



# Adsorption and desorption studies on hazardous dye Naphthol Yellow S

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## ARTICLE INFO

### Article history:

Received 23 November 2009

Received in revised form 23 June 2010

Accepted 23 June 2010

Available online 30 June 2010

### Keywords:

De-oiled mustard  
Activated carbon  
Naphthol Yellow S  
Adsorption  
Desorption  
COD

## ABSTRACT

In the present study, the batch technique was adopted under a variety of conditions, viz., amount of adsorbent, contact time, concentration, temperature and pH. By using UV spectrophotometer, concentration of dye was measured before and after adsorption. Dye removal data were fitted into the Langmuir and Freundlich adsorption isotherm equations. The values of their corresponding constants were determined. Thermodynamic parameters like free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of the systems were calculated by using Langmuir constant. The estimated values for ( $\Delta G$ ) were  $-8.027 \times 10^3$  and  $-28.46 \times 10^3$  kJ mol<sup>-1</sup> over activated carbon and activated de-oiled mustard at 303 K (30 °C), indicate toward a spontaneous process. The adsorption process followed pseudo-first-order model. The values of % removal and  $k_{ad}$  for dye systems were calculated at different temperatures ranging (303–323 K). Desorption studies indicate that elution by dilute NaOH through the fixed bed of the adsorbents columns could be regenerated and a quantitative recovery of Naphthol Yellow S can be achieved.

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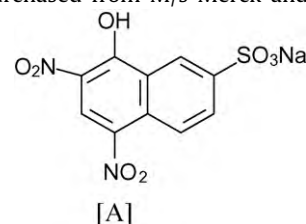
## 1. Introduction

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries [1]. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade [2]. Furthermore, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities [3]. There are various conventional methods for removing dyes including coagulation and flocculation [4], oxidation or ozonation [5,6] and membrane separation [7]. However, these methods are not widely used due to their high cost and economic disadvantage. Chemical oxidations are generally not feasible on large scale in industries. In contrast, an adsorption technique is by far the most versatile and widely used. If the adsorption system is designed correctly it will produce a high-quality treated effluent. Most commercial systems currently use activated carbon as sorbent to remove dyes in wastewater because of its excellent adsorption ability. Apart from the high-quality product obtained, the processes have proved economically feasible [8]. The most common adsorbent materials are: alumina, silica [9], metal hydroxides [10] and activated carbon [11]. Commercially available activated carbon as an adsorbent has yielded excellent results. Possessing high specific surface area, activated carbon frequently exhibits high removal efficiency for most dissolved compounds. However, the cost of activated carbon and

regeneration problems necessitated the search for other low cost adsorbents [12–16]. Over the years, waste materials from agricultural products, such as rice straw, coconut husk, peat moss, rice husk [17] and gram husk [18], etc., have been exploited as possible alternatives to activated carbon to remove hazardous chemicals [19]. Gupta et al. [20–22] and Jain et al. [23–26] have also utilized various adsorbents for the removal of dyes from wastewater. The aim of the present study is to determine the efficiency of removal of Naphthol Yellow S using activated carbon (AC) and activated de-oiled mustard (ADM).

## 2. Materials and methods

The dye under consideration is Naphthol Yellow S (A) (C<sub>10</sub>H<sub>4</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>8</sub>S; Mol. Wt. 358.20), which is highly water soluble dye of nitro group was obtained from M/s Merck. The stock solution (0.01 mol dm<sup>-3</sup>) and all other solutions of Naphthol Yellow S were prepared in double-distilled water, and the same was used for the necessary dilution. All reagents used in the present work were of analytical grade. The adsorbent de-oiled mustard was collected from a local oil mill, while activated carbon (AC) was purchased from M/s Merck and used as received.



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Measurements of pH of the solutions were carried out on a digital pH meter DB 1011. Usual 2 h open reflux method was applied for the COD determination and it was found that for the dye solutions COD values are substantially reduced. COD digestion apparatus (Spectra-Lab-2015 S) was used for determining COD of the solutions. A spectronic 20D+ thermospectronic spectrophotometer was used to measure the absorbance at 430 nm.

Scanning electron microscopy was performed using a Philips SCI quanta 400 instrument. The zero point charge of the activated de-oiled mustard was determined by the potentiometric mass titrations (PMT) [27]. The physical characteristics of the de-oiled mustard prepared as adsorbent is 43% proteins, 2.05% oil, 1.22% allylisothiocyanate (AIT) and 2.75% phytic acid [28].

### 2.1. Adsorbent development

The adsorbent material, activated carbon was used as received. The other material, de-oiled mustard, was cleaned, thoroughly washed with distilled water, and then dried in an oven. Thereafter, it was treated with hydrogen peroxide (30%) at 60 °C for 24 h to oxidize the adhering organic impurities and washed repeatedly with doubly distilled water. The amount of hydrogen peroxide 0.5 mL g<sup>-1</sup> of used in the oxidation of the adhering organic matter of de-oiled mustard. The resulting material was washed with double-distilled water and filtered and again dried to 100 °C for 1 h in the vacuum oven. The material was grounded and sieved to desired particle sizes such as <106, 106–125, 125–180, 180–212, 212–250, 250–300, >300 BSS mesh (British Standard Size). Finally, granules of activated de-oiled mustard (ADM) thus obtained were stored in separate vacuum desiccators until required.

### 2.2. Adsorption studies

Adsorption studies were performed by the batch technique at 30, 40 and 50 °C, temperatures. Adsorption isotherms recorded at a fixed pH range (2–9) over the concentration range  $1.0 \times 10^{-5}$  to  $9.0 \times 10^{-5}$  mol dm<sup>-3</sup> of Naphthol Yellow S solutions, prepared by diluting 0.01 mol dm<sup>-3</sup> of stock solution in a series of 100 ml graduated conical flask containing 30 ml of solution of each concentration. Adsorption was achieved by adding a known amount of each adsorbent of a specific sieve size into the dye solution of known concentration and pH, and the conical flask were agitated intermittently. Once the equilibrium was established, supernatant liquid was filtered off using Whatmann filter paper No. 42 and uptake of the dye was determined spectrophotometrically.

### 2.3. Sorption kinetics

The initial solution Naphthol Yellow S concentration was  $9 \times 10^{-5}$  mol dm<sup>-3</sup> for all experiments, except for those carried out to examine the effect of the initial concentration of Naphthol Yellow S. For kinetic studies, the batch technique was used because of its simplicity. For dye removal kinetic experiments 12 mg of AC and 120 mg of ADM were contacted with 30 ml of Naphthol Yellow S solutions in a beaker agitated vigorously by a mechanic stirrer using a water bath maintained at constant temperature at 30 °C. The stirring speed was kept constant at 200 rpm for AC and 400 rpm for ADM. At predetermined intervals of time, solutions were analyzed for the final concentration of Naphthol Yellow S by using a UV–vis spectrophotometer set at wavelength of 430 nm, maximum absorbance. The dye uptake  $Q$  (mol g<sup>-1</sup>) was determined as follows:

$$Q = \frac{(C_0 - C)V}{W} \quad (1)$$

where  $C_0$  and  $C$  are the initial and final dye concentrations (mol L<sup>-1</sup>), respectively,  $V$  is the volume of solution (L), and  $W$  is the sorbent weight (g).

Calibration experiments were carried out to exclude the experimental mistake raised from sorption of Naphthol Yellow S on wall of the glass vessels. All the experiments were carried out in triplicate and the mean values are presented.

### 2.4. Batch equilibrium studies

The procedures of equilibrium tests were basically identical to those of kinetic experiments. The aqueous samples were taken at preset time intervals, and the concentrations of dye were similarly measured.

### 2.5. Desorption studies

Regeneration is the most significant aspect of the adsorption study. Continuous emphasis was being placed on waste minimization, recovery and reuse. Studies were carried out on column. The column operations was carried by using corning glass column of 30 cm length and 1 cm internal diameter, after packing it with a known amount, 300 mg AC of 125–180 BSS mesh and 400 mg of ADM of 106–125 BSS mesh, on a glass wool support. The weighed adsorbent was made in to slurry with water and kept overnight and then fed slowly in to column, displacing the heel of water, to avoid air entrapment. The slurry of the adsorbent was prepared in water only and kept overnight before feeding. The column was then loaded with a dye solution of appropriate concentration, which was allowed to percolate downwards under gravitational force at a flow rate of 0.5 mL per minute. Then the amount of dye desorbed was estimated spectrophotometrically at  $\lambda_{max}$  430 nm. After about 90% of exhaustion column operations were shut down. Thus desorption studies help in the recycling and regeneration of the spent adsorbent and the dye.

## 3. Results and discussion

### 3.1. Characterization of adsorbent

For morphological characteristics SEM of adsorbent AC and ADM was carried out. The AC and ADM were analyzed by Scanning electron microscope (SEM) as shown in Fig. 1. SEM is widely used to study the morphological features and surface characteristics of the adsorbent materials. In the present study, SEM photographs of AC and ADM reveals surface texture and porosity. The surface area of AC and ADM as calculated by Brunauer–Emmett–Teller (BET) method is  $929.7 \pm 2.1$  and  $326.5 \pm 3.4$  m<sup>2</sup> g<sup>-1</sup>, respectively. Scanning electron microscopy was performed using a Philips SCI quanta 400 instrument. The zero point charge of the activated de-oiled mustard was found to be 8.2.

### 3.2. Adsorption studies

The effect of adsorbent dose on the removal of Naphthol Yellow S was studied by varying the amount of AC from 0.1 to 0.6 and 1 to 6 g L<sup>-1</sup> for ADM. Experiments were carried out at fixed pH 5.4, concentration  $9.0 \times 10^{-5}$  mol dm<sup>-3</sup> and at different temperatures. It is apparent from Fig. 2(a) for AC and (b) for ADM that, initially the rate of increase in the percentage of dye removal was found to be rapid from 0.1 to 0.5 g L<sup>-1</sup> which then slowed down as the dose increased from 0.5 to 0.6 g L<sup>-1</sup> for AC, while in case of ADM, dye removal increased as the dose of adsorbent increases from 1 to 4 g L<sup>-1</sup>, which then constant as the dose increased from 4 to 6 g L<sup>-1</sup>. The initial rise in adsorption with adsorbent dose is probably due to a stronger driving force and larger surface area. The subsequent slow rise in the curves is due to adsorption and intra-particle diffusion taking place simultaneously with the dominance of adsorption with a rise in adsorbent dose, there is a less commensurate increase

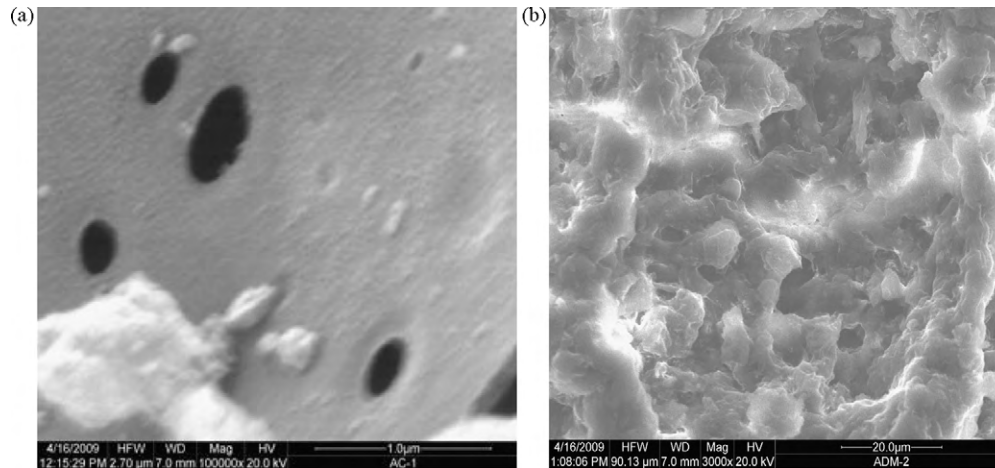


Fig. 1. SEM micrographs of (a) AC and (b) ADM adsorbents.

in adsorption resulting from lower adsorptive capacity utilization of adsorbent [29,30]. Hence all further studies were carried out using  $0.5 \text{ g L}^{-1}$  for AC and  $4 \text{ g L}^{-1}$  for ADM, respectively.

The experimental results of adsorptions at various concentrations (from  $1 \times 10^{-5}$  to  $10 \times 10^{-5} \text{ mol dm}^{-3}$ ) shown in Fig. 3 reveals that percent adsorption decreased with increases in initial dye concentration, but the actual amount of dye adsorbed per unit mass of adsorbent increased with increases in dye concentration. This means that the adsorption is highly dependent on initial concentration of dye. At lower concentration, the ratio of the initial number of dye molecules to the available surface area is low. Subsequently, the fractional adsorption becomes independent of initial concentration. Equilibrium have established at 20 min for AC and 80 min for ADM for all concentrations. However, at high concentration the available sites of adsorption become fewer and hence the percentage removal of dye is dependent upon initial concentration [31,32].

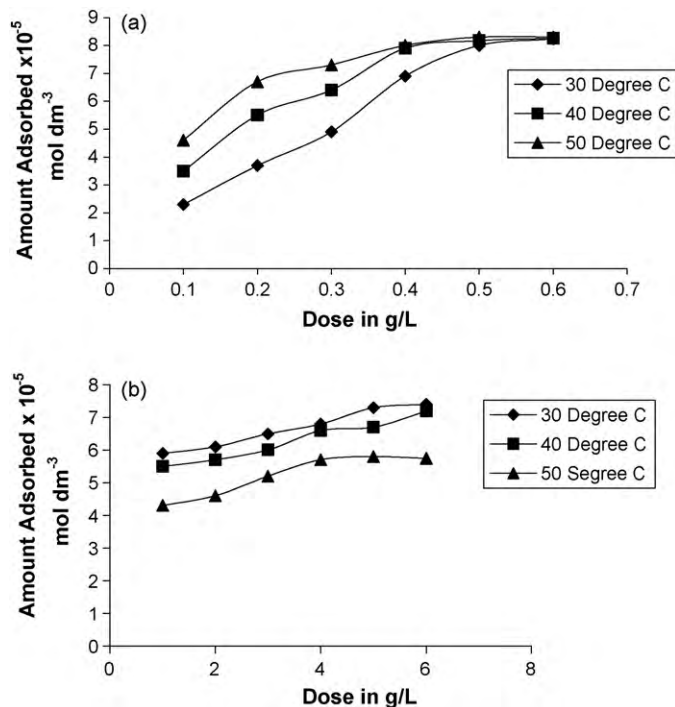


Fig. 2. Effect of amount of adsorbent for the removal of Naphthol Yellow S ( $9 \times 10^{-5} \text{ mol dm}^{-3}$ ) by (a) AC- $0.5 \text{ g L}^{-1}$  and (b) ADM- $4 \text{ g L}^{-1}$  at pH 5.4 and different temperatures.

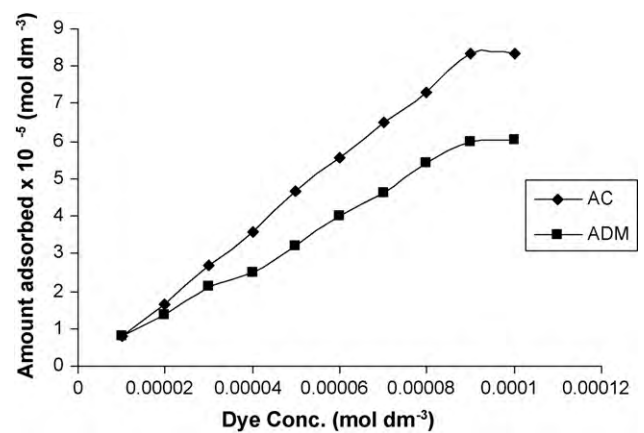


Fig. 3. Effect of initial dye concentration for the removal of Naphthol Yellow S by (a) AC- $0.5 \text{ g L}^{-1}$  and (b) ADM- $4 \text{ g L}^{-1}$  at  $30^\circ \text{C}$  and pH 5.4.

It was observed that the percent removal of dye decreases from 94.41% to 82.60% for AC and 81.4% to 65.8% for ADM. Fig. 3 reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the dyes on the adsorbent surface.

The pH of the aqueous solution is an important controlling parameter in the adsorption process [33]. For AC, it was observed that the percentage of dye removal was not affected by pH variation indicating AC is very efficient adsorbent in all media. This indicates the strong force of interaction between the dye and adsorbent that either  $\text{H}^+$  or  $\text{OH}^-$  ions could not influence the adsorption capacity. In other words, the adsorption of Naphthol Yellow S dye on AC does not involve ion exchange mechanism. Whereas adsorption of dye onto ADM is influenced by the pH of the solution and zero point charge of the adsorbent (pHzpc). The zero charge of ADM for (pHzpc) has been found to occur at pH 8.2. The adsorption of dye was higher at solution pH < pHzpc. This could be due to more positive charges at the ADM surface. It was evident that the adsorbent showed better adsorption capacity in the lower pH [34]. This may be due to the higher adsorption of the dye anion by positively charged surface of the adsorbent. It was observed from the experiment that the maximum uptake of dye takes place at pH 2.5, 99.1% colour removal in case of AC and for ADM at pH 2.5, 77.4% (Fig. 4) colour removal. The  $\text{pK}_a$  of hydroxyl group is found to be 15 and that of sulfonate group is reported to be 3.0 which is in good agreement with lower pH where best adsorption is obtained.



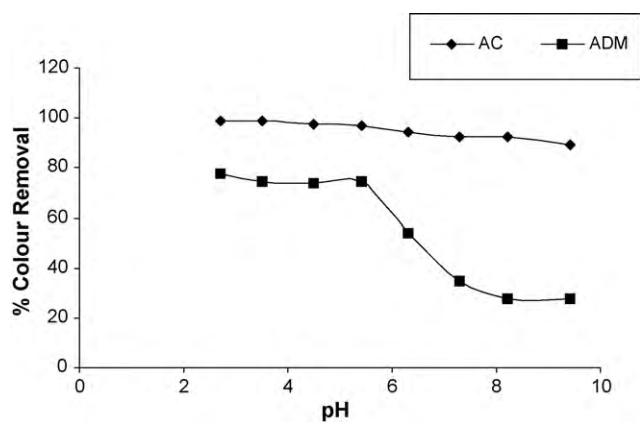


Fig. 4. Effect of pH for the removal of Naphthol Yellow S ( $9 \times 10^{-5} \text{ mol dm}^{-3}$ ) by (a) AC- $0.5 \text{ g L}^{-1}$  and (b) ADM- $4 \text{ g L}^{-1}$  at  $30^\circ\text{C}$ .

For process in which adsorption on the exterior surface of the adsorbent or transport through an external surface flow is the rate limiting reaction, the rate is expected to vary as the reciprocal of the surface diameter of the adsorbent particle for a given total weight of adsorbent. Sorption studies were performed at different particle sizes, i.e. <106, 106–125, 125–180, 180–212, 212–250, 250–300, >300 BSS mesh were taken at a fixed dose  $0.5 \text{ g L}^{-1}$  for AC and  $4 \text{ g L}^{-1}$  for ADM and pH 5.4. Maximum adsorption that could be achieved for AC was 90% and for ADM 67% at <106 BSS mesh size (Fig. 5). High rate of adsorption is due to the availability of more specific surface area on the adsorbent as adsorption process is dependent on the surface morphology. For larger particles, the diffusion resistance to mass transport is higher and most of the internal surface of the particle may not be utilized for adsorption and consequently, the amount of dye adsorbed is small [35]. Whereas the breaking of large particle tends to open tiny cracks and channels on the particle surface, providing added surface area (for small particles) removes more dye in the initial stages of the adsorption process than the large particles. Thus the increase in the rate of the Naphthol Yellow S adsorption by both adsorbents is interpreted in terms of the surface area [36].

The adsorption of the Naphthol Yellow S at the affixed concentration on AC and ADM was studied as a function of the retention time in order to determine the equilibrium time. The adsorption of Naphthol Yellow S dye was very fast initially for both the adsorbents and thereafter the rate leveled off gradually and then attained a more or less constant value (equilibrium) beyond which there was no significant increase in colour removal (Fig. 6). The time required

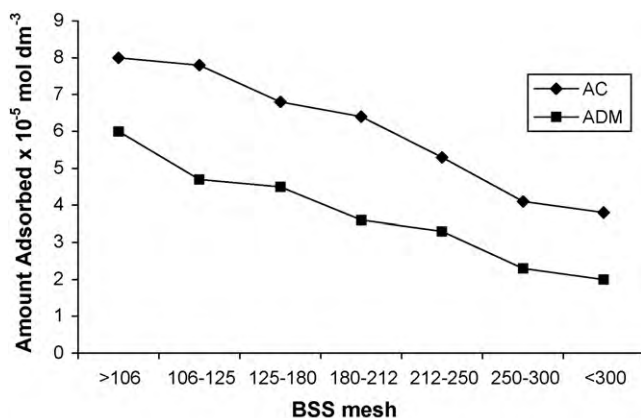


Fig. 5. Effect of particle size for the removal of Naphthol Yellow S by (a) AC- $0.5 \text{ g L}^{-1}$  and (b) ADM- $4 \text{ g L}^{-1}$  at  $30^\circ\text{C}$  and pH 5.4.

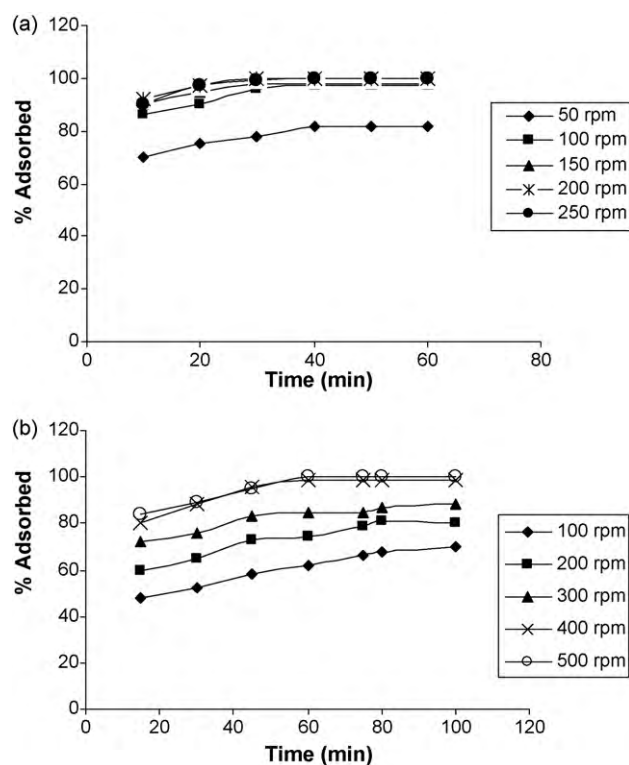


Fig. 6. Effect of agitation speed on the sorption kinetics of Naphthol Yellow S by (a) AC- $0.5 \text{ g L}^{-1}$  and (b) ADM- $4 \text{ g L}^{-1}$  at  $30^\circ\text{C}$  and pH 5.4.

to attain equilibrium was 20 min for AC and 80 min for ADM. This is due to, for a particular experiment, the rate of adsorption decreased with time, it gradually approached a maximum adsorption and owing to continuous decrease in the concentration driving force and it also indicate that the adsorbent is saturated at this level [37].

Taking into account that the sorption kinetics is influenced by mass transfer parameters, such as agitation speed, five agitation speeds were selected from 50 to 200 rpm for AC and 100 to 500 rpm for ADM to study their effects on the sorption of Naphthol Yellow S (Fig. 6). Increase in the speed of agitation enhances the rate of adsorption. The amount of dye sorption increases with the increase of the agitation speed from 50 to 250 rpm for AC and 100 to 500 rpm for ADM. This may be explained that with low agitation speed a greater contact time would be required for reaching equilibrium. By increasing the speed of agitation, the randomness increases during the adsorption process, resulting in better contact between the adsorbate and adsorbent in the system and hence enhancing the rate of adsorption [38]. It was observed that equilibrium was attained faster at 200 rpm than at 50 rpm for AC and 400 rpm for ADM. Thus it can be noticed that the sorption rate has a slight increase with increasing the speed of agitation.

The temperature effect on decolourization rate is significant. Adsorption studies were carried out at different temperatures, i.e.  $30^\circ\text{C}$ ,  $40^\circ\text{C}$  and  $50^\circ\text{C}$  for AC and ADM. The rate of uptake of dye with AC increased with increase in temperature as shown in Fig. 7(a) for AC, thereby indicating process to be endothermic in nature. It is apparent that the maximum adsorption for AC occurred at  $50^\circ\text{C}$  and adsorption follows the order  $30^\circ\text{C} < 40^\circ\text{C} < 50^\circ\text{C}$ . For ADM the percentage removal of Naphthol Yellow S decreases with rise in temperature from  $30^\circ\text{C}$  to  $50^\circ\text{C}$  as shown in Fig. 7(b) for ADM indicating the process to be exothermic in nature [39]. This may be due to the relative escaping tendency of dye molecules from the solid phase to the bulk phase with increase in temperature of the solution [40]. It was observed that the maximum adsorp-

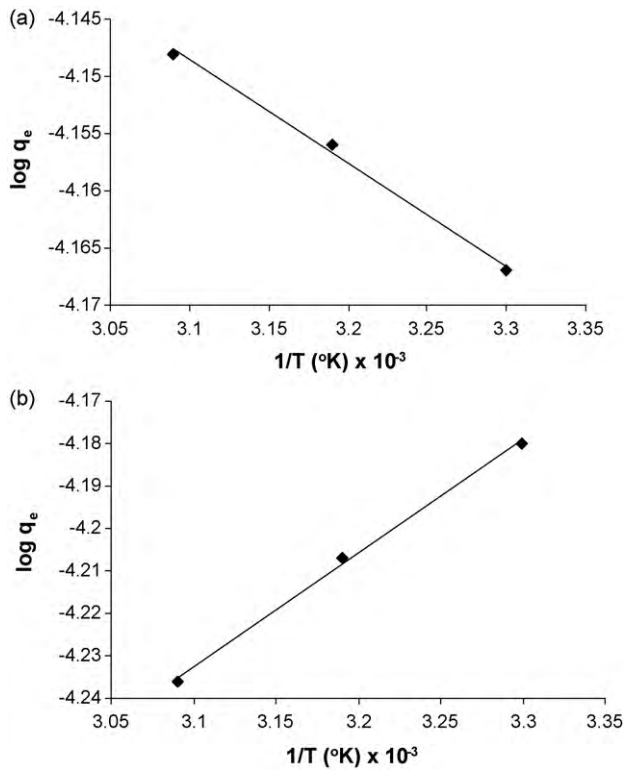


Fig. 7. Effect of temperature for the removal of Naphthol Yellow S by (a) AC-0.5 g L<sup>-1</sup> and (b) ADM-4 g L<sup>-1</sup> at pH 5.4.

tion for ADM occurred at 30 °C and adsorption follows the order 30 °C > 40 °C > 50 °C.

#### 4. Adsorption isotherms

The equilibrium adsorption isotherm is fundamental in describing the interaction behaviour between solutes and adsorbents, and is important in the design of an adsorption system.

##### 4.1. Freundlich isotherm

The adsorption data of activated carbon and activated de-oiled mustard are best fitted into the linear form of Freundlich equation:

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

where  $q_e$  is the amount adsorbed (mol g<sup>-1</sup>),  $C_e$  is the equilibrium concentration of adsorbate (mol L<sup>-1</sup>). The Freundlich isotherm describes equilibrium on a heterogeneous surface where energy of the adsorption was not equivalent for all adsorption sites, thus allowing multi-layer adsorption. The value of  $K_f$  can be used as an alternative measure of adsorption capacity, while  $1/n$  determines the adsorption intensity. The more heterogeneous the surface will bring the  $1/n$  value closer to zero [41,42]. Values of  $K_f$  and  $n$  were calculated from the slope and intercept of the Freundlich plots,

respectively (Table 1). The magnitude of the exponent 'n' gives an indication of the favourability and  $k_f$  the capacity of the adsorbent/adsorbate system. Result from this experiment shows the  $n$  values ranging between 1 and 10, indicating beneficial adsorption. Linear plot of  $\log q_e$  versus  $\log C_e$  shows that the adsorption of Naphthol Yellow S dye from an aqueous solution on both adsorbents also follows Freundlich isotherms. Similar observations were reported for the adsorption of Direct Red 12B dye on biogas residual slurry [43], and also for the adsorption of methylene blue on adsorbent materials produced from sewage sludge [44].

##### 4.2. The Langmuir isotherm

Langmuir adsorption isotherm has been successfully applied to many other real sorption processes [45]. A basic assumption of Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Theoretically, therefore, a saturation value is reached beyond which no further sorption can take place. A linear form of this expression is:

$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0} C_e \quad (3)$$

where  $q_e$  is the amount adsorbed (mol g<sup>-1</sup>),  $C_e$  is the equilibrium concentration of the adsorbate (mol L<sup>-1</sup>),  $Q^0$  and  $b$  are Langmuir constants related to maximum adsorption capacity and energy of adsorption relatively. When  $1/q_e$  plotted against  $1/C_e$ , a straight line with slope  $1/bQ^0$  is obtained which shows that the adsorption of Naphthol Yellow S follows Langmuir isotherm. Langmuir constants are calculated and values of these constants at different temperatures are given in Table 2. It must be pointed out that  $Q^0$  and  $b$  are empirical constants and are really secondary parameters obtained graphically using Eq. (3). So a definite conclusion regarding the trend cannot be obtained by comparing  $b$  and  $Q^0$  values separately. In such cases the better alternative is to compare  $bQ^0$  value which shows the same trend as shown in Table 2.

The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor for equilibrium parameter,  $R_L$  [46], defined as follows:

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

where  $C_0$  is the initial concentration of dye and  $b$  is the Langmuir constant. The values of  $R_L$  indicate the type of isotherm to be irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavorable ( $R_L > 1$ ). Values of separation factor for both the adsorbents are found to be less than unity, confirming thereby the favorable adsorption process in both cases. The same method has already been adopted [47] to confirm the favourability of a Langmuir type of adsorption.

##### 4.3. Thermodynamic parameters

The thermodynamic parameters for the adsorption of Naphthol Yellow S by both adsorbents such as the enthalpy change ( $\Delta H^\circ$ ),

Table 1  
Freundlich constants for the adsorption of Naphthol Yellow S Over AC and ADM at pH 5.4 and different temperatures.

Temperature	Activated carbon				Activated de-oiled mustard			
	$K_f$	$n$	$R^2$	%RSD <sup>a</sup>	$K_f$	$n$	$R^2$	%RSD <sup>a</sup>
30 °C	95.829	2.325	0.8835	0.65	1.7466	1.0353	0.955	0.94
40 °C	27.308	1.9212	0.9856	0.82	1.2835	0.9823	0.9287	1.02
50 °C	7.7889	1.6244	0.9973	0.91	2.7790	1.008	0.9116	1.11

<sup>a</sup> Average of three replicate measurements.

**Table 2**  
Langmuir constants for the adsorption of Naphthol Yellow S over AC and ADM at pH 5.4 and different temperatures.

Temperature	Activated carbon					Activated de-oiled mustard				
	$b$ (mol g <sup>-1</sup> )	$Q^0$ (L mol <sup>-1</sup> )	$bQ^0$	$R^2$	% RSD <sup>a</sup>	$b$ (mol g <sup>-1</sup> )	$Q^0$ (L mol <sup>-1</sup> )	$bQ^0$	$R^2$	% RSD <sup>a</sup>
30 °C	24.192	0.0311	0.750	0.8808	0.68	3.130	0.2827	0.88	0.9681	0.89
40 °C	32.45	0.0363	1.180	0.9072	0.98	0.985	0.6701	0.66	0.9394	1.02
50 °C	10.67	0.1062	1.133	0.900	0.93	2.927	0.1455	0.42	0.856	1.24

<sup>a</sup> Average of three replicate measurements.

**Table 3**  
Thermodynamic parameters for the uptake of Naphthol Yellow S over AC and ADM at pH 5.4.

Adsorbent	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )			$\Delta H^\circ$ (kJ mol <sup>-1</sup> ) (30 °C)	$\Delta S^\circ$ (JK <sup>-1</sup> mol <sup>-1</sup> ) (30 °C)
	30 °C	40 °C	50 °C		
Activated carbon	$-8.0 \times 10^3$	$-8.3 \times 10^3$	$-8.5 \times 10^3$	$9.345 \times 10^3$	57.33
Activated de-oiled mustard	$-2.8 \times 10^3$	$-2.9 \times 10^3$	$-3.06 \times 10^3$	$-91.52 \times 10^3$	-292

the Gibbs free energy change ( $\Delta G^\circ$ ) and the entropy change ( $\Delta S^\circ$ ) can be calculated from the variation of Langmuir constant with temperature ( $T$ ) using the following thermodynamic relations [48] (Table 3):

$$\Delta G^\circ = -RT \ln b \quad (5)$$

$$\Delta H^\circ = \frac{-R(T_2 T_1)}{(T_2 - T_1)} \ln \left( \frac{b_2}{b_1} \right) \quad (6)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (7)$$

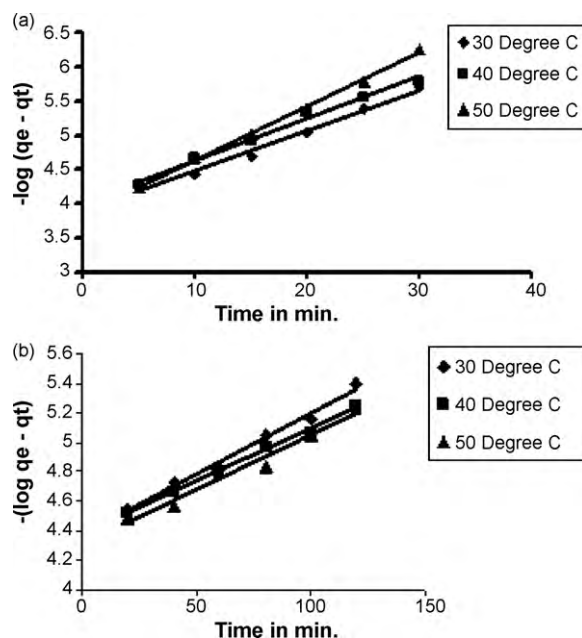
where  $b$ ,  $b_1$ ,  $b_2$  are the equilibrium constants at different temperatures and obtained from the slopes of adsorption isotherms at different concentrations. Negative free energy values for both the systems indicate the spontaneity of the adsorption process. It was also seen that  $\Delta G^\circ$  values decreases with increasing temperatures, which once again reveals higher adsorption at higher temperatures. The positive value of  $\Delta H^\circ$  confirms the endothermic nature of adsorption of dye over AC, whereas in case of ADM the increase in temperature affects the solubility and the chemical potential of the adsorbate, the latter being a controlling factor in adsorption. It has been reported earlier [49] that if the solubility of the adsorbate increases with an increase in temperature, the chemical potential decreases and both the effects, i.e. solubility and normal temperature, work in same direction, causing a decrease in adsorption. The amount of dye adsorbed decreased from 6.8 (81.4%) to 5.7 (57.2%) mol g<sup>-1</sup> for ADM with the rise in temperature of dye solutions from 30 to 50 °C. This was confirmed by the thermodynamic parameters like free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) changes during the removal process. The negative value of enthalpy change ( $\Delta H^\circ$ ) for the processes (ADM) confirmed their exothermic nature [50,51] while negative entropy ( $\Delta S^\circ$ ) reflects the affinity of ADM towards Naphthol Yellow S [50,52].

#### 4.4. Adsorption rate constant

The kinetic study of adsorption processes provides useful data regarding the efficiency of the adsorption and the feasibility for scale-up operations. The kinetic data of adsorption can be evaluated using different types of mathematical models [53] of which the one most widely used is Lagergren's rate equation. The kinetics of the adsorption process was analyzed using the first-order rate equation [54]:

$$\log(q_e - q_t) = \log q_e - k_{ad} \left( \frac{t}{2.303} \right) \quad (8)$$

where  $q_e$  and  $q_t$  signify the amount adsorbed at equilibrium and at any time  $t$ , respectively. For both the systems, the graphs (Fig. 8(a)



**Fig. 8.** Lagergren plots for Naphthol Yellow S adsorption over AC and ADM at pH 5.4 and different temperatures.

for AC and (b) for ADM) obtained for  $\log(q_e - q_t)$  versus  $t$  exhibit straight lines and confirm the adsorption process to follow first-order rate kinetics in each case. The  $k_{ad}$  values evaluated, for each system, from the respective Lagergren plot are presented in Table 4.

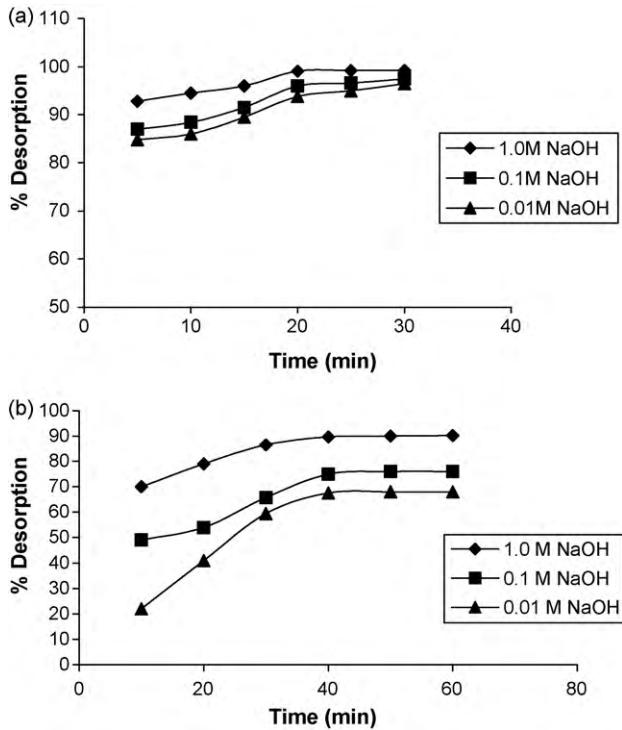
#### 5. Recovery of hazardous dye Naphthol Yellow S

To assess the practical utility of the adsorbents, bulk adsorption were done by employing column operations. Adsorption column chromatography method [55] is adopted. Recovery of the adsorbed Amaranth and regeneration of column was made by eluting dilute NaOH solution (Fig. 5). Three different concentration of NaOH, i.e. 1.0, 0.1 and 0.01 mol dm<sup>-3</sup> which was passed at a flow rate of 5 mL min<sup>-1</sup> and fractions collected after every 10 min, which were analyzed spectrophotometrically. It has been observed from Fig. 9(a) for AC and (b) for ADM that maximum dye 99% desorbed of from AC and about 90% of dye desorbed from ADM with 1.0 mol dm<sup>-3</sup> NaOH. After complete recovery of the dye the column was finally washed with the hot water.

**Table 4**  
Values of rate constant for the uptake of Naphthol Yellow S over AC and ADM at pH 5.4.

Temperature	Activated carbon		Activated de-oiled mustard	
	$k_{ad}$	%RSD <sup>a</sup>	$k_{ad}$	%RSD <sup>a</sup>
30 °C	$135.4 \times 10^{-3}$	0.85	$18.88 \times 10^{-3}$	0.91
40 °C	$140.94 \times 10^{-3}$	0.93	$16.35 \times 10^{-3}$	1.3
50 °C	$180.5 \times 10^{-3}$	1.06	$17.04 \times 10^{-3}$	1.7

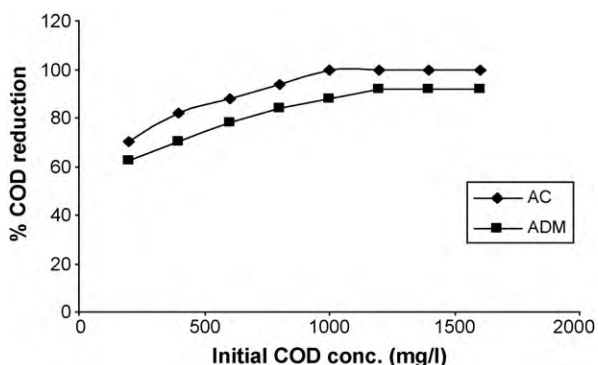
<sup>a</sup> Average of three replicate measurements.



**Fig. 9.** Desorption profile of Naphthol Yellow S of AC and ADM using different concentrations of NaOH.

## 6. Chemical oxygen demand (COD)

The chemical oxygen demand test is widely used as an effective technique to measure the organic strength of wastewater. Comparison of the COD value of the initial dye solution with treated adsorbed solution indicates that the COD value is substantially reduced from 1860 to 186 mg L<sup>-1</sup> and 232 mg L<sup>-1</sup> for AC and ADM, respectively. The ADM seems to be fairly active adsorbent even at higher initial concentrations. At lower initial concentrations, the ratio of the initial number of moles available to the adsor-



**Fig. 10.** Effect of initial COD concentration on % COD reduction by AC and ADM.

bent surface area is low and subsequently the fractional adsorption becomes independent of initial concentration (Fig. 10). At higher concentrations, the available sites of adsorption become fewer and hence the % removal of COD depends upon the initial concentration. The treated filtrate of AC and ADM with the percent COD removal efficiency of 90.0% and 87.5% indicates the usefulness of adsorptive treatment of wastewater.

## 7. Conclusion

The adsorption isotherm and kinetics of Naphthol Yellow S were studied. The following results were obtained:

1. The present work is an attempt to develop a versatile, economic and reliable method for the removal of hazardous dye Naphthol Yellow S from wastewater. Preliminary batch studies indicate that ADM can adsorb almost 81.4% to 65.8% for ADM of the Naphthol Yellow S from its aqueous solutions in the concentration range  $(1.0-9.0) \times 10^{-5}$  mol dm<sup>-3</sup>, at 30 °C.
2. The adsorption data also confirm the validity of Freundlich and Langmuir adsorption isotherm.
3. The adsorption capacities were affected by the changes in temperature. The uptake decreased with the increase in temperature in case of ADM indicating exothermic nature of the process.
4. A pseudo-first-order kinetic model agreed well with the dynamical behaviour for the adsorption of Naphthol Yellow S on AC and ADM under different temperatures.
5. Desorption studies indicate that by eluting dilute NaOH through the fixed bed of the adsorbents their columns can be regenerated and a quantitative recovery of Naphthol Yellow S can be achieved. The percentage removal of dye was almost similar in both cases.
6. In view of all these findings, it may be concluded that the developed adsorbent is very useful, economic, and reproducible for the removal of Naphthol Yellow S. Thus it may be safely concluded that de-oiled mustard is quite economic than available commercially adsorbents for controlling the water pollution by dyes.

## References

- [1] O. Gulnaz, A. Kaya, F. Matyar, B. Arikian, Sorption of basic dyes from aqueous solution by activated sludge, *J. Hazard. Mater.* 108 (2004) 183–188.
- [2] E. Blanca, Barragán, Carlos Costa, M. Carmen Márquez, Biodegradation of azo dyes by bacteria inoculated on solid media, *Dyes Pigments* 75 (2007) 73–81.
- [3] K. Santhy, P. Selvapathy, Removal of reactive dyes from wastewater by adsorption on coir pith activated carbon, *Bioresour. Technol.* 97 (2006) 1329–1336.
- [4] J.J.M. Orfao, A.I.M. Silva, J.C.V. Pereira, S.A. Barata, I.M. Fonseca, P.C.C. Faria, M.F.R. Pereira, Adsorption of reactive dyes on chemically modified activated carbons—influence of pH, *J. Colloid Interf. Sci.* 296 (2006) 480–489.
- [5] P.K. Malik, S.K. Saha, Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst, *Sep. Purif. Technol.* 31 (2003) 241–250.
- [6] A. Vogelpohl, S.M. Kim, Advanced oxidation processes (AOPs) in wastewater treatment, *J. Ind. Eng. Chem.* 10 (2004) 33–40.
- [7] G. Ciardelli, L. Corsi, M. Marussi, Membrane separation for wastewater reuse in the textile industry, *Resour. Conserv. Recycl.* 31 (2001) 109–113.
- [8] S. Senthilkumar, P.R. Varadarajab, K. Porkodi, C.V. Subbhuraam, Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies, *J. Colloid Interf. Sci.* 284 (2005) 78–82.

- [9] S.Y.M. Josefa, E. De Oliveira, Heavy metals removal in industrial effluents by sequential adsorption treatment, *Adv. Environ. Res.* 7 (2003) 263–272.
- [10] F.-C. Wu, R.-L. Tseng, Preparation of highly porous carbon from fir wood by KOH etching and CO<sub>2</sub> gasification for adsorption of dyes and phenols from water, *J. Colloid Interf. Sci.* 294 (2006) 21–30.
- [11] D.J. Malik, V. Strelko Jr., M. Streat, A.M. Puziy, Characterization of novel modified active carbons and marine algal biomass for the selective adsorption of lead, *Water Res.* 36 (2002) 1527–1538.
- [12] V.K. Gupta, A. Mittal, V. Gajbe, J. Mittal, Adsorption of basic fuchsin using waste materials-bottom ash and deoiled soya-as adsorbents, *J. Colloid Interf. Sci.* 319 (2008) 30–39.
- [13] V.K. Gupta, R. Jain, S. Varshney, Electrochemical removal of the hazardous dye Reactofix Red 3 BFN from industrial effluents, *J. Colloid Interf. Sci.* 312 (2007) 292–296.
- [14] V.K. Gupta, R. Jain, S. Varshney, V.K. Saini, Removal of Reactofix Navy Blue 2 GFN from aqueous solutions using adsorption techniques, *J. Colloid Interf. Sci.* 307 (2007) 326–332.
- [15] V.K. Gupta, R. Jain, S. Varshney, Removal of Reactofix golden yellow 3 RFN from aqueous husk—an agricultural waste, *J. Hazard. Mater.* 142 (2007) 443–448.
- [16] V.K. Gupta, A. Mittal, V. Gajbe, J. Mittal, Removal and recovery of the hazardous azo dye Acid Orange 7 through adsorption over waste materials: bottom ash and de-oiled soya, *Ind. Eng. Chem. Res.* 45 (2006) 1446–1453.
- [17] V.K. Gupta, A. Mittal, R. Jain, M. Mathur, S. Sikarwar, Adsorption of Safranin T from wastewater using waste materials-activated carbon and activated rice husk, *J. Colloid Interf. Sci.* 303 (2006) 80–86.
- [18] R. Jain, S. Sikarwar, Photocatalytic and adsorption studies on the removal of dye Congored from wastewater, *Int. J. Environ. Pollut.* 27 (2006) 158–178.
- [19] H.L. Chiang, J.H. Tsai, G.H. Chang, F.T. Jeng, Diffusion of hydrogen sulphide and methyl mercaptan onto microporous alkaline activated carbon, *Chemosphere* 41 (2000) 1227–1232.
- [20] V.K. Gupta, I. Ali, Suhas, Removal of Rhodamine B, Fast green and Methylene blue from wastewater using red mud an aluminum industry waste, *Ind. Eng. Chem. Res.* 43 (2004) 1740–1747.
- [21] V.K. Gupta, A. Mittal, L. Krishnan, V. Gajbe, Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash, *Sep. Purif. Technol.* 40 (2004) 87–96.
- [22] V.K. Gupta, A. Mittal, V. Gajbe, Adsorption and desorption studies of a water soluble dye, quinoline yellow, using waste materials, *Ind. Eng. Chem. Res.* 284 (2005) 89–98.
- [23] R. Jain, A. Mittal, M. Mathur, S. Sikarwar, Removal of the hazardous dye Rhodamine B from photocatalytic and adsorption treatments, *J. Environ. Manage.* 85 (2007) 956–960.
- [24] R. Jain, S. Sikarwar, Removal of hazardous dye congo red from waste material, *J. Hazard. Mater.* 152 (2008) 942–948.
- [25] R. Jain, S. Varshney, S. Sikarwar, Electrochemical techniques for the removal of Reactofix Golden yellow 3 RFN from industrial wastes, *J. Colloid Interf. Sci.* 313 (2007) 248–253.
- [26] R. Jain, S. Sikarwar, Adsorptive removal of Erythrosine dye onto activated deoiled mustard, *J. Hazard. Mater.* 164 (2009) 627–633.
- [27] N. Fiol, I. Villaescusa, Determination of sorbent point zero charge: usefulness in sorption studies, *Environ. Chem. Lett.* 7 (2009) 79–84.
- [28] Improvement in the Nutritive Value of Mustard Seed Cake, Institute of Chemistry, University of Punjab, 1986.
- [29] S.P. Raghuvanshi, R. Singh, C.P. Kaushik, A.K. Raghav, Kinetics study of methylene blue dye by bioadsorption on baggase, *Int. J. Appl. Ecol. Environ. Res.* 2 (2004) 35–43.
- [30] S. Saiful Azhar, A. Ghaniey Liew, D. Suhardy, K. Farizul Hafiz, M.D. Irfan Hatim, Dye removal from aqueous solution by using adsorption on treated sugarcane bagasse, *Am. J. Appl. Sci.* 2 (2005) 1499–1503.
- [31] C. Namasivayam, N. Muniasamy, K. Gayathri, M. Rani, K. Renganathan, Removal of dyes from aqueous solution by cellulosic waste orange peel, *Bioresor. Technol.* 57 (1996) 37–43.
- [32] C. Namasivayam, R.T. Yamuna, Adsorption of direct red by biogas residual slurry, *Environ. Pollut.* 89 (1995) 1–7.
- [33] M. Ajmal, R.A.K. Rao, R. Ahmad, J. Ahmad, Adsorption studies on citrus reticulate: removal and recovery of Ni(II) from electroplating wastewater, *J. Hazard. Mater.* B79 (2000) 117–131.
- [34] A. Shukla, Y.H. Zhang, P. Dubey, J.L. Margrave, S.S. Shukla, The role of saw dust in the removal of unwanted materials from water, *J. Hazard. Mater.* 95 (2002) 137–152.
- [35] S.P. Raghuvanshi, R. Singh, C.P. Kaushik, Kinetics study of Methylene blue dye bioadsorption on baggase, *Appl. Ecol. Environ. Res.* 2 (2004) 35–43.
- [36] G. Karthikeyan, Pius Anitha, G. Alagumuthu, Kinetic and thermodynamic studies on adsorption of fluoride by dolomite, *Ind. J. Chem. Technol.* 9 (2002) 397–401.
- [37] M.S. Chiou, H.Y. Li, Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads, *J. Hazard. Mater.* B 93 (2002) 233–248.
- [38] K.K. Panday, G.V. Prasad, N. Singh, Copper(II) removal from aqueous solutions by fly ash, *Water Res.* 19 (1985) 869–873.
- [39] S.D. Khattri, M.K. Singh, Adsorption of basic dyes from aqueous solution by natural adsorbents, *Indian J. Chem. Technol.* 6 (1999) 112–116.
- [40] K.K. Panday, G. Prasad, V.N. Singh, Copper(II) removal from aqueous solution by fly ash, *J. Chem. Technol. Biotechnol.* 34 (1984) 367–374.
- [41] S. Mohan, J. Karthikeyan, Removal of lignin and tannin colour from aqueous solution by adsorption onto activated charcoal, *Environ. Pollut.* 97 (1997) 183–187.
- [42] P. Atkins, *Physical Chemistry*, Oxford University Press, Oxford, U.K., 1970.
- [43] C. Namasivayam, R.T. Yamuna, Adsorption of direct red 12B by biogas residual slurry: equilibrium and rate processes, *Environ. Pollut.* 89 (1995) 1–7.
- [44] M. Otero, F. Rozada, L.F. Calvo, A.I. Garcia, A. Moran, Kinetic and equilibrium modeling of the methylene blue removal from solution by adsorbent materials produced from sewage sludges, *Biochem. Eng. J.* 15 (2003) 59–68.
- [45] M.S. Chiou, H.Y. Li, Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked Chitosan beads, *J. Hazard. Mater.* B 93 (2002) 233–248.
- [46] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore and solid-diffusion kinetics in fixed bed adsorption under constant pattern conditions, *Ind. Eng. Chem. Fund.* 5 (1996) 212–223.
- [47] T.W. Weber, R.K. Chakrabarti, Pore and solid diffusion models for fixed bed adsorbents, *J. Am. Inst. Chem. Eng.* 20 (1974) 228–238.
- [48] O. Yavuz, Y. Altunkaynak, F. Guzel, Removal of copper, nickel and manganese from aqueous solution by kaolinite, *Water Res.* 37 (2003) 948–952.
- [49] G.S. Gupta, G. Prasad, V.N. Singh, Removal of chrome dye from aqueous solutions by mixed adsorbents: fly ash and coal, *Water Res.* 24 (1990) 45–50.
- [50] S.D. Khattri, M.K. Singh, Colour removal from synthetic dye wastewater using a bioadsorbent, *Water Air Soil Pollut.* 120 (2000) 283–294.
- [51] A.K. Singh, P.N. Tiwari, Removal of basic dye from industrial wastewater by adsorption, *Indian J. Chem. Technol.* 10 (2003) 211–216.
- [52] V.K. Gupta, M. Gupta, S. Sharma, Process development for the removal of lead and chromium from aqueous solutions using red mud—an aluminium industry waste, *Water Res.* 5 (2001) 1125–1134.
- [53] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part 1. Solids, *J. Am. Chem. Soc.* 38 (1916) 2221–2295.
- [54] K. Vasanth Kumar, V. Ramamurthy, S. Sivasenan, Modeling the mechanism involved during the sorption of methylene blue onto flyash, *J. Colloid Interf. Sci.* 284 (2005) 14–21.
- [55] B.D. Bhole, B. Gangula, A. Madhuram, D. Deshpande, J. Joshi, Biosorption of methyl violet, basic fuchsin and their mixture using dead fungal biomass, *Curr. Sci.* 86 (2004) 1641–1645.