Oiled Soya system clearly indicate that the ongoing process is much favored at higher temperature. All evaluated r-values are portrayed in Table 7.

3.4. Rate constant study

The adsorption kinetics of the ongoing process is well described by popularly and frequently used Lagergren's first order rate equation [50]. The specific rate constants for both the systems was calculated using following mathematical form:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \tag{7}$$

where q_e and q_t denote the amount adsorbed at equilibrium and at any time t, respectively. The linear graph of $\log(q_e - q_t)$ versus time suggests involvement of first order kinetics (Figs. 10 and 11) in both the cases. The values of rate constant (k_{ad}) for both the adsorbents were calculated using the values of slopes of these straight lines at different temperatures (Table 8).

3.4.1. Rate expression and treatment of data

To interpret the experimental data, it is essential to recognize the adsorption process steps, which govern the overall removal rate in each case. The ingenious mathematical treatment recommended by Boyd et al. [51] and Reichenberg [52]

Table 6
Thermodynamic parameters for the uptake of Metanil Yellow

Adsorbent	$-\Delta G^\circ$ (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° (J/(K mol))
	30 °C	40 °C	50 °C		
Bottom Ash	25.014	24.915	24.721	−29.493	14.675
De-Oiled Soya	23.390	25.055	27.226	34.728	191.776

Bottom Ash: adsorbent dose = 0.1 g, particle size = 100 BSS mesh, pH 2.0; De-Oiled Soya: adsorbent dose = 0.05 g, particle size = 36 BSS mesh, pH 2.0.

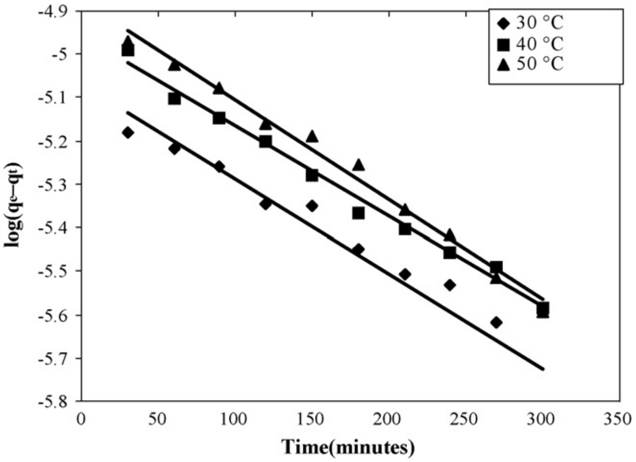


Fig. 10. Lagergren's plot of time vs. $\log(q_e - q_t)$ for Metanil Yellow–Bottom Ash system at different temperatures.

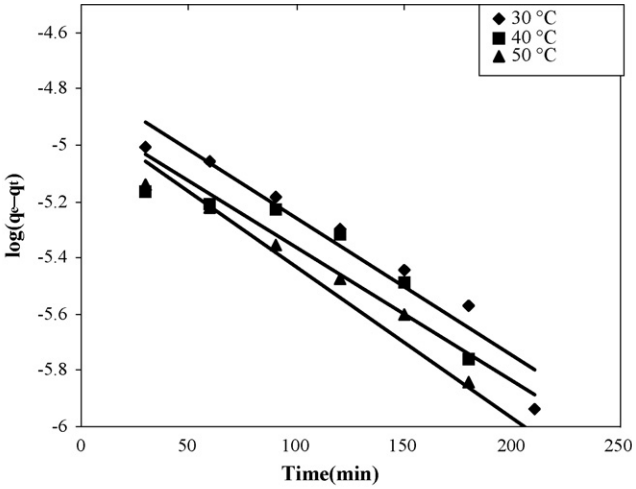


Fig. 11. Lagergren's plot of time vs. $\log(q_e - q_t)$ for Metanil Yellow–De-Oiled Soya system at different temperatures.

was employed to identify whether the process is particle diffusion or film diffusion. During the adsorption of an adsorbate by a porous adsorbent, adsorbate undergoes either particle diffusion or film diffusion or is adsorbed on the interior surface of the adsorbent. The third process is very rapid and is not rate-limiting step in the adsorption [53]. The remaining two steps have three possibilities:

Case 1. If external transport > internal transport, rate is governed by particle diffusion.

Table 8
Rate constant of adsorption (k_{ad}) for the adsorption of Metanil Yellow over Bottom Ash and De-Oiled Soya

Adsorbent	k_{ad} ($\times 10^{-3}$)		
	30 °C	40 °C	50 °C
Bottom Ash	−5.07	−4.84	−5.30
De-Oiled Soya	−11.28	−11.05	−12.44

Case 2. If external transport < internal transport, rate is governed by film diffusion.

Case 3. If external transport ≈ internal transport, there occurs the formation of a liquid film surrounded by the adsorbent particles, as the transport of the adsorbate ions to the boundary does not occur at a considerable rate.

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

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

$$F = \frac{Q_t}{Q_\infty} \tag{9}$$

$$B = \frac{\pi^2 D_i}{r_0^2} = \text{time constant} \tag{10}$$

where F is the fractional attainment of equilibrium at time t, Q_t and Q_∞ amounts adsorbed after time t and after infinite time, respectively, B the time constant, B_t the time constant after time t, D_i the effective diffusion coefficient of adsorbate in adsorbent phase, r_0 the radius of adsorbent particle and n is the Freundlich constant of the adsorbate. Based on values of F, B_t values were derived from Reichenberg's table and B_t versus time graph was plotted to distinguish between the film diffusion and particle diffusion adsorption rates.

In the present investigations, the pictorial presentation of the B_t versus time graph (Figs. 12 and 13) exhibit linearity with straight lines without passing through the origin in case of adsorption of the dye over Bottom Ash and De-Oiled Soya at different temperatures and concentrations. This suggests rate-determining process as film diffusion.

The effective diffusion coefficient (D_i) values are calculated from the slopes of B_t versus time graph for both the adsorbents

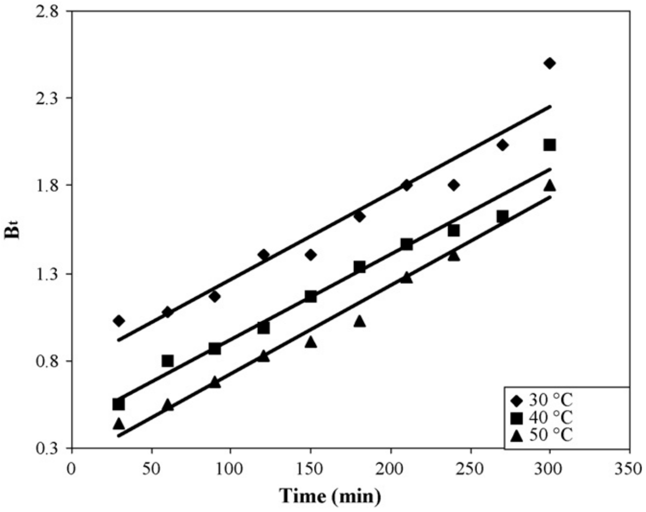


Fig. 12. Plot of time vs. B_t for Metanil Yellow–Bottom Ash system at different temperatures.

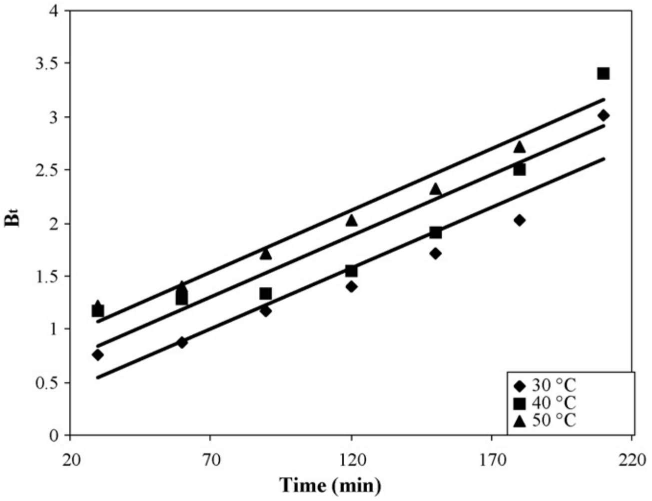


Fig. 13. Plot of time vs. B_t for Metanil Yellow–De-Oiled Soya system at different temperatures.

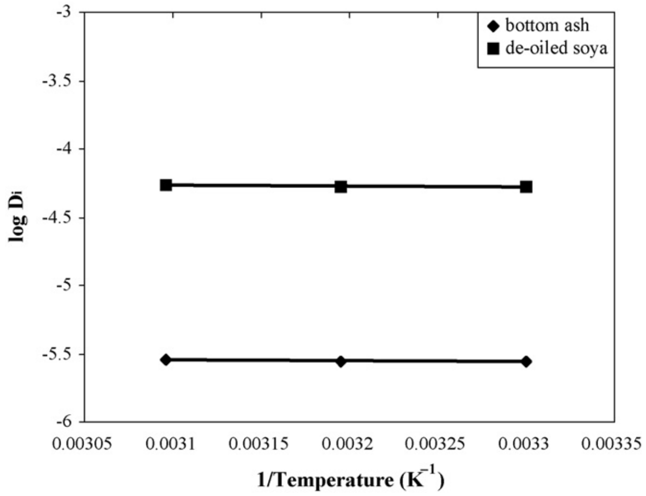


Fig. 14. Plot of 1/temperature vs. log D_i for Metanil Yellow–Bottom Ash system and Metanil Yellow–De-Oiled Soya system.

at 30, 40 and 50 °C. It is clear from Fig. 14 plotted between 1/temperature and log D_i that values of D_i also increases with increasing temperature, indicating thereby an increase in the mobility of the ions with increase in temperature. The energy of activation (E_a), entropy (ΔS°) and pre-exponential constant (D_0), values were evaluated using following relations and are shown in Table 9.

$$D_i = D_0 \exp\left(-\frac{E_a}{RT}\right) \tag{11}$$

$$D_0 = \left(\frac{2.72d^2kT}{h}\right)\exp\left(\frac{\Delta S^{\#}}{R}\right) \tag{12}$$

where d is the average distance between two successive sites of the adsorbent, k the Boltzmann constant, h the Plank's constant, E_a the energy of activation, T the temperature and R is the universal gas constant. The negative values of ΔS° obtained for both the systems reflect that the internal structure of the adsorbents do not undergo any note worthy change during the adsorption of the dye.

3.5. Column studies

Fixed bed adsorption process has been widely used to remove toxic dye from industrial wastewaters. The column adsorption studies were undertaken to understand the practical utility of adsorption process. Bulk removal of the adsorbate by column studies proves to be more advantageous over batch studies as the exhaustion capacity of column is usually found to be relatively higher than the batch capacity [54]. This is because of establishment of continuous larger concentration gradient at the interface zone as the influent passes through the column. Thus, for both the adsorbents, fixed bed column studies were carried out by well-established methods [55,56].

3.5.1. Dye adsorption in columns

Through the prepared columns 10×10^{-5} M dye solution was passed at the rate of 0.5 mL/min. Breakthrough curves of eluted volume against concentration of the eluted dye for both the systems are plotted and depicted in Fig. 15. It is found that out of 19.44 mg of the dye taken in the solution, 8.595 mg gets adsorbed over 0.5 g of Bottom Ash, while 6.838 mg of the dye was adsorbed over total 0.125 g of De-Oiled Soya out of 21.96 mg of the dye. Breakthrough curves obtained in both the cases are used in calculating parameters like, length of the primary adsorption zone (δ), total time involved for the establishment of primary adsorption zone (t_x), time for the primary adsorption zone to move down its length (t_δ), time for initial formation of primary adsorption zone (t_f), mass rate flow of the adsorbent (F_m) and fractional capacity of the column (f) by using following relations:

$$t_x = \frac{V_x}{F_m} \tag{13}$$

$$t_\delta = \frac{V_x - V_b}{F_m} \tag{14}$$

Table 9
Values of effective diffusion coefficient (D_i), pre-exponential constant (D_0), activation energy (E_a) and entropy of activation (ΔS°) for the diffusion of Metanil Yellow adsorbing over Bottom Ash and De-Oiled Soya

Adsorbent	D_i			D_0	E_a (J mol^{-1})	ΔS° (J/(K mol))
	30 °C	40 °C	50 °C			
Bottom Ash	2.800×10^{-6}	2.800×10^{-6}	2.850×10^{-6}	3.850×10^{-6}	813.340	−307.565
De-Oiled Soya	5.221×10^{-5}	5.312×10^{-5}	5.359×10^{-5}	7.96×10^{-5}	1060.788	−721.954

Table 10
Fixed bed adsorber calculations

Adsorbent	C_0 ($\times 10^{-5}$ M)	C_x ($\times 10^{-5}$ M)	C_b ($\times 10^{-5}$ M)	V_x (ml)	V_b (ml)	F_m (mg/cm^2)	D (cm)
Bottom Ash	10	9.90	2.60	510	50	0.02293	0.5
De-Oiled Soya	10	9.90	2.62	560	60	0.02293	0.8

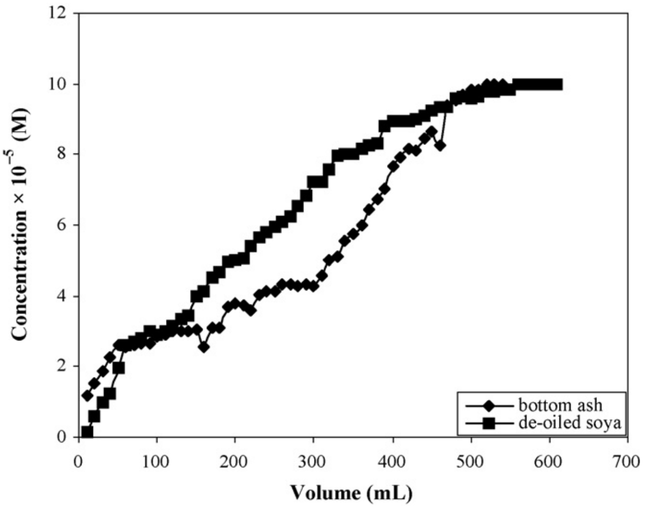


Fig. 15. Breakthrough curves for Metanil Yellow–Bottom Ash and Metanil Yellow–De-Oiled Soya columns.

$$\frac{\delta}{D} = \frac{t_\delta}{t_x - t_f} = \frac{t_\delta}{t_x + t_\delta(f-1)} = \frac{V_x - V_b}{V_b + f(V_x - V_b)} \qquad (15)$$

$$f = 1 - \frac{t_f}{t_\delta} = \frac{M_s}{(V_x - V_b)C_0} \qquad (16)$$

$$\text{percentage saturation} = \frac{D + \delta(f-1)}{D} \times 100 \qquad (17)$$

The calculated values of all these parameters are presented in Tables 10 and 11. Table 11 indicates that the values of t_x and t_δ for the Metanil Yellow–Bottom Ash adsorption are less than those for the Metanil Yellow–De-Oiled Soya system. The data obtained reveals that the time taken for the initial formation of primary adsorption zone (t_f) for both the systems is nearly 2 h. For both the systems the fractional capacity *f*, at breakpoint was calculated around 0.99. An additional 460 and 500 mL of adsorbate quantity per unit cross-sectional area will result in complete exhaustion of the capacity of adsorbent.

3.5.2. Column regeneration and dye recovery

The recovery of the dye and column regeneration was carried out using dilute sodium hydroxide solution (pH 13) through the exhausted column under specified conditions of flow rate, column bed, etc., and results obtained are depicted in Fig. 16. In case of Bottom Ash and De-Oiled Soya total 310 mL of dilute NaOH was found sufficient for the desorption of Metanil Yellow.

Table 11
Parameters for fixed bed adsorber

Adsorbent	t_x (min)	t_δ (min)	t_f (min)	δ (cm)	Percentage saturation (%)
Bottom Ash	22241.67	20061.11	100	0.915	99.15
De-Oiled Soya	24422.22	21805.56	120	0.897	99.38

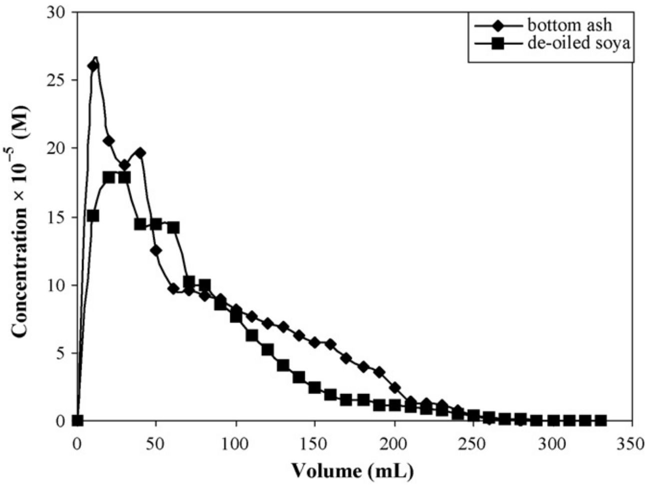


Fig. 16. Desorption of Metanil Yellow from Bottom Ash and De-Oiled Soya columns.

Fig. 16 exhibits that the collection of 50% of the desorbed dye was achieved by first 70 mL of the eluent for Bottom Ash column and 24 more aliquots of 10 mL each were sufficient to recover remaining amount of the dye. Total percentage recovery of the dye was almost 88.44%. Similarly, during the regeneration of De-Oiled Soya column, 50% of the dye could be desorbed by 60 mL of the eluent and remaining amount of dye was obtained by eluting 25 more aliquots of 10 mL each. In this way total about 89.45% of the dye was recovered. Both the columns were then washed with hot water at the flow rate of 0.5 mL min^{-1}.

4. Conclusions

The result obtained in this study clearly establishes that both waste materials—Bottom Ash and De-Oiled Soya, can be used as promising adsorbents for the removal of Metanil Yellow from waste waters and adsorption of the dye over these materials is dependent on pH, sieve sizes of adsorbents, concentration of dye, temperature, etc., Langmuir and Freundlich models were successfully applied to confirm involvement of monolayer adsorption in the present case and also to predict the adsorption capacities of the two adsorbents. Calculated values for enthalpy change (ΔH°) were found to be −29.493 kJ mol^{-1} for Bottom Ash and +34.728 kJ mol^{-1} for De-Oiled Soya, respectively, which confirmed the ongoing process is exothermic in case of Bottom Ash and endothermic for De-Oiled Soya. The entropy change (ΔS°) and free energy (ΔG°) suggested random and feasible nature of the adsorption process in both the cases. The kinetics of the process indicated the dye removal via film diffusion for both the adsorbent systems. Efficient adsorption capacity of the adsorbents was established by performing column operations. By using sodium hydroxide as an eluent, percentage recovery was found 88.44 and 89.45%, respectively. Thus, a conclusion can be drawn that adsorption technique can be a viable and effective alternative for wastewater treatment and both Bottom Ash and De-Oiled Soya can act as excellent and economical adsorbers.

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