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Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product

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Abstract Application of saw dust for the removal of an anionic dye, tartrazine, from aqueous solutions has been investigated. The experiments were carried out in batch mode. Effect of the parameters such as pH, initial dye concentration and temperature on the removal of the dye was studied. Equilibrium was achieved in 70 min. Maximum adsorption of dye was achieved at pH 3. Removal percent was found to be dependent on the initial concentration of dye solution, and maximum removal was found to be 97% at 1 mg/L of tartrazine. The removal increases from 71% to 97% when the initial concentration of dye solution decreases from 15 mg/L to 1 mg/L. The equilibrium adsorption data were analyzed by Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The (Langmuir) adsorption capacity of the adsorbent is found to be 4.71 mg/g at 318 K. Kinetic modeling of the process of removal was carried out and the process of removal was found to follow a pseudo second order model and the value of rate constant for adsorption process was calculated as $2.7 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ at 318 K. The thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined and the negative values of ΔG° indicated that the process of removal was spontaneous at all values of temperatures. Further, the values of ΔH° indicated the endothermic nature of the process of removal.

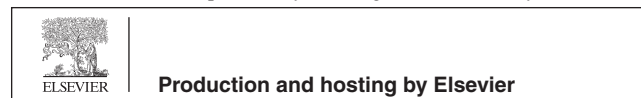
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1. Introduction

Many industrial processes use a variety of synthetic chemical dyes for various uses (Lata et al., 2008). The industries like

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paper and pulp manufacturing, dyeing of cloth, textiles, leather treatment, printing, food products etc. used dyes and the effluents released from these industries bear large amounts of colored wastes. It has been estimated that about 800,000 tons of synthetic dyes are produced annually and ~50% of these are azo dyes (Greluk and Hubicki, 2011). Dyes have complex aromatic molecular structure and are generally resistant to light, temperature and oxidizers. This characteristic feature makes the dye non-degradable and therefore causes bioaccumulation in living organisms, leading to severe diseases and disorders.

Nowadays great attention has been focused on elimination of the effluents bearing dyes due to their potential toxicity and visibility problems. Various methods of treatment for dye/color removal are adopted in order to decrease their impact on the environment. These methods include adsorption, coagulation/flocculation, photo-catalytic decolonization, ozonation, microbial decomposition, wet air oxidation, sono-chemical and electrochemical methods. Among various methods of dye removal, adsorption has been reported to be the most effective method that provides promising results. Among the adsorbent materials, one of the most extensively explored adsorbents is activated carbon. However, its use is limited due to its high cost so researchers look out for low cost adsorbent materials for as alternates to activated carbon. Many scientific workers have investigated the feasibility of cheaper substitutes such as coconut husk (Low and Lee, 1990), orange peel (Arami et al., 2005), wheat bran (Sulak et al., 2007), meranti saw dust (Ahmad et al., 2009), spent tea leaves (Nasuha et al., 2010) etc. for the removal of pollutants from aqueous solutions.

Present investigation addresses the application of raw (unmodified) saw dust as an adsorbent for the removal of tartrazine, a hazardous dye from its aqueous solutions. Saw dust is a solid waste/by product produced in huge quantities at saw mills. Sawdust mainly consists of cellulose and lignin, and many hydroxyl groups; such as tannins or other phenolic compounds (Shukla et al., 2002). Growing interest in the use of sawdust for the removal process has been stimulated by the significant results that have been reported by various workers. Tartrazine is a coal tar derivative, azo dye: usually present in many drugs, food products and cosmetics. Due to its wide applicability in various industrial processes and its hydrophilic nature, its presence can be noticed as a yellow menace in effluents. The contact of the dye is reported to result in various types of health problems like hypersensitivity (Lockey, 1977), mutagenic and carcinogenic effects (Chung, 1983), allergy and asthma (Pohl et al., 1987), skin eczema (Devlin and David, 1992) and immunosuppressive effects (Koutsoqeorqopoulou et al., 1998). This leads to raise concern regarding its use as well as its removal from aqueous solutions. Effect of various process parameters on the removal has been reported in this communication. The experimental data have been tested for different isotherm models. Thermodynamic parameters like change in free energy, enthalpy and entropy for the process of removal have been determined and reported.

2. Materials and methods

2.1. Adsorbent

Saw dust was procured from the local timber factory from Allahabad, India. Saw dust was washed several times with

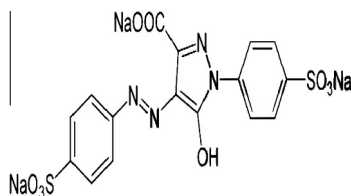


Figure 1 Chemical structure of Tartrazine or Acid Yellow 23.

normal tap water followed by distilled water to remove adhered dust particles. The cleaned material was kept in an oven for 24 h at 110 °C. The dried mass was then crushed and sieved. The fraction of the particles between 0.425 and 0.6 mm (geometric mean size: 0.5 mm) was selected and used in the adsorption experiments as such without any further modification.

2.2. Adsorbate

An anionic dye, 4, 5-dihydro-5-oxo-1-(4-sulfophenyl)-4-[(4-sulfophenyl) azo]-1H pyrazole-3- carboxylic acid trisodium salt also known as Tartrazine (Acid Yellow 23, FD & C Yellow 5, E102) with molecular formula $C_{16}H_9N_4Na_3O_9S_2$ and molecular weight 534.4 shown in Fig. 1 was obtained from Alfa Aesar, Great Britain with CAS No- 1934-21-0 and CI No-19140. Stock solution of the dye was made by dissolving its required amount in double distilled water. The stock solution was further diluted with distilled water to obtain the standard solutions of 1 mg/L, 5 mg/L, 10 mg/L and 15 mg/L.

2.3. Characterization of adsorbent

Infrared spectra of the adsorbents were obtained using a Fourier transform infrared spectrometer (ABB Model FTLA-2000, Canada). For the FT-IR study, finely ground adsorbent has been intimately mixed with KBr (Merck) in a ratio of 1:100 in order to prepare a translucent pellet. From these FT-IR spectra the presence of functional groups on the adsorbent were confirmed.

The surface morphology of the adsorbents was investigated by scanning electron microscope (Jeol JSM 6390LV). The SEM micrograph of saw dust at bar length equivalent to 200 μ m with 400 magnifications, at a working voltage of 30 kV was reported.

2.4. Batch adsorption studies

In the present study batch adsorption experiments were carried out to achieve the optimum operating conditions for the removal of the selected dye. 50 mL solution of known initial concentration was taken in 250 mL Erlenmeyer flasks and a known amount of saw dust, the adsorbent was added to the solutions. The mixture was shaken mechanically at a constant speed of 180 rpm using a water bath shaker (Mac-Macro Scientific Works, Pvt Ltd, New Delhi, India). The samples were withdrawn after predetermined time viz. equilibrium time and thereafter the adsorbent was separated from the solutions by centrifugation using a centrifuge (Remi, Model-R-8CBL, India). The residual concentration of the dye in the supernatant was estimated spectrophotometrically with a double beam spectrophotometer (Model-2203 Systronics, Ahmedabad, India) at 426 nm.

2.5. Determination of pH_{zpc}

For the determination of pH_{zpc} of the adsorbent, 50 mL of 0.01 M NaCl solutions were taken in different Erlenmeyer flasks of 250 mL and 0.5 g of adsorbent was introduced in each of them. Now pH values of these solutions were adjusted in 2 to 12 range by 0.1 M HCl/NaOH solutions. These flasks were

kept for 48 h and the final pH of the solutions was measured. Graphs were plotted between pH_{final} versus $\text{pH}_{\text{initial}}$. The point of intersection of the curve of pH_{final} versus $\text{pH}_{\text{initial}}$ was recorded as pH_{zpc} of the saw dust.

2.6. Adsorption kinetics and equilibrium studies

Adsorption kinetics investigations were carried out by agitating 50 mL of dye solution of known initial concentration with 5 g/L of adsorbent at a temperature of 318 K, at a pH of 3.0 ± 0.1 and at 180 rpm for different time intervals. The amount of dye adsorbed onto the adsorbent at equilibrium, q_e (mg/g), was calculated by the following expression:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where C_0 and C_e are the initial and equilibrium dye concentrations in mg/L respectively, V is the volume of solution (L) and M is the mass of the adsorbent (g). The amount of adsorption at time t , q_t (mg/g) was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (2)$$

where C_0 and C_t (mg/g) are the liquid phase concentrations of the dye at initial and any time t , respectively. V is the volume of solution (L) and M is the mass of the dry adsorbent (g).

Similarly, the adsorption isotherm experiments were conducted by contacting 5 g/L of saw dust with 50 mL of dye solutions of various initial concentrations (1 mg/L, 5 mg/L, 10 mg/L, and 15 mg/L). The samples were agitated on a water bath at 180 rpm at 298 K, 308 K, and 318 K for 70 min.

Blank experiments were also conducted by using dye solutions without adsorbent to ensure that no dye was adsorbed onto the containers and with adsorbent and water only to check that no leaching occurred, which would rather interfere with the measurement of dye concentrations on a spectrophotometer. All adsorption experiments were performed in triplicate and the mean values were used in data analysis.

3. Results and discussions

3.1. Characterization

Fig. 2 shows the SEM micrograph of saw dust (400 X). It is clear from this image that the surface is rough and highly corrugated. Saw dust is a heterogeneous material consisting of particles of irregular shapes having considerable layers with pores of varying size and provides a fair possibility for the dye to be adsorbed.

Sawdust is basically composed of cellulose as well as lignin, and all these components contribute as active sites for the adsorption of dye molecules. Fig. 3 displays the FT-IR spectra of sawdust in its natural form and dye loaded form. The spectra exhibited several peaks representing that saw dust is composed of various functional groups which possibly help in binding of the dye molecules. The appearance of a peak in natural saw dust at 3497 cm^{-1} represents $-\text{OH}$ stretching (Samiey and Ashoori, 2012). The peak at 2852 cm^{-1} corresponds to the presence of $-\text{CH}_2$ stretching of aliphatic groups. The peaks at 1637 cm^{-1} and 1321 cm^{-1} indicate the presence of $\text{C}=\text{C}$ stretching of phenol group and $\text{C}-\text{N}$ stretching of the amine

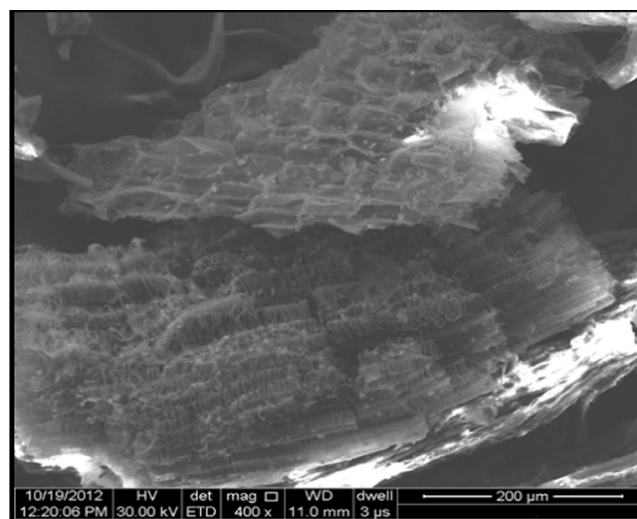


Figure 2 SEM micrograph of saw dust (400 X).

group respectively. Whereas peaks appearing at 1119 cm^{-1} and 1032 cm^{-1} in the spectrum contribute to $\text{C}-\text{O}$ stretching of the phenolic group and a strong $\text{C}-\text{O}$ bond due to ether group of cellulose, respectively (Ahmad et al., 2009). The spectra of the dye loaded saw dust showed similar characteristics as the saw dust in natural form except for slight changes. The FT-IR spectrum of the dye loaded adsorbent indicates that the peaks are slightly shifted from their position and the intensity gets altered. These results indicated the involvement of some functional group in the adsorption of dye ions on the surface of the saw dust through weak electrostatic interaction or Van der Waals forces. Therefore, there is no possibility of chemical bonding in this process. Thus the FT-IR of the surface moieties remained unchanged.

3.2. Effect of pH

The effect of pH on the removal of tartrazine has been investigated. Solution pH plays an important role in controlling the

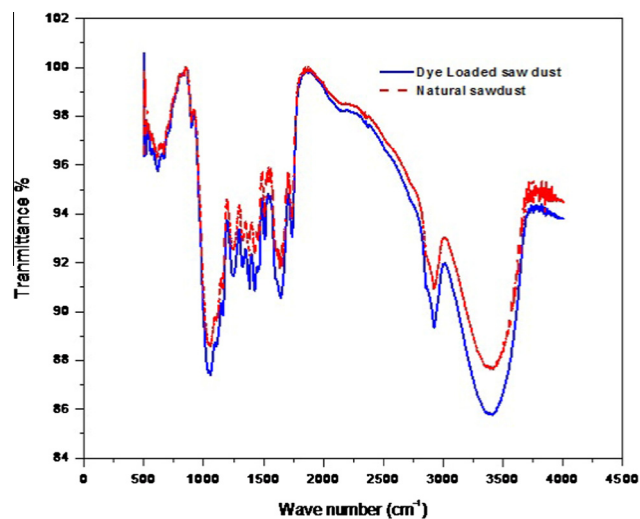


Figure 3 Comparative FT-IR spectra of saw dust before and after adsorption of dye.

surface charge of the adsorbent, the degree of ionization of the adsorbate in the solution as well as dissociation of various functional groups on the active sites of the adsorbent (Wawrzukiewicz and Hubicki, 2009). In most cases, pH is termed as the 'master variable'. The adsorption experiment of anionic dye tartrazine was performed in 2–12 pH range at 318 K for 70 min. The equilibrium sorption capacity was lowest at pH 12 (0.163 mg/g) and maximum adsorption of the dye was achieved at pH 3 (0.19 mg/g). This can be explained as in the aqueous solutions, the anionic dye exists in dissociated form as anionic dye ions:



For $\text{pH} < 6$, a significantly high electrostatic force of attraction exists between the positively charged surface of saw dust and anionic dye, hence enhancing the dye uptake. However, with the increase of pH, the positively charged sites of the adsorbent get decreased and the surface of the adsorbent became negatively charged. This condition does not favor the uptake of anionic dye from the system and leads to electrostatic repulsion (Ozcan et al., 2004). At high pH, OH^- ions compete effectively with dye ions causing a decrease in sorption of the dye from aqueous solutions. Also, change in pH affects the adsorptive process through the dissociation of functional groups on the adsorbent surface that tends to shift in equilibrium characteristics of the adsorption process. The present findings are supported by earlier workers who have reported the removal of Tartrazine onto Chitin and Chitosan (Dotto et al., 2012).

3.3. Zero point charge of adsorbent

The influence of pH on the dye removal can be illustrated on the basis of isoelectric point of the adsorbent surface. Solution pH is a significant parameter which affects the dye adsorption process. It also alters the surface charge of the adsorbent, the ionization extent of different pollutants, as well as the structure of the dye molecules (Ai et al., 2011). The presence of various ligands such as carboxyl, phosphate and amino group on lignin and cellulose based materials in the ionic state contributes to the reaction with dye ions. At pH_{zpc} , the acidic and basic functional groups no longer contribute to the pH of the solutions. The zero point charge, pH_{zpc} , of saw dust was found to be 6.32. At a pH of the solution below pH_{zpc} the surface of the sorbent is positively charged and can attract anions from the solution. When the solution pH is greater than pH_{zpc} the surface of saw dust is negatively charged and attracted cations. In the present case, a lower pH is favorable for dye removal as at low pH, the number of positively charged sites is increased which favor the adsorption of negatively charged dye ions because of the electrostatic force of attraction.

3.4. Effect of initial dye concentration and contact time

A given amount of adsorbent has the capacity to adsorb only a fixed amount of adsorbate species. Thus initial concentration of the adsorbate solution is very important. Fig. 4 shows the graph plotted between the amount of dye adsorbed (q_t) versus time, t , at different initial dye concentrations. The time variation plot indicates that the removal of dye is rapid in initial stages but when it approaches equilibrium, it slows down

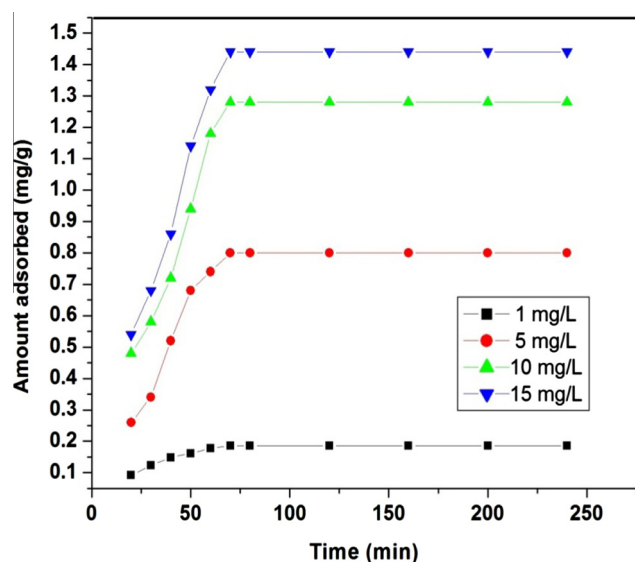


Figure 4 Effect of initial dye concentration on adsorption of tartrazine. Experimental conditions: adsorbent dosage 5 g/L, contact time 240 min, pH 3.

gradually. This may be due to the availability of vacant surface sites during the preliminary stage of adsorption, and after a certain time period the vacant sites get occupied by dye molecules which lead to create a repulsive force between the adsorbate on the adsorbent surface and in bulk phase. The attainment of equilibrium takes place after agitating the solutions containing the adsorbent up to 70 min and once equilibrium was attained, the percentage of adsorption of dye did not show any appreciable change with time. This suggests that after equilibrium is attained, further treatment does not provide more removal. In batch adsorption, the rate of removal of the adsorbate from aqueous solutions is controlled mainly by the transport of dye molecules from the surrounding sites to the interior sites of the adsorbent particles (Ahmad et al., 2009). From the corresponding plot it can be observed that the amount of dye adsorbed (mg/g) varies with varying initial dye concentration and increases with increase in initial dye concentration and after equilibrium, it becomes constant due to the driving force offered by the increased solute concentration which is sufficient enough to overcome the resistance to mass transfer between the solid and liquid phases. Hence the adsorption will enhance with higher initial concentration. When the initial dye concentration increased from 1 mg/L to 15 mg/L at 318 K and $\text{pH} 3.0 \pm 0.1$, the sorption capacity increased from 0.186 to 1.44 mg/g while the removal percentage of dye decreased from 97% to 71%. At a higher concentration range the fractional removal is always higher whereas for low concentration ranges the percentage removal of the dye is higher (Sharma and Uma, 2010).

3.5. Adsorption kinetics

3.5.1. Lagergren pseudo first order equation

The rate constant of adsorption is determined from the following first order rate expression (Lagergren, 1898):

Table 1 FT-IR study of sawdust in natural form and dye loaded form.

Frequency (cm ⁻¹)		Assignment
Before adsorption	After adsorption	
3497	3492	OH stretching
2852	2854	C-H stretching
1637	1632	C=C stretching
1321	1315	C-N stretching
–	1112	C-O stretching
1302	1026	–OCH3 group

Table 2 Kinetic parameters for the adsorption of Tartrazine onto saw dust.

Kinetic models and its parameters	Temperatures (K)		
	298	308	318
q_e , exp (mg g ⁻¹)	0.182	0.192	0.194
<i>Pseudo-first order kinetic</i>			
q_e , cal (mg g ⁻¹)	1.3	0.92	0.961
k_1 (min ⁻¹)	0.04	0.07	0.086
R^2	0.987	0.9495	0.958
SSE%	0.452	0.311	0.297
<i>Pseudo-second order kinetics</i>			
q_e , cal (mg g ⁻¹)	0.84	0.36	0.32
k_2 (g mg ⁻¹ min ⁻¹)	0.9×10^{-3}	1.2×10^{-3}	2.7×10^{-3}
h (mg g ⁻¹ min ⁻¹)	6.3×10^{-4}	1.5×10^{-3}	2.3×10^{-3}
R^2	0.995	0.988	0.989
SSE%	0.109	0.06	0.0514
<i>Intraparticle diffusion</i>			
k_i (mg g ⁻¹ min ^{1/2})	0.031	0.267	0.034
C (mg g ⁻¹)	0.016	0.037	0.040
R^2	0.982	0.941	0.964
Di (cm ² /s)	1.13×10^{-3}	1.6×10^{-3}	2.07×10^{-3}

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) \cdot t \quad (4)$$

where q_e is the amount of dye adsorbed (mg/g) at equilibrium, q_t is the amount of dye adsorbed at time t (min) and k_1 is the rate constant of adsorption of pseudo first order. The values of the rate constant, k_1 , were determined from the linear plots of the graph and their values are given in Table 2. On perusal of the values of k_1 (Table 2), it is clear that the corresponding values of R^2 are non-significant and that is why the figure and other details of this model are not discussed. However, the values of k_1 were found to be $4.0 \times 10^{-2} \text{ min}^{-1}$ at 298 K. (See Table 1).

3.5.2. Pseudo-second order kinetics equation

The kinetics of the adsorption process may also be described in pseudo-second order rate equation (Ho and McKay, 1998). The linearized form of t equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

$$h = k_2 q_e^2 \quad (6)$$

where the equilibrium adsorption capacity (q_e) and the second order constant k_2 (g/mg min) can be determined experimentally from the slope and intercept of plot t/q_t versus t (Fig. 5). k_2 and q_e determined from the model are presented in Table 2 along

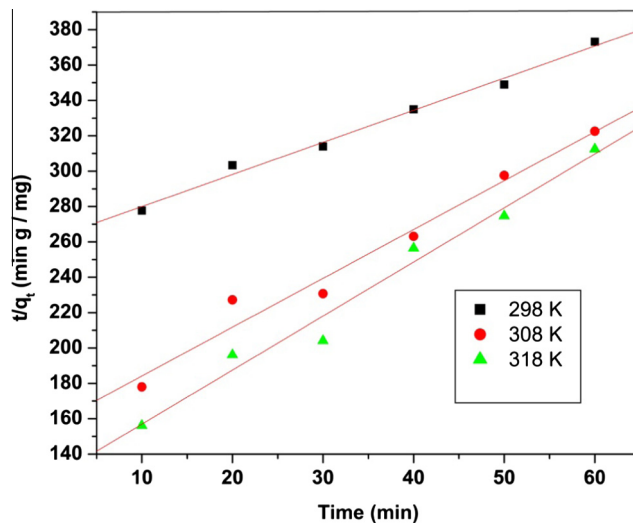


Figure 5 Pseudo-second order kinetic plot for adsorption of tartrazine over saw dust. Experimental condition: pH 3, adsorbent dosage 5 g/L, contact time 70 min.

with corresponding correlation coefficients. The calculated and experimental values of q_e are presented in Table 2 and it is observed that the rate constants of pseudo second order

kinetics model increased from 9.0×10^{-4} g/mg min to 2.7×10^{-3} g/mg min with an increase in temperature indicating that the sorption system process reached equilibrium faster at high temperature. This may be due to an increase in the probability of collision between active surface binding sites and the adsorbate and a decrease in thickness of boundary layer of the adsorbent at high temperature. Besides the value of R^2 , the applicability of kinetic models is verified through the sum of error squares (Lata et al., 2008) given by:

$$SSE\% = \frac{\sqrt{\sum(q_{e,cal} - q_{e,exp})^2}}{N} \quad (7)$$

where N is the number of data points.

The higher value of R^2 and the lower value of SSE (Table 2) calculated in the case of pseudo second order kinetic model indicates better fitness of the data and indicates that the adsorption follows pseudo second order kinetics. A similar observation was reported for adsorption of tartrazine onto fly ash and a resin (Pura and Atun, 2009; Baraka, 2012). The calculated results are given in Table 3.

Arrhenius (1889) proposed the relationship between the rate constant and temperature which could be described using the following expression (Zhang et al., 2011):

$$k_2 = k_0 e^{-E_a/RT} \quad (8)$$

This can be rearranged to linear relationship as:

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT} \quad (9)$$

here k_2 is the rate constant of the pseudo second order adsorption kinetics rate, k_0 is the frequency factor, R is the gas constant (8.314 J/mol K) and E_a (kJ/mol) is the activation energy for the adsorption process. The magnitude of the activation energy can indicate the type of sorption. The activation energy was obtained from the slope of $\ln k_2$ values versus $1/T$ using Eq. (10) and is found to be 19.79 kJ/mol.

$$\ln k_2 = -2385 \frac{1}{T} + 4.35 \quad (R^2 = 0.9642) \quad (10)$$

For adsorption processes with an activation energy less than 40 kJ/mol (Zhang et al., 2011), the main interaction between the dye and saw dust is probably physisorption.

3.5.3. Intraparticle diffusion model

Kinetic data were further analyzed using the intraparticle diffusion model (Weber and Morris, 1963). The above kinetic models were not able to identify the diffusion mechanism, thus this model was proposed. It is an empirical model that describes dye uptake and varies almost proportionally with $t^{1/2}$ rather than with the contact time, t :

$$q_t = K_{id} t^{0.5} + C \quad (11)$$

where q_t is the quantity of dye ions adsorbed at time t in mg/g, K_{id} is the initial rate of intra particular diffusion ($\text{mg/L min}^{-1/2}$) and C is the y-intercept which gives information about the thickness of the boundary layer. When adsorbate in solution is mixed with the adsorbent, there occurs transport of the dye into the pores of particles from the solution through the interface between the solution and the adsorbent. In the case of intra particle diffusion, the plot of q_t versus $t^{1/2}$ will be linear passing through the origin, and if not linear, then some other mechanism along with intra particle diffusion will also be involved. The graph plotted is non-linear over the whole time range, implying that more than one process affected the adsorption.

3.5.4. Sorption mechanism

For proper corroboration of the adsorption process, the rate determining step is an important factor. Adsorption process is governed by either external mass transfer or intraparticle diffusion or both i.e. solute transfer processes. The overall rate of adsorption is controlled by either film diffusion or pore diffusion. It is clear from Fig. 6 that the adsorption process at the

Table 3 Isotherm constants for the removal of Tartrazine on sawdust at different temperatures.

Adsorption isotherms and their constants	Temperatures (K)		
	298	308	318
<i>Langmuir adsorption isotherm</i>			
K_L (L g ⁻¹)	3.12	4.20	7.14
a_L (L mg ⁻¹)	0.92	1.13	1.52
(mg g ⁻¹)	3.39	3.72	4.71
R_L	0.067	0.55	0.043
R^2	0.974	0.977	0.982
<i>Freundlich adsorption isotherm</i>			
K_f (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	0.79	0.96	1.23
n	4.90	5.81	6.21
R^2	0.974	0.965	0.954
<i>Temkin adsorption isotherm</i>			
K_T (L mg ⁻¹)	1.09	1.39	1.56
B	0.285	0.266	0.258
R	0.978	0.989	0.989
<i>D-R adsorption isotherm</i>			
q_m (mg g ⁻¹)	1.24	1.35	1.48
P (mol ² kJ ⁻²)	0.051	0.039	0.031
E (kJ mol ⁻¹)	3.01	3.62	3.86
R^2	0.986	0.997	0.997

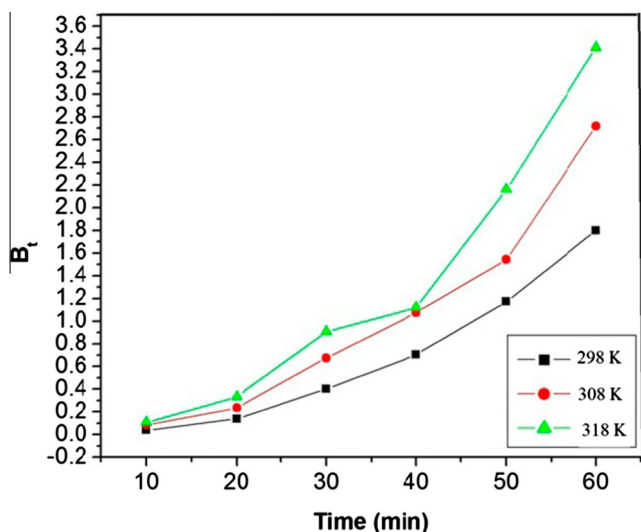


Figure 6 Plot of B_t versus t (Boyd plot) at three different temperatures.

selected values of temperature has been divided into two phases. The initial curved portion of the plot indicates boundary layer effect while second linear portion due to pore diffusion. The biphasic nature of intraparticle diffusion plot confirms that both film and pore diffusion are involved in the process of dye removal. In order to differentiate between particle diffusion and film diffusion, Boyd kinetic expression (Boyd et al., 1947) was employed to the experimental data. Film diffusion occurs when external transport is greater than internal transport and in the case of particle diffusion internal transport is greater than external transport (Mittal et al., 2007).

A quantitative treatment of the sorption process can be investigated by using the following expressions:

$$F = 1 - \frac{6}{\Pi^2} \sum_1^{\infty} \left(\frac{1}{n^2} \right) \exp(-n^2 B_t) \quad (12)$$

$$F = \frac{q_t}{q_e} \quad (13)$$

Here q_e is the amount of dye adsorbed at infinite time (mg/g), q_t the amount of dye adsorbed at any time, F is the fraction of the solute adsorbed at any time t and B_t is mathematical fraction of F .

$$B = \frac{\Pi^2}{r^2} D_i \quad (14)$$

where B is time constant and values of B were calculated from the slope of ' B_t versus t ' plot, D_i is the effective diffusion coefficient of adsorbents and r represents radius of the particle (0.25 mm).

The F value can be used to determine the corresponding B_t values using the Richenberg's table (Richenberg, 1953). Film diffusion and particle diffusion adsorption rate are determined with the help of B_t versus time plot (Fig. 6). The linearity of these plots was used to distinguish between film diffusion and pore diffusion controlled rates of adsorption. A straight line passing through the origin indicates that adsorption processes are governed by pore diffusion mechanisms for the present study. However it is observed from Fig. 6 that the relation between B_t and t is linear (average $R^2 = 0.974$), but does not

pass through origin. This result confirms that surface diffusion is the rate limiting step where external transport of dye is more than internal transport. The values of effective diffusion coefficient D_i ($\text{cm}^2 \text{s}^{-1}$) are calculated at 298 K, 308 K and 318 K and are summarized in Table 2. As reported earlier (Singh et al., 2011), in the case of intra particle diffusion or pore diffusion as a rate-limiting step in the adsorption process, a D_i value is of the order of (10 to 11) $\text{cm}^2 \text{s}^{-1}$. In this study, the average value of D_i obtained is $1.59 \times 10^{-3} \text{cm}^2 \text{s}^{-1}$, which is 7 orders of magnitude greater than the value quoted by Singh et al. This indicates that pore diffusion is not the rate limiting step. Similar results have been reported by Aravindhyan et al. (2007) and Zou et al., 2011. The increasing values of effective diffusion coefficient D_i indicate that as temperature increases from 298 K to 318 K the mobility of ions rises due to the decrease of retarding force acting on diffusing ions of the dye.

3.5.5. Adsorption isotherms

The experimental data for the removal of tartrazine were tested with different isotherm models namely Langmuir, Freundlich, Dubinin and Radushkevich and Temkin models.

3.5.6. Langmuir model

This model assumes monolayer coverage of adsorbent and adsorption occurs over specific homogenous sites on the adsorbent (Langmuir, 1918).

The linear form of the Langmuir isotherm model is given by the following equation (Sharma et al., 2008):

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} (C_e) \quad (15)$$

where in C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed per specified amount of adsorbent (mg/g), K_L (L/g) and a_L (L/mg) are the Langmuir isotherm constants.

Linear plots obtained for C_e/q_e versus C_e (Figure not shown) at each temperature with R^2 values close to unity reflect that Langmuir isotherm holds well for tartrazine – sawdust system. Straight lines obtained were used for calculating the value of K_L from the intercept and the value of a_L from the slope. The theoretical monolayer capacity is Q_0 and it is numerically equal to K_L/a_L . The values of constants Q_0 , a_L and K_L were calculated and presented in Table 3. It is evident from Table 3 that with the increase in temperature, the values of monolayer adsorption capacity (Q_0) increase from 3.39 to 4.71 mg/g for saw dust. This indicates that higher temperature enhanced adsorption capacity. The adsorption capacities of tartrazine over a variety of adsorbents are compared and reported in Table 4. The adsorption capacity of this study was found to be larger than adsorption capacity accounted by several workers.

3.5.7. Freundlich model

It is an empirical equation (Freundlich, 1906) which indicates that the adsorption process takes place on a heterogeneous surface and adsorption capacity is related to the concentration of dye at equilibrium. The linear form of this isotherm is given by the following expression:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (16)$$

where K_F [$\text{mg/g}(\text{L/mg})^{1/n}$] is roughly an indicator of the sorption capacity as well as the strength of adsorptive bond and n is

Table 4 Comparison of the adsorption capacity of sawdust with various adsorbents.

Adsorbent	Adsorption capacity (Q°) (mg g^{-1})	References
Bottom ash	1.01×10^{-5}	Mittal et al. (2006)
Deoiled soya	2.12×10^{-5}	Mittal et al. (2006)
Hen feather	6.4×10^{-5}	Mittal et al. (2007)
Activated carbon	18.581×10^3	Gupta et al. (2010)
Coconut husk carbon	3.366×10^3	Gupta et al. (2010)
Polyaniline nano layer composite	2.47	Ansari et al. (2011)
Chitin	30	Dotto et al. (2012)
Chitosan	350	Dotto et al. (2012)
Sawdust	4.71	This study

the heterogeneity factor that represents the bond distribution. Thus a plot of $\ln q_e$ versus $\ln C_e$ was obtained as straight lines at different temperatures (Figure not shown) from which values of correlation coefficients and Freundlich constants K_F and $1/n$ were calculated from the intercept and slope respectively and are presented in Table 3. An increase in the value of K_F is observed with the increase of temperature, indicating an increase in dye – adsorbent interaction at higher temperature. The values of n were found to be greater than 1 at all temperatures which may be attributed to the distribution of surface sites or any factor responsible for a decrease in dye-sawdust interaction with increasing surface density.

3.5.8. Temkin model

The Temkin isotherm model contains a factor that explicitly takes into account the interactions between adsorbate and adsorbent species (Temkin and Pyzhev, 1940). It further implies that the heat of adsorption of all the molecules in the layer would decrease linearly with the coverage involved in this interaction. The linear form of the Temkin model is expressed as follows:

$$q_e = B \ln K_T + B \ln C_e \quad (17)$$

where

$$B = \frac{RT}{b} \quad (18)$$

where K_T is the Temkin equilibrium binding constant (L/mg) corresponding to maximum binding energy and constant B is related to the heat of adsorption. The adsorption data were analyzed according to equation 18. A plot of q_e versus $\ln C_e$ yielded linear lines (Figure not shown) which enable the determination of the isotherm constants K_T and B from intercepts and slopes respectively. The values of constants along with R^2 values are listed in Table 3. The values of R^2 suggest that this model also does not satisfy the experimental data.

3.5.9. Dubinin radushkevich model

The D–R isotherm model is applied to estimate the apparent free energy and characteristics of adsorption. The isotherm is an analog of the Langmuir type but it is more general because it is used to determine the occurrence of adsorption on both homogenous and heterogeneous surfaces. The linear form of D–R isotherm (Dubinin et al., 1947) can be expressed as:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (19)$$

where q_m is the D–R monolayer capacity (mg/g), β is the activity coefficient related to mean sorption energy (mol^2/kJ^2) and ε

is the Polyani potential (Polyani, 1932) which can be calculated using the following expression:

$$\varepsilon = RT \ln \left[1 + \left(\frac{1}{C_e} \right) \right] \quad (20)$$

where R is the gas constant (8.314 J/mol K) and T is the absolute temperature in K. The mean adsorption energy, E (kJ/mol) was calculated with the help of the following equation:

$$E = \frac{1}{\sqrt{(-2\beta)}} \quad (21)$$

The values of parameters were determined from the straight line plots of $\ln q_e$ versus ε (Figures not shown). The values of D–R constants are given in Table 3. The adsorption potential is independent of the temperature, but it depends on the nature of adsorbent and adsorbate. E is the mean free energy of adsorption for the transfer of one mole of the adsorbate ion from infinity to the surface of the adsorbent thus providing information regarding the nature of adsorption either chemical, ion exchange or physical adsorption. In the case of E smaller than 8 kJ/mol, the physical forces dominate, in case E is in the range of 8–16 kJ/mol, the adsorption is governed by chemical ion exchange mechanism (Rafatullah et al., 2009). In this study, the adsorption energies are 3.01, 3.62 and 3.86 kJ/mol for temperatures 298 K, 308 K and 318 K respectively suggesting that the adsorption process is dominated by physical forces at all the temperatures.

The regression parameters and correlation coefficients (R^2) presented in Table 3, indicate that the adsorption data best fitted the Dubinin-Radushkevich adsorption isotherm. The good fit of the D–R isotherm (all R^2 values > 0.98) suggest that this isotherm is appropriate under industrial conditions.

3.5.10. Effect of temperature and thermodynamic parameters

The removal of tartrazine was studied at different temperatures viz. 298 K, 308 K and 318 K for the determination of adsorption isotherm and thermodynamic parameters. It had been investigated from the experiment that with the rise of temperature from 298 K to 318 K the amount of dye uptake increases from 3.39 to 4.71 mg/g. As the rate of diffusion of the dye molecules is a temperature controlled process, variation in temperature alters the equilibrium capacity of the adsorbent for a particular adsorbate. In the present study increase in temperature leads to fast diffusion of dye molecules across the external boundary layer and internal pores of the adsorbent particles due to less resistance offered by viscous forces in the aqueous phase. Also, in some cases the solubility of the adsorbate molecules is affected which finally has significant effect on the removal process. The increase in adsorption capacities of adsorbents at

Table 5 Values of thermodynamic parameters for the removal of Tartrazine onto sawdust.

Temperature (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
298	-0.75	48.26	166
308	-1.74		
318	-2.13		

high temperature may also be attributed to the pore size enlargement (Demirbas et al., 2008).

Thermodynamic parameters such as change in free energy (ΔG), enthalpy changes (ΔH) and entropy changes (ΔS) were determined using the following equations (Meena et al., 2008)

$$K_c = \frac{q_e}{C_e} \quad (22)$$

where K_c is equilibrium constant, q_e and C_e are the equilibrium concentrations of dye ions on adsorbent (mg/g) and in solution (mg/L) respectively. The change in free energy (ΔG) can be calculated from the relation:

$$\Delta G^\circ = -RT \ln K_c \quad (23)$$

where, T is the temperature in Kelvin and R is the gas constant (8.314 J/molK).

Enthalpy change (ΔH) was calculated from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (24)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \frac{1}{T} \quad (25)$$

ΔH° and ΔS° were obtained from the slope and intercept of Von't Hoff plots of $\log K_c$ versus $1/T$ (Figure not given). The values of the thermodynamic parameters are presented in Table 4. Positive value of ΔH° thermodynamically substantiates the assumption that the adsorption of dye on the adsorbent surface is endothermic. The negative value of ΔG° indicates the feasibility and spontaneity of the adsorption process. The value of ΔS° had been estimated to be so large which indicated an increase of entropy as a result of adsorption. Before adsorption, the ions of dyes near the adsorbent surface were in ordered form than in the subsequent adsorbed state and the ratio of free dye ions to the interacting dye ions with the adsorbent will be higher than in the adsorbed state. As a result the distribution of rotational and translational energy will increase with increasing adsorption by producing a positive entropy value and at solid-liquid interface there will be increased randomness. Adsorption is then likely to occur spontaneously at high temperature because $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$. (See Table 5).

4. Conclusions

On the basis of the above studies, the following can be concluded:

- Characterization of saw dust was carried out which revealed the presence of various functional groups on the adsorbent surface and that the surface of the adsorbent was rough and suitable for adsorption.

- Saw dust has shown a potential to remove tartrazine from aqueous solution.
- Initial concentration of the dye plays an important role in the removal process.
- Kinetics of the process removal was studied and the values of rate constants were determined. The dye removal was found to be governed by film diffusion mechanism where external transport of the adsorbate over surface of the adsorbent is greater than internal transport which was confirmed by the Boyd plot and the process of removal was found to follow second order kinetics.
- Thermodynamic parameters were calculated for the removal of dye and their values indicated that the process of removal was spontaneous and endothermic.
- The data were found to best fitted in D-R isotherm model.

It can therefore be concluded that saw dust offers promise as an economically viable alternative for sequestering of the dye from the aqueous solution. The work can be extended for the removal of dyes from effluents as well.

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