

Removal and recovery of hazardous triphenylmethane dye, Methyl Violet through adsorption over granulated waste materials

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Abstract

Bottom Ash a power plant waste material and De-Oiled Soya, an agricultural waste product have been successfully used for the removal and recovery of a hazardous triphenylmethane dye—Methyl Violet, from wastewaters. The characterization of each adsorbent has been carried out by I.R. and D.T.A. curves. Batch adsorption studies have been made by measuring effects of pH, sieve size, amount of adsorbent, contact time, temperature, concentration of the adsorbate solution, etc. Kinetic studies have been used to determine the nature of rate controlling step of the processes and confirm the applicability of the first order rate expression in the ongoing adsorption process. Various thermodynamic parameters have also been calculated by applying the linear forms of Langmuir and Freundlich adsorption isotherms. The linear nature of adsorption isotherms obtained shows the dependence of the processes on the Freundlich and Langmuir isotherm models. Furthermore, to ascertain the adsorption processes to be particle diffusion or film diffusion mechanism, Boyd and Reichenberg's expressions have been applied. For both the adsorbents, column operations have been carried out for the bulk removal of the dye. The adsorbed dye has been recovered by eluting hydrochloric acid of pH 3 through exhausted columns.

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1. Introduction

Methyl Violet, molecular formula $C_{24}H_{28}ClN_3$ (Fig. 1) is a triphenylmethane dye soluble in water, ethanol, methanol, diethylene glycol and dipropylene glycol. It is a dark green powder dye stable under ordinary conditions and has a poor resistance towards light and to chemical bleaches [1]. As described by Conn [2], Methyl Violets are the mixtures of tetramethyl, pentamethyl, hexamethyl and pararosanilines, thus the dye is also known as crystal violet or Methyl Violet 10 B. The dye is chiefly used in copying papers, in heterograph and printing inks. It imparts deep violet colour in paints and printing inks. It is also used to obtain shades of deep colours that can be applied for the dyeing of cotton, silk, paper, bamboo, weed, straw and leather. The commonest use of Methyl Violet is in Gram's Stain

for the demonstration and primary classification of bacteria. It is also used as an antiallergen and bactericide, the Flemming triple stain with iodine and Newton's crystal violet technique. Methyl Violets are metachromatic and are sometimes used to demonstrate amyloid [2].

The dye Methyl Violet is widely used in analytical chemistry laboratories as a pH indicator to test pH ranges from 0 to 1.6. At the low pH, Methyl Violet takes on to yellow colour and it becomes bluish violet at an alkaline end [2]. From the chemical structure of the dye it is observed that there are three aromatic rings attached to a central carbon atom. Presence of several double bonds accounts for the delocalization of the electrons sufficient enough to adsorb visible light. Hence, Methyl Violet shows absorption maxima at 584 nm, imparting violet blue colour.

The toxic nature of the dye can be explained by considering the fact that on decomposition it gives out hazardous products, such as carbon monoxide (CO), carbon dioxide (CO₂), nitrogen oxides and hydrogen chlorides [1]. These products are toxic and may cause severe health problems to mankind as well as animals. Thus, Methyl Violet attracts noteworthy attention to innovate

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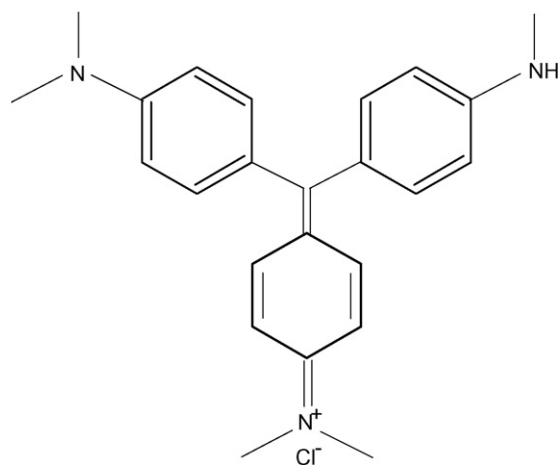


Fig. 1. Chemical structure of Methyl Violet.

effective techniques for its removal. The toxic information reveals that the dye may cause severe skin and eye irritation, a physical contact with the dye causes irritation with redness and pain. The dye is harmful if swallowed. Inhalation of Methyl Violet may also cause irritation to respiratory tract, whereas ingestion causes irritation to gastrointestinal tract [1].

As far as the removal of Methyl Violet is concerned, techniques such as chemical oxidation, coagulation, electrolysis, ultra filtration, froth floatation, solvent extraction, ion-exchange, reverse osmosis, etc., have been used to study for the removal of different dyes over different adsorbents [3–7]. All these techniques were found inefficient and incompetent because of the stability of the dye towards light, oxidizing agents and aerobic digestion. The dye also shows fairly high solubility in the aqueous media thus it is difficult to remove with the above-mentioned chemical methods for the wastewater treatments. On the basis of comprehensive investigation the adsorption technique was successfully applied and was found to be most appropriate and efficient one [8,9].

In recent past the wastes of some prime industries have been successfully utilized to remove this toxic dye. Four species of *Pseudomonas*, namely *Ps. alcaligenes*, *Ps. mendocina*, *Ps. putida* biovar B and *Ps. stutzeri*, were able to remove Methyl Violet with simultaneous reduction in chemical oxygen demand (COD), total organic carbon (TOC) and ammonical nitrogen from the waste effluent [10]. Apart from this the removal of Methyl Violet from aqueous solution has also been successfully tried by using perlite [11] and poly (acrylamide-co-acrylic acid) hydrogels [12]. Gupta et al. [13–18] have also contributed in this direction and used various adsorbents for the removal of different organic dyes. Continuing the efforts in that direction, we have tried Bottom Ash and De-Oiled Soya, after converting them into productive and efficient adsorbents for the removal and recovery of the dye from aqueous solutions [19–23].

The adsorbent material Bottom Ash is the unburned waste material of thermal coal-fired power generation plants that remains in the bottom of the incinerator furnace. It is a dark gray black granular sand size material. Bottom Ash generally is not hazardous and non-toxic usually disposed off in a land-

fill or dumped near the surrounding land [24]. This ash makes the agricultural land uncultivable and infertile [25]. Other adsorbent, De-Oiled Soya is a by-product of soyabean oil extracting mills. It is a dry, brownish white, porous, flaky material, which is obtained after extracting all possible nutrients of soyabeans. The product is manufactured under careful processing conditions but sometimes due to improper processing anti-metabolites like Lipoxygenase and Trypsin inhibitors liberates, which makes the De-Oiled Soya bitter in taste and non-edible for human as well as animals. When extracted with more than 170 ppm of hexane solvent, De-Oiled Soya becomes toxic to the animals and even cannot be used as a fishmeal [26–30]. Soyabean in India has experienced a phenomenal increase both in area and production during the last two decades and the country has become one of the leading producers of the soyabean crop. In India, Madhya Pradesh is the leading state in producing soyabean and many soyabean industries surround our city.

2. Materials and methods

Methyl Violet a triphenylmethane dye (molecular weight = 393.96) was procured from M/s Merck. Bottom Ash is a waste material collected from thermal power station (TPS) of M/s Bharat Heavy Electrical Limited (B.H.E.L), Bhopal (India). It is a dark grayish black, granular, incombustible material. The sub-bituminous coal used by TPS, B.H.E.L, Bhopal was obtained from M/s South Eastern Coal Field Limited, Chirmiri, Sarguja (India). Another potential and valuable adsorbent De-Oiled Soya is a by-product of soyabean oil industries, which is obtained after extracting almost all nutrients and proteins from the soyabean. It is given by M/s Surya Agro Oils, Bhopal, India as free gift. All reagents used in this investigation were of A.R. grade. Double distilled water was used for preparing solutions throughout the study.

All pH measurements were carried out with a micro-processor based pH meter model number HI 8424, M/s Henna Instruments, Italy. Concentration of the dye solutions were estimated using absorbance recorded on UV/VIS spectrophotometer model number 117 (M/s Systronics, Ahmedabad, India) over the wavelength of 584 nm. Scanning electron microscopy was performed using a Philips SEM 501 electron microscope. Philips X-ray diffractometer employing nickle filtered $\text{Cu}\alpha$ radiations was used for X-ray measurements. The surface area of the adsorbent was determined by using Quantasorb Model QS-7. The IR spectral studies were carried out on infra-red spectrometer (HP FT-IR).

2.1. Material development

Present study deals with the efforts made to utilize these waste materials, by converting them into efficient, low cost adsorbents, for the removal of some toxic dyes. As a result it was planned to first activate the Bottom Ash and De-Oiled Soya. Both the waste materials were first thoroughly washed with distilled water and dried. This dried material was then treated with hydrogen

per oxide at room temperature for 24 h to oxidize the adhering organic matter. The resulting products were then dried in an oven at 100 °C to remove the moisture. The activated De-Oiled Soya obtained from this process was sieved to obtain desired particle size, such as 0.425–0.15 mm (36 mesh), 0.15–0.08 mm (100 mesh), ≤ 0.08 mm (170 mesh), etc., whereas the Bottom Ash was further activated in presence of air in a Muffle furnace at 500 °C for 15 min. Temperature and time was optimized by observing the surface properties of the adsorbent, obtained during the activation of material, at different intervals of time and varying temperature. The material thus obtained was sieved to different sizes, same as De-Oiled Soya. Finally, the products obtained were stored in separate vacuum desiccators until required.

2.2. Adsorption studies

Adsorption studies were mainly carried out by batch technique to obtain rate and equilibrium data. The experiments were performed to observe the effect of pH, temperature, particle size, amount of adsorbent, concentration, contact time, etc. Adsorption studies with both the adsorbents were carried out at 30, 40, 50 °C. A known amount of adsorbent was taken in 100 mL airtight volumetric flasks containing 25 mL each of different adsorbate solution of known concentration. These flasks were then shaken intermittently to attain equilibrium condition of adsorption. The solution obtained was then filtered using Whatmann filter paper (No. 41) and analyzed spectrophotometrically by measuring the absorbance at λ_{max} of 584 nm. For the present work concentration range from 1×10^{-5} to 8×10^{-5} M was selected at a desired pH. The optimization of the entire concentration range was decided after a good deal of investigation.

2.3. Kinetic studies

To assess the applicability of the adsorption process it is necessary to determine the kinetic parameters, which were carried out through batch technique. A series of volumetric flasks of 100 mL capacity, containing 25 mL dye solution of known concentration were kept in water bath maintained at a desired temperature and pH and then agitated by mechanical shaker. After a definite time interval solutions were filtered and the filtrate thus obtained were then analyzed spectrophotometrically.

2.4. Column studies

The column study of each adsorbent Bottom Ash and De-Oiled Soya was carried out by using two glass columns, each of total length 30 cm and 1 cm internal diameter, packed with a known amount of adsorbent on a glass wool support. The weighed amount of each adsorbent was made into slurry with water and kept overnight. The slurry was then fed slowly into the column over a heel of water to minimize air entrapment in the column. Afterwards each column was loaded with dye solution of suitable concentration and was allowed to percolate at a flow rate of 0.5 mL min⁻¹ and 0.4 mL min⁻¹ for Bottom Ash and De-Oiled Soya, respectively, under the influence of gravity. In each case several 5–10 mL aliquots of effluents were collected and analyzed spectrophotometrically. Once the effluent concentration matches with the concentration of loaded dye, column operations were shut down.

2.5. Column regeneration

The regeneration of the exhausted fixed bed of the column was made by eluting HCl solution of pH 3. The total recovery of the dye was achieved by percolating total 340 mL of eluent in case of Bottom Ash and 70 mL in case of De-Oiled Soya through the column at a flow rate of 0.4 mL min⁻¹. After complete recovery of the dye both the columns were washed with hot water.

3. Results and discussion

3.1. Characterization of adsorbent materials

The characterization of the activated Bottom Ash and De-Oiled Soya was carried out by conventional chemical methods. The chemical composition and physicochemical properties obtained are presented in Table 1. The differential thermal analysis (DTA) curves of activated Bottom Ash and De-Oiled Soya exhibit their good thermal stability and negligible weight loss was accounted. The scanning electron microscopic photographs of Bottom Ash and De-Oiled Soya accounts for their surface texture and porosity thus these adsorbents can be approximated as spheres. The *d*-spacing values provided by the X-ray spectrum of the adsorbents indicate presence of

Table 1
Chemical constituents of adsorbents

	Constituents						
	Moisture	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O
Bottom Ash							
Percentage by weight (%)	15	45.4	10.3	9.7	15.3	3.1	1.0
	Constituents						
	Moisture	Fibre	SiO ₂	P	Ca		
De-Oiled Soya							
Percentage by weight (%)	11	6	2	0.7	0.2		

mainly alumina (Al_2O_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Beaverite [$\text{Pb}(\text{Cu}, \text{Fe}, \text{Al})_3(\text{SO}_4)_2(\text{OH})_6$], borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and kaolinite [$2\{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\}$]. From the IR spectrum, the bands at 3467, 2930, 2676, 1502, 1097 and 790 cm^{-1} were obtained, which indicate the presence of laumontite, amber, mulite, azurite, bavenite and kaolinite in the Bottom Ash. The sharp adsorption bands in the region of $3700\text{--}3500\text{ cm}^{-1}$ apparently reveal the presence of free hydroxyl groups. In case of De-Oiled Soya the presence of gorthite ($4[\text{FeO} \cdot \text{OH}]$), corundum ($2[\alpha\text{-Al}_2\text{O}_3]$), coesite (SiO_2), laumontite ($4[\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}]$) was supported by the bands obtained at 479.6, 779.1, 1113.5, 3459 cm^{-1} .

3.2. Adsorption studies

3.2.1. Effect of pH

The adsorption behaviour of both the adsorbents was studied at varying pH range of 2.0–10.0. The percentage removal of the dye Methyl Violet by Bottom Ash and De-Oiled Soya are plotted in Fig. 2. The graph clearly indicates that each adsorption process is highly pH dependent and the maximum uptake of the dye takes place at around pH 8.0. It was observed that in both the cases at the acid end of its measuring range the dye Methyl Violet exhibits a yellow colour, while at the alkaline end it becomes bluish violet. Thus, all further studies were carried out at the higher pH 8.0. From Fig. 2 it is observed that rate of removal of the dye increases with increase in pH up to 8.0 and thereafter remains constant.

3.2.2. Kinetic studies

In the present work, it is observed that the kinetic parameters govern the overall efficiency of the adsorption process and thus it becomes essential to determine the applicability of the ongoing process. The studies include parameters, such as effect of time, sieve size, amount of adsorbent and the initial adsorbate concentration.

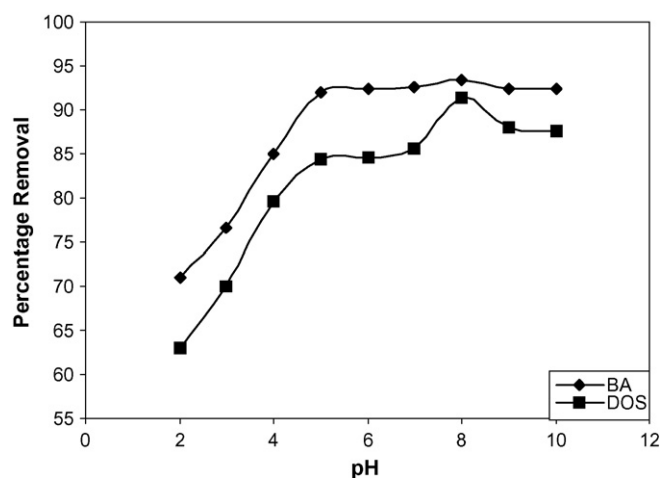


Fig. 2. Effect of pH on percentage removal of Methyl Violet adsorbed on Bottom Ash and De-Oiled Soya systems at 30°C [Bottom Ash: dye concentration = $3 \times 10^{-5}\text{ M}$, adsorbent dose = 0.1 g, particle size = 0.15–0.08 mm (100 BSS mesh); De-Oiled Soya: dye concentration = $3 \times 10^{-5}\text{ M}$, adsorbent dose = 0.05 g, particle size = 0.15–0.08 mm (100 BSS mesh)].

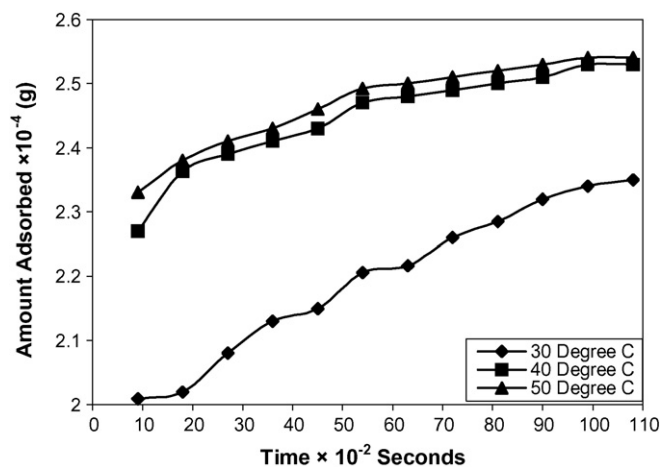


Fig. 3. Effect of uptake of Methyl Violet on Bottom Ash with time at different temperatures [dye concentration = $3 \times 10^{-5}\text{ M}$, adsorbent dose = 0.1 g, particle size = 0.15–0.08 mm (100 BSS mesh), pH 8.0].

3.2.3. Effect of time of contact

Preliminary studies imply that the rate of removal of the dye Methyl Violet was rapid during the initial phase of the adsorption process and within the first hour of time of contact almost 72.3, 81.6, and 83.3% of the dye was adsorbed over Bottom Ash at 30, 40 and 50°C , respectively. Whereas, for the De-Oiled Soya within an hour almost 72.6, 81.3, and 82.0% of the dye was removed successfully at 30, 40 and 50°C , respectively. Figs. 3 and 4 clearly specify that for both the adsorbents the equilibrium could be achieved in almost 2 h of the contact time. The half-lives for each adsorption process were also calculated and found increasing with the increase in the time.

3.2.4. Effect of sieve size

The batch adsorption experiments were carried out using three different particle sizes at desired pH, time, amount of adsorbent and temperature. The chosen particle sizes for both the adsorbents were 36 BSS mesh, 100 BSS mesh and 170 BSS mesh. The study shows that with the decrease in the particle

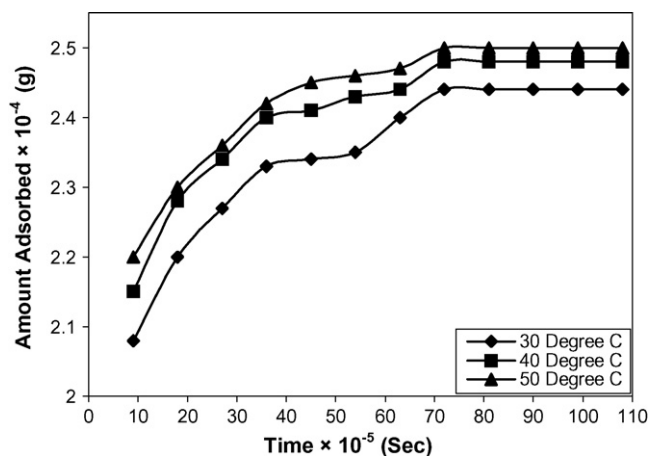


Fig. 4. Effect of contact time on adsorption of Methyl Violet by De-Oiled Soya at different temperatures [dye concentration = $3 \times 10^{-5}\text{ M}$, adsorbent dose = 0.05 g, particle size = 0.15–0.08 mm (100 BSS mesh), pH 8.0].

Table 2
Effect of sieve size of different adsorbents on the rate of adsorption of Methyl Violet

Adsorbent	Bottom Ash			De-Oiled Soya			
	Particle size (mm)	0.15–0.425 (36 mesh)	0.08–0.15 (100 mesh)	≤0.08 (170 mesh)	0.15–0.425 (36 mesh)	0.08–0.15 (100 mesh)	≤0.08 (170 mesh)
Amount adsorbed × 10 ⁻⁴ (g)	2.29	2.57	2.61	2.47	2.67	2.70	
t _{1/2}	169.972	150.814	148.407	157.166	144.930	143.250	

Bottom Ash: dye concentration = 3×10^{-5} M, adsorbent dose = 0.1 g, pH 8.0, temperature = 30 °C; De-Oiled Soya: dye concentration = 3×10^{-5} M, adsorbent dose = 0.05 g, pH 8.0, temperature = 30 °C.

Table 3
Effect of amount of different adsorbents on the rate of uptake of Methyl Violet at 30 °C for 180 min

Adsorbent	Bottom Ash				De-Oiled Soya				
	Amount of adsorbent (g)	0.025	0.050	0.100	0.150	0.025	0.050	0.075	0.100
Amount Adsorbed × 10 ⁻⁴ (g)	2.57	2.56	2.66	2.74	2.57	2.65	2.67	2.68	
t _{1/2} × 10 ³	1.13	1.11	1.06	1.09	1.13	1.10	1.09	1.08	

Bottom Ash: dye concentration = 3×10^{-5} M, particle size = 0.15–0.08 mm (100 BSS mesh), pH 8.0; De-Oiled Soya: dye concentration = 3×10^{-5} M, particle size = 0.15–0.08 mm (100 BSS mesh), pH 8.0.

size of adsorbents, rate of adsorption increases, whereas half-life of each system decreases. The adsorbent of particle sizes was selected for the entire experimentation due to the sufficient adsorption capacity. The data obtained are listed in Table 2.

3.2.5. Effect of adsorbent dose

The effect of the adsorbent dose on the removal of the dye Methyl Violet was studied by varying the amount of adsorbent Bottom Ash from 0.025 to 0.15 g and of De-Oiled Soya from 0.025 to 0.1 g at different time intervals, fixed pH, temperature and adsorbate concentration. The results obtained are presented in Table 3. Figs. 5 and 6 clearly show an increase in the adsorption with the increase in the amount of adsorbents. These figures also specify that in both the cases rate of removal of the dye increases with the increase in the time of contact. The half-life of the process was also determined at varying doses for each adsorbent and reveals that the half-life increases with increasing amount.

3.2.6. Effect of concentration

The adsorption experiments were carried out in the concentration range of the dye ranging from 1×10^{-5} to 8×10^{-5} M at a fixed pH 3.0, time of contact, amount of adsorbents and 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 Figs. 7 and 8. Fig. 7 clearly shows that for the Bottom Ash the uptake is almost 83, 88.65 and 91% at low concentration and about 82.16, 87 and 90% at higher concentrations of the dye at all the temperatures. However, in case of De-Oiled Soya at 30, 40 and 50 °C, the uptake of the dye is about 87.5, 92 and 96% in the low concentration range and 85.5, 88.5 and 93.3% at high concentration, respectively. These results also signify good efficacy of both the adsorbents towards Methyl Violet.

The rate of removal of the dye with both the adsorbents at optimum pH and adsorbate concentration was found quiet rapid and kinetic experiments exhibit that the adsorption equilibrium

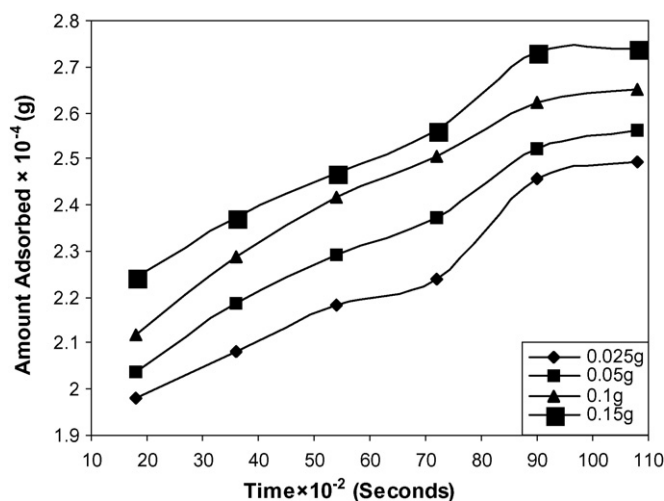


Fig. 5. Effect of amount adsorbed over Bottom Ash at different time intervals at 30 °C [dye concentration = 3×10^{-5} M, particle size = 0.15–0.08 mm (100 BSS mesh), pH 8.0].

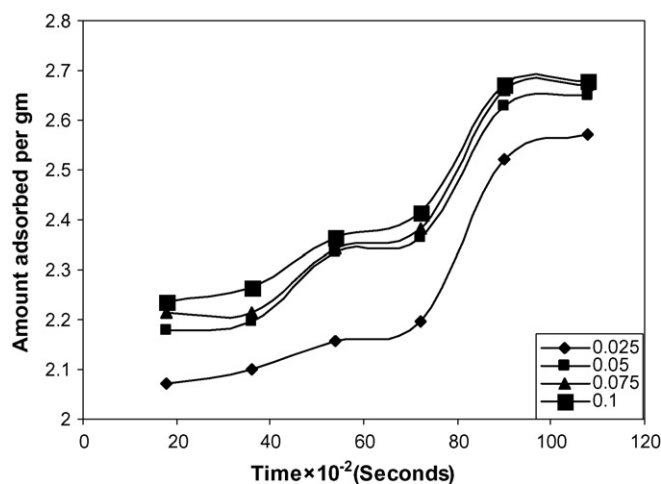


Fig. 6. Effect of amount adsorbed over De-Oiled Soya at different time intervals at 30 °C [concentration = 3×10^{-5} M, particle size = 0.15–0.08 mm (100 BSS mesh), pH 8.0].

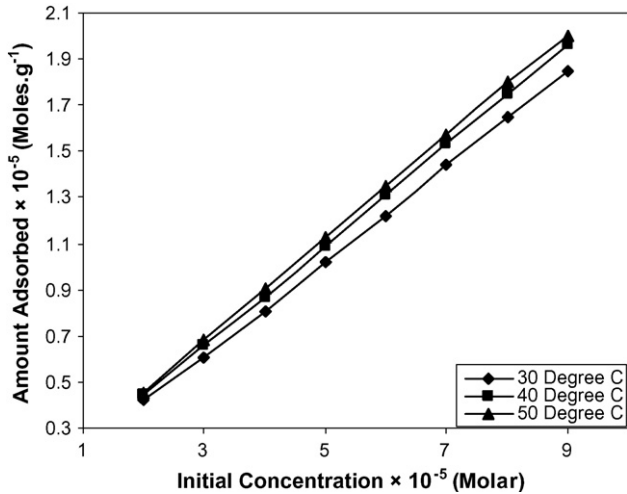


Fig. 7. Adsorption isotherm of Methyl Violet on Bottom Ash at different temperatures [adsorbent dose = 0.1 g, particle size = 0.15–0.08 mm (100 BSS mesh), pH 8.0].

was attained within about two hours for the Bottom Ash and in about one hour for the De-Oiled Soya (Figs. 3 and 4). Thus, in the entire temperature range almost 82–86% and 88–92% adsorption of the dye were accomplished over Bottom Ash and De-oiled Soya, respectively. Based on above results, the half-lives of both adsorptions were also calculated and found increasing with increase in time.

3.2.7. Thermodynamic adsorption parameters

In order to examine the thermodynamic parameters of the ongoing process the well-known Langmuir (Eq. (1)) and Freundlich (Eq. (2)) models were successfully applied at the different temperatures 30, 40 and 50 °C.

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \tag{1}$$

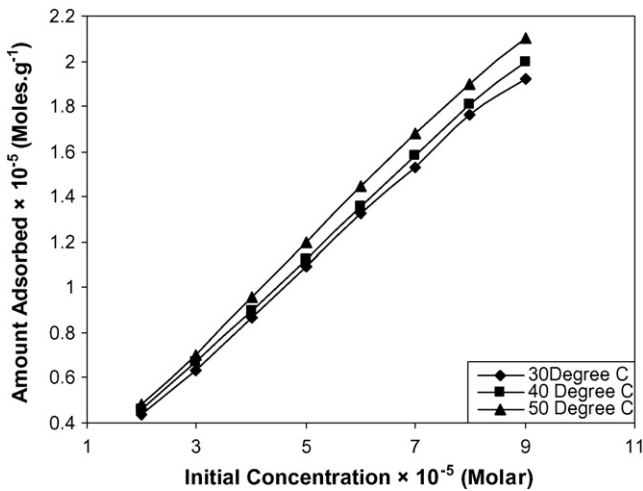


Fig. 8. Adsorption isotherm of Methyl Violet on De-Oiled Soya at different temperatures [adsorbent dose = 0.05 g, particle size = 0.15–0.08 mm (100 BSS mesh), pH 8.0].

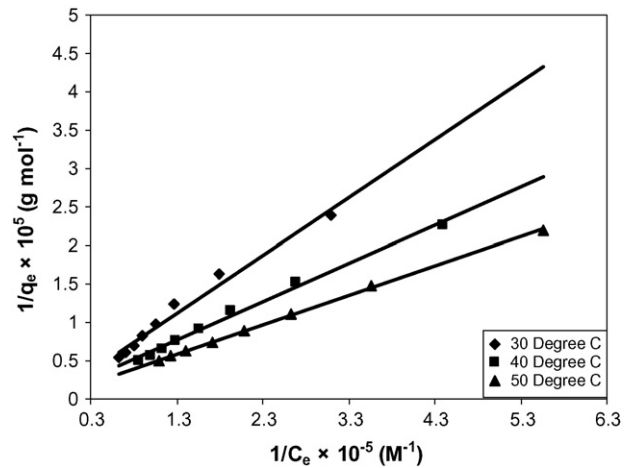


Fig. 9. Langmuir adsorption isotherm for Methyl Violet on Bottom Ash at different temperatures [adsorbent dose = 0.1 g, particle size = 0.15–0.08 mm (100 BSS mesh), pH 8.0].

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \tag{2}$$

where Q_o and b are Langmuir constants, while K_F and n are Freundlich constants.

The Langmuir and Freundlich plots for Bottom Ash system and De-Oiled Soya system are presented in Figs. 9–12, respectively. These graphs clearly reveal that adsorption over each adsorbent satisfies Langmuir as well as Freundlich isotherm models. The values of Freundlich and Langmuir constants calculated at different temperatures (30, 40 and 50 °C) are depicted in Table 4. From the values of K_F it is observed that the K_F remains constant with the rise in temperature for both the systems.

The plot of $1/q_e$ versus $1/C_e$ exhibit linearity at all temperatures for Bottom Ash and De-Oiled Soya which shows the adsorption of the dye Methyl Violet in accordance to Langmuir isotherm. The Q_o values calculated from the intercepts of the Langmuir plots showed an increase with the increasing

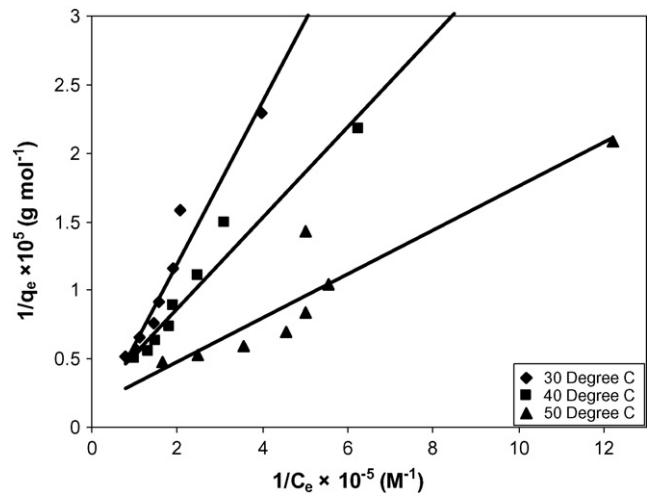


Fig. 10. Langmuir adsorption of Methyl Violet–De-Oiled Soya adsorption at different temperatures [adsorbent dose = 0.05 g, particle size = 0.15–0.08 mm (100 BSS mesh), pH 8.0].

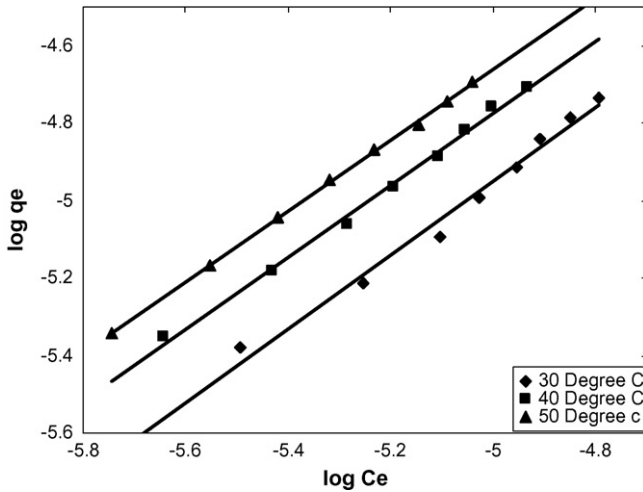


Fig. 11. Freundlich adsorption isotherm for Methyl Violet adsorption on Bottom Ash at different temperatures [adsorbent dose=0.1 g, particle size =0.15–0.08 mm (100 BSS mesh), pH 8.0].

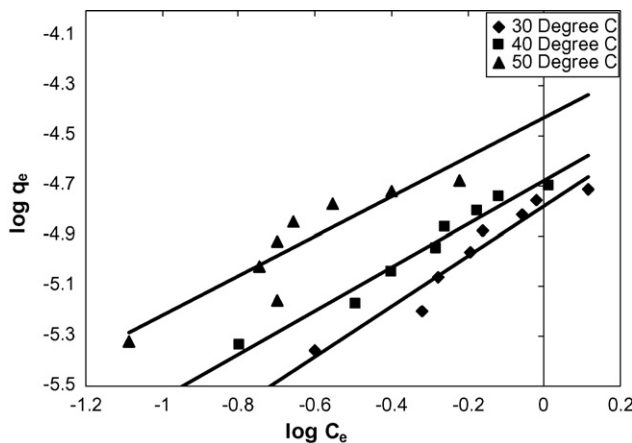


Fig. 12. Freundlich adsorption isotherm of Methyl Violet–De-Oiled Soya adsorption at different temperatures [adsorbent dose =0.05 g, particle size =0.15–0.08 mm (100 BSS mesh), pH 8.0].

Table 5
Parameters indicating the shape of isotherms

Adsorbent	r value		
	30 °C	40 °C	50 °C
Bottom Ash	1.71×10^{-6}	1.41×10^{-6}	1.38×10^{-6}
De-Oiled Soya	7.16×10^{-6}	5.36×10^{-7}	3.36×10^{-7}

temperature and confirm the endothermic nature of the process.

To identify the feasibility and favourability of the adsorption process, an approach recommended by Weber and Chakrabarti [31] was adopted and the dimensionless constant, separation factor (*r*) [32] was calculated in each case using the following equation:

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

where *b* signifies the Langmuir constant and *C*₀ the initial concentration. The values of ‘*r*’ were found to be less than unity for Bottom Ash and De-oiled Soya (Table 5) and indicate highly favourable sorption for both adsorbents.

The thermodynamic parameters were calculated using Langmuir isotherms and listed in Table 6. These parameters, changes in the standard Gibb’s free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) for the adsorption process were obtained using expressions mentioned below in Eqs. (4)–(6).

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

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

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

where *b*, *b*₁ and *b*₂ are the equilibrium constants at 30, 40 and 50 °C, respectively, and *R* is the universal gas constant.

The negative free energy values indicate the feasibility of the process and its spontaneous nature. On the other hand, the positive value of enthalpy change (ΔH°) once again confirms an

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

Adsorbent	Langmuir constants					
	$Q_0 \times 10^{-5}$ (mol/g)			$b \times 10^{10}$ (L/mol)		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Bottom Ash	6.82×10^{-9}	8.47×10^{-9}	1.1×10^{-8}	1.95×10^{10}	2.37×10^{10}	2.41×10^{10}
De-Oiled Soya	3.58×10^{-8}	4.84×10^{-9}	6.30×10^{-9}	4.66×10^9	6.22×10^{10}	9.91×10^{10}
Adsorbent	Freundlich constants					
	<i>n</i>			<i>K_F</i>		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Bottom Ash	0.1044	0.1074	0.1095	1.000	1.000	1.000
De-Oiled Soya	0.0992	0.1148	0.1260	1.001	1.001	1.001

Bottom Ash: adsorbent dose =0.1 g, particle size =0.15–0.08 mm (100 BSS mesh), pH 8.0; De-Oiled Soya: adsorbent dose =0.05 g, particle size =0.15–0.08 mm (100 BSS mesh), pH 8.0.

Table 6
Values of thermodynamics parameters for the adsorption of Methyl Violet 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	5.97×10^5	6.22×10^5	6.42×10^5	3.87×10^4	2104.473
De-Oiled Soya	5.61×10^5	6.46×10^5	6.80×10^5	1.23×10^6	5929.712

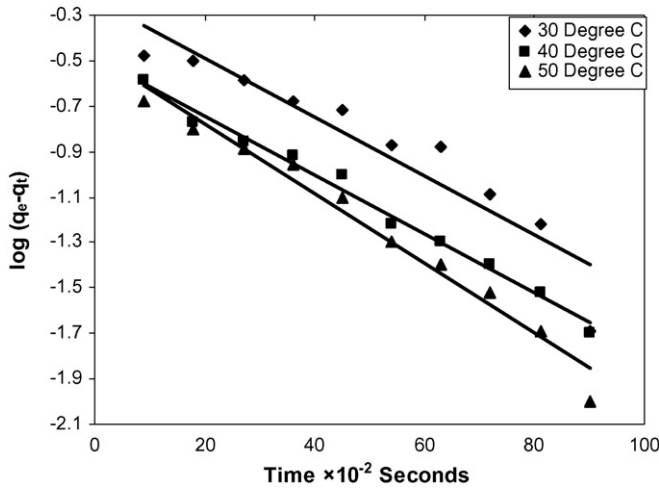


Fig. 13. Lagergren's plot for Methyl Violet–Bottom Ash System.

endothermic nature of the enduring process. Further, the positive values of entropy change (ΔS°) render good affinity of the adsorbent material towards the dye.

3.2.8. Adsorption rate constant study

The specific rate constant for each adsorption process was calculated using following Lagergren's first order rate expression [33].

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

where q_e and q_t are the amount adsorbed at equilibrium and at time t , respectively. The plot of $\log(q_e - q_t)$ versus time gives a straight line (Figs. 13 and 14) and confirms the applicability of first order rate expression of Lagergren's in each system. The values of the rate constant, k_{ad} were obtained from Lagergren's plot at 30, 40 and 50 °C, respectively, and are represented in Table 7.

In the presented work, for the proper interpretation of the experimental data, it is necessary to identify the steps governing the overall removal rate in the adsorption process. Kinetic data

Table 7
Values of specific rate constant (K_{ad}) obtained for different adsorbents at different temperatures

Adsorbent	K_{ad} (min ⁻¹)		
	30 °C	40 °C	50 °C
Bottom Ash	-2.97×10^{-2}	-3.01×10^{-2}	-3.54×10^{-2}
De-Oiled Soya	-3.55×10^{-2}	-3.98×10^{-2}	-4.398×10^{-2}

as obtained by the batch method has been treated by the expressions given by Boyd et al. [34], which is in accordance with the observations of Reichenberg [35]. The data thus obtained very well distinguishes between the particle diffusion and the film diffusion. The three sequential steps in the adsorption of the organic/inorganic compounds by porous adsorbents are:

- i. Film diffusion, where adsorbate ions travel towards the external surface of the adsorbent.
- ii. Particle diffusion, where adsorbate ions travel within the pores of the adsorbent excluding a small amount of adsorption that occurs on the exterior surface of the adsorbent.
- iii. Adsorption of the adsorbate ions on the interior surface of the adsorbent.

Amongst the above three steps the third step is considered to be very fast thus it cannot be treated as rate limiting step [36]. The remaining two steps provide following information:

- a. External Transport > Internal Transport, where rate is governed by particle diffusion;
- b. External Transport < Internal Transport, where the rate is governed by film diffusion;
- c. External Transport \approx Internal Transport, which indicates that the transport of adsorbate ions to the boundary may not be possible at a significant rate thus, formation of a liquid film surrounding the adsorbent particles takes place through the proper concentration gradient.

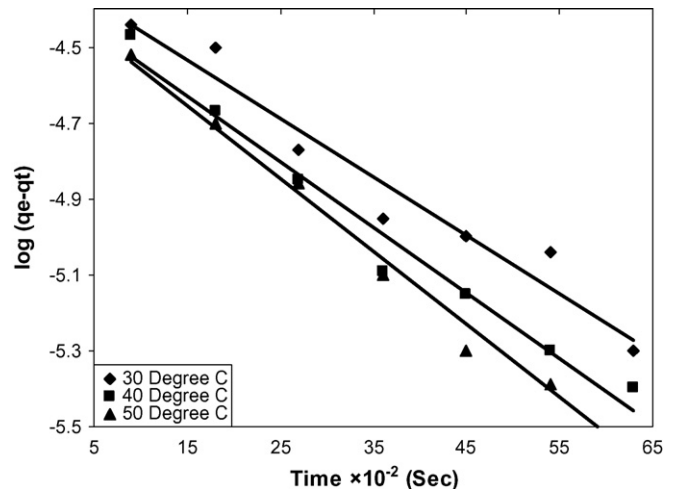


Fig. 14. Lagergren's plot for De-Oiled Soya system.

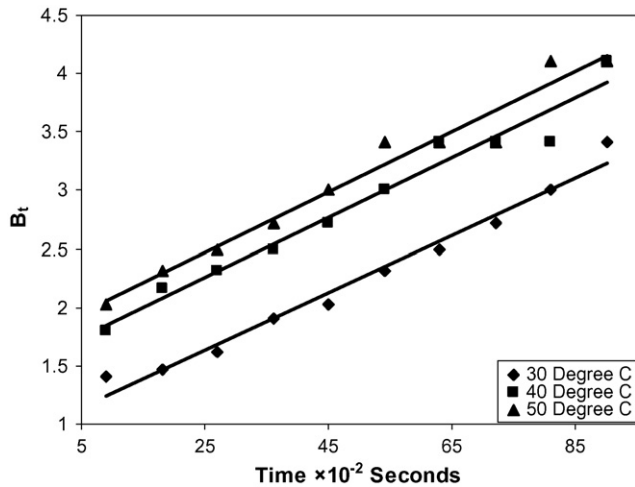


Fig. 15. Plot of time vs. B_t for Methyl Violet–Bottom Ash System at different temperatures.

Thus, to examine the mechanism involved in the adsorption process, a quantitative treatment of the sorption data was used and various parameters were evaluated by using the following equations:

$$F = 1 - \frac{6}{\pi^2} \sum_1^{\infty} \left(\frac{1}{n^2} \right) \exp(-n^2 B_t) \quad (8)$$

$$B = \frac{\pi^2 D_i}{r_0^2} = \text{time constant} \quad (9)$$

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 Freundlich constant of the adsorbate. The F (fractional attainment) is acquired by applying following equation:

$$F = \frac{Q_t}{Q_{\infty}} \quad (10)$$

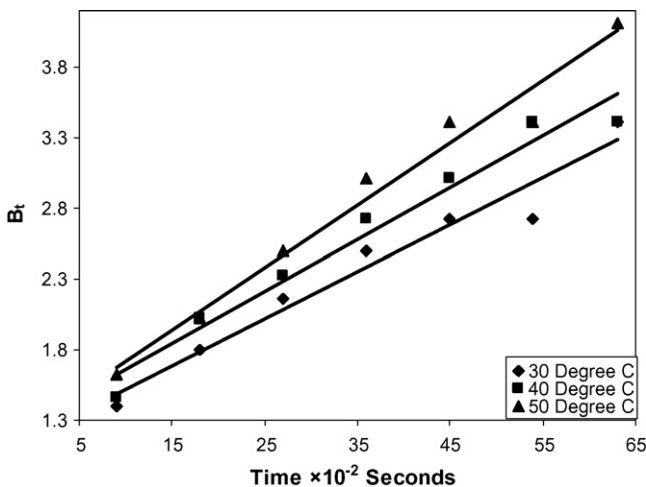


Fig. 16. Plot of B_t vs. time for Methyl Violet–De-Oiled Soya system at different temperatures.

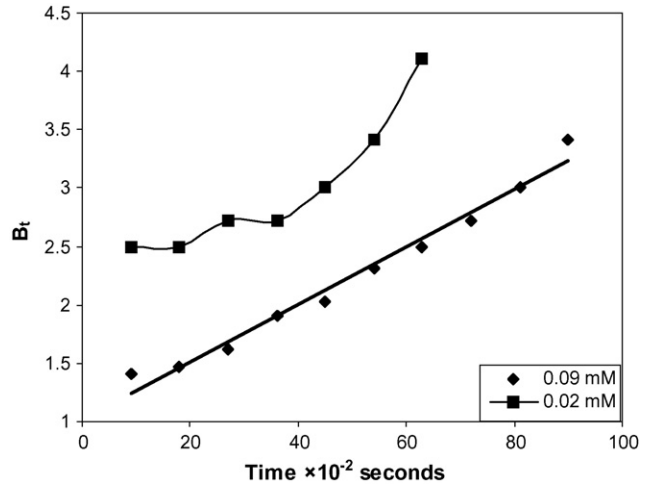


Fig. 17. B_t vs. time plot of Methyl Violet–Bottom Ash adsorption at different concentrations at 30 °C.

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

To distinguish whether the ongoing process is particle diffusion or the film diffusion the kinetic parameters of the process for Bottom Ash and De-Oiled Soya was performed at two different concentrations 9×10^{-5} and 2×10^{-5} M. For the values of F , the corresponding values of B_t were obtained from Reichenberg’s table [35]. From the plot of B_t versus time a clear distinction can be made between the film diffusion and particle diffusion controlled rates of adsorption. The nature of the graphs (Figs. 15–18) indicates the ongoing adsorption processes to be governed through film diffusion mechanism at all concentrations for Bottom Ash and De-Oiled Soya.

The effective diffusion coefficient (D_i) values for each adsorption process at the three different temperatures 30, 40 and 50 °C are represented in Table 8. 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 pores of different widths and different electronic fields along the diffusion path. Moreover, as the temperature

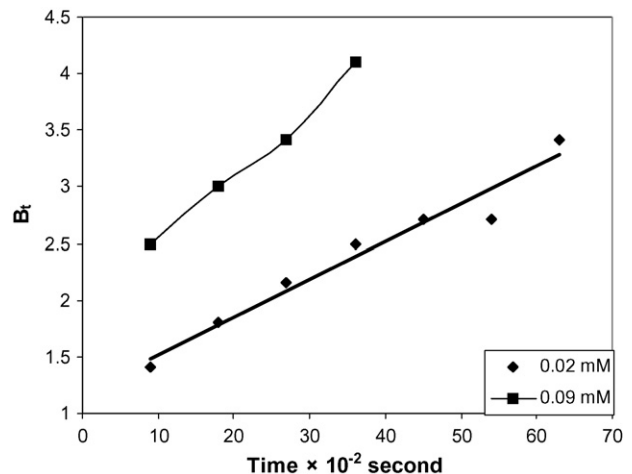


Fig. 18. B_t vs. time plot for Methyl Violet–DOS adsorption system at different concentrations at 30 °C.

Table 8

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

Adsorbent	D_i (m^2/s)			D_o (m^2/s)	E_a ($J\ mol^{-1}$)	ΔS^\ddagger ($J\ K^{-1}\ mol^{-1}$)
	30 °C	40 °C	50 °C			
Bottom Ash	1.40×10^{-11}	1.43×10^{-11}	1.48×10^{-11}	3.02×10^{-11}	1934.482	-98.92
De-Oiled Soya	1.90×10^{-11}	2.09×10^{-11}	2.52×10^{-11}	1.81×10^{-9}	11502.438	-64.89

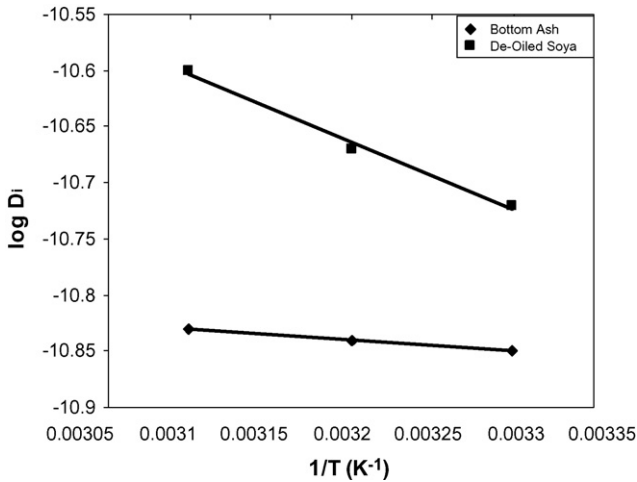


Fig. 19. Plot of $\log D_i$ vs. $1/T$ for Methyl Violet adsorption system.

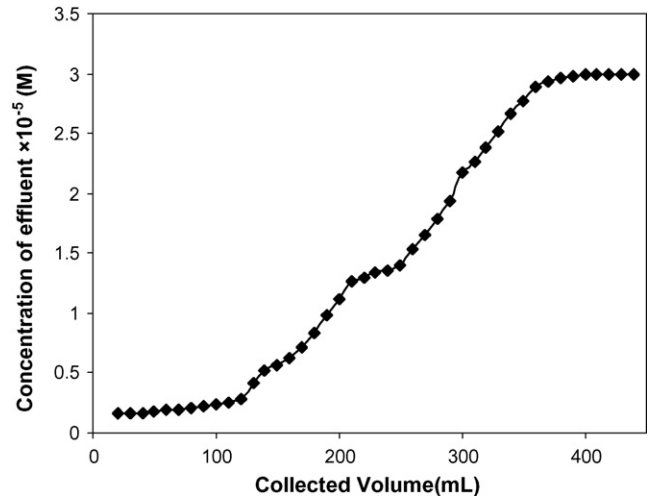


Fig. 20. Breakthrough curve for Methyl Violet–Bottom Ash system.

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. 19 was found to be linear for each system.

To determine energy of activation (E_a) and change in entropy of activation (ΔS^\ddagger) of the ongoing adsorption processes, following well-known Arrhenius equation was employed.

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

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

The values of ΔS^\ddagger , E_a , and pre-exponential constant (D_o) are listed in Table 8. The negative ΔS^\ddagger values indicates that no significant change occur in the internal structure of both the adsorbents throughout the adsorption process [37–39].

3.3. Column studies

To judge the feasibility of the ongoing process and practical utility as well, straightforward approach of Weber [3] was adopted for the design of the fixed bed adsorber for the removal of the dye Methyl Violet. The two separate glass columns were packed with Bottom Ash and De-Oiled Soya, respectively, over a glass wool support. The column was then loaded with the dye solution of 3×10^{-5} M concentration at a controlled flow rate of $0.5\ mL\ min^{-1}$ for Methyl Violet–Bottom Ash system, while the dye solution for 1×10^{-5} M concentration was percolated at a flow rate of $0.4\ mL\ min^{-1}$ for the Methyl Violet–De-Oiled

Soya system. The breakthrough curves obtained for the Methyl Violet–Bottom Ash system and Methyl Violet–De-Oiled Soya system (Figs. 20 and 21) were used to calculate the values of V_b , V_x , C_b and C_x , which were then used to evaluate the column parameters, such as t_x (the time involved in establishing primary adsorption zone), t_f (time of initial formation of primary adsorption zone), f (the fractional capacity of the column), δ (the length of primary adsorption zone), F_m (the mass rate of flow to the adsorbent) and percentage saturation of columns at the breakpoint, by applying following Eq. (3):

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

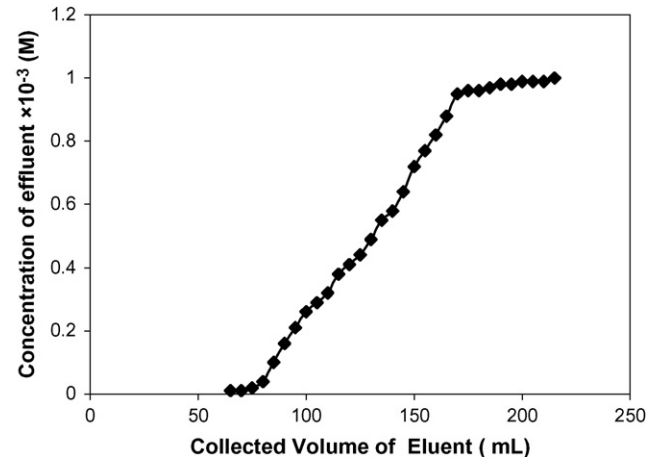


Fig. 21. Breakthrough curve for Methyl Violet–De-Oiled Soya system.

Table 9
Fixed bed adsorber calculations for Bottom Ash and De-Oiled Soya columns

Adsorbent	C_o (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	3.0×10^{-5}	2.94×10^{-5}	0.41×10^{-5}	370	130	240	7.527×10^{-3}	1.0
De-Oiled Soya	1.0×10^{-3}	0.95×10^{-3}	0.04×10^{-3}	170	80	90	2.007×10^{-4}	0.5

Table 10
Parameters for fixed bed adsorbers—Bottom Ash and De-Oiled Soya

Adsorbent	t_x (min)	t_δ (min)	t_f (min)	f	δ (cm)	Percentage saturation
Bottom Ash	49153.077	31883.077	260	0.992	0.6520	99.47
De-Oiled Soya	846863.931	448339.728	200	0.999	0.5297	99.88

$$t_\delta = \frac{V_x - V_b}{F_m} \quad (14)$$

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

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

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

where M_s is the amount of adsorbate adsorbed in the primary adsorption zone from break point to exhaustion, D the length of column and C_o is the initial concentration of adsorbate.

At the complete exhaustion of the columns the column capacity of each column was calculated by taking the total area to the point, where the effluent plot joins the effluent and dividing this value by the weight of the adsorbent filled in the column. The data obtained is presented in Tables 9 and 10 and found that the time required for the movement of a zone through its own length in the column and the time taken for the initial formation of the primary adsorption zone for the Methyl Violet–Bottom Ash system is greater than Methyl Violet–De-Oiled Soya system. The percentage saturations at the breakpoint are found 99.47 and 99.88% for both Bottom Ash and De-Oiled Soya, respectively.

3.4. Column regeneration and dye recovery

Methyl Violet shows an extremely good adsorption towards the basic medium. Hence, desorption of the dye was carried out in the acidic medium. Desorption studies for both the adsorbents were performed by eluting hydrochloric acid of pH 3 through the exhausted columns. Fig. 22 indicates that a large amount (about 93.0%) of the dye was removed by eluting first 40 mL of the eluent for exhausted Bottom Ash column and 30 more aliquots of 10 mL each removes the remaining amount of the dye. While for exhausted De-Oiled Soya column the first aliquot of 10 mL removes about 87% of the dye and the rest of the dye was removed in six more aliquots of 10 mL each. During the entire column study 54 and 80% of the dye was recovered for Bottom Ash and De-Oiled Soya, respectively. Finally both the columns were washed with hot water at a flow rate of 0.5 mL min⁻¹.

The adsorption efficiency of the two adsorbents was determined by refilling the column with dye solution of

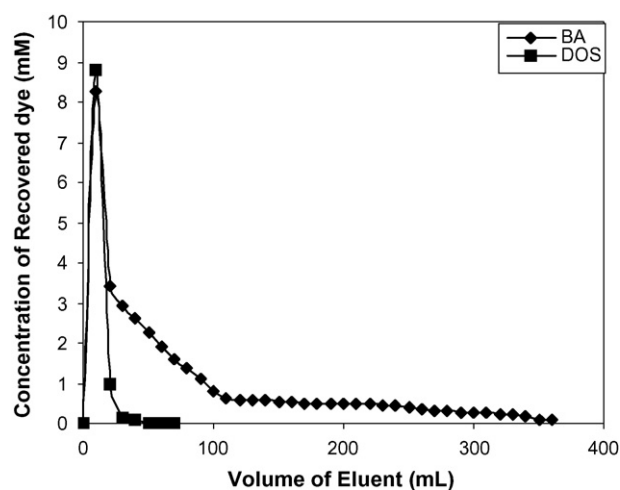


Fig. 22. Desorption of Methyl Violet from Bottom Ash and De-Oiled system.

known concentration. Breakthrough capacities for Methyl Violet–Bottom Ash column were found as 93, 80, 64 and 40% mg g⁻¹ and for Methyl Violet–De-Oiled Soya column 95, 82, 67 and 52% mg g⁻¹ during first, second, third, and fourth cycles, respectively.

4. Conclusions

The entire experimentation concludes that both the waste materials possess extremely good potential to remove the hazardous triphenylmethane dye—Methyl Violet. The effect of process parameters like contact time, concentration of the dye, temperature, and pH on the extent of Methyl Violet adsorption from solution have been investigated and it is found that the adsorption of the dye over both the materials is dependent upon all these variables. The results obtained are well fitted in the linear forms of Freundlich and Langmuir adsorption isotherms. The results of batch adsorption shows that for the Bottom Ash, at all the temperatures, almost 83–91% adsorption could be achieved at low concentration range and about 82–90% in the higher concentration range of the dye. However, in case of De-Oiled Soya almost 87.5 to 96% of the adsorption is observed in the low concentration range and 85.5–293% at high concentration.

Results of kinetic experiments indicate that the adsorption reaction follow Lagergren's first order rate reaction with respect to dye solution concentration. It also confirms an involvement of film diffusion at all the concentrations for Bottom Ash and De-Oiled Soya. It further shows that within the first hour of time of contact almost 72.3, 81.6, and 83.3% of the dye was adsorbed over Bottom Ash at 30, 40 and 50 °C, respectively. Whereas, for the De-Oiled Soya within an hour almost 72.6, 81.3, and 82.0% of the dye was removed at 30, 40 and 50 °C, respectively.

The column studies for both the adsorbents further suggest that Bottom Ash and De-Oiled Soya show 99.47 and 99.88% adsorption, respectively. These values are higher than the batch operations. Desorption studies imply that the quantitative recovery and regeneration of the dye was successfully done in the acidic medium. Thus, overall studies very well describes that the two adsorbents, which were converted into low cost efficient and productive adsorbents act as excellent adsorbents.

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