# Equilibrium and Thermodynamic Studies on the Adsorption of the Dye Tartrazine onto Waste "Coconut Husks" Carbon and Activated Carbon

## Vinod K. Gupta,\*,<sup>†,‡</sup> Rajeev Jain,<sup>§</sup> Meenakshi Shrivastava,<sup>§</sup> and Arunima Nayak<sup>†</sup>

Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India, Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran, 31261, Saudi Arabia, and Department of Environmental Chemistry, Jiwaji University, Gwalior 474011, India

Removal of tartrazine by an agricultural waste, coconut husks (CH), was investigated and compared with activated carbon (AC). The effect of pH, temperature, amount of adsorbent, contact time, initial dye concentration, and particle size on the extent of adsorption by the two adsorbents was investigated. The maximum adsorption capacity was obtained for pH 2.5, adsorbent dose of  $3.3 \text{ g} \cdot \text{L}^{-1}$ , particle size > 0.15 mm, contact time of 210 min, temperature of 30 °C, and dye concentration of  $6 \cdot 10^{-5}$  M for the CH–tartrazine system and pH 2.5, adsorbent dose of  $0.3 \text{ g} \cdot \text{L}^{-1}$ , particle size > 0.15 mm, contact time of 40 min, temperature of 50 °C, and dye concentration of  $6 \cdot 10^{-5}$  M for the AC–tartrazine system. The negative values of  $\Delta G^{\circ}$  indicated that the dye adsorption process is spontaneous in nature. The positive value of  $\Delta H^{\circ}$  shows the endothermic nature of the AC–tartrazine system, whereas the negative value of  $\Delta H^{\circ}$  indicates the exothermic nature of the CH–tartrazine system. The adsorption was found to undergo pseudo first-order adsorption kinetics. A significant amount of the dye (99 % for AC and 92 % for CH) was recovered by using 1.0 M NaOH as an eluting agent. The results revealed that CH can be used as a economically viable alternative to AC.

## 1. Introduction

Contamination of the environment from a variety of sources has become an increasingly serious problem in recent years. The release of dyes into wastewaters by various industries poses serious environmental problems due to their persistence and recalcitrance in nature. The presence of dyes in waterways is easily detectable even when released in small concentrations. For some dyes, a dye concentration of less than 1 mg  $\cdot$ L<sup>-1</sup> in receiving water bodies is highly visible, so that even small quantities of dyes can color large water bodies. This is not only unsightly, but the coloration of the water by the dyes may have an inhibitory effect on photosynthesis affecting aquatic ecosystems. Dyes may also be problematic if they are broken down aerobically in the sediment, as toxic amines are often produced due to incomplete degradation by bacteria.<sup>1</sup> Some of the dyes or their metabolites are either toxic or mutagenic and carcinogenic.<sup>2,3</sup> The treatment of textile wastewaters to reduce visual color and dissolved organic contaminants to meet increasing environmental demands has continued to attract the interest of research groups. The nondegradable nature of dyes and their stability toward light and oxidizing agents complicates the selection of a suitable method for their removal. Many methods are available for the removal of dyes from waters.<sup>3–12</sup> Among these methods, adsorption is by far the most versatile and widely used method because of its ability to separate a wide range of chemical compounds and its easy operational procedures and facilitation of recovery of costly organic and inorganic

<sup>†</sup> Indian Institute of Technology Roorkee.

§ Jiwaji University.

materials.<sup>13</sup> One of the major challenges associated with adsorption by activated carbon (AC) is its cost effectiveness. Hence, research of the recent past has mainly focused on utilizing waste materials as alternatives to AC. A number of agricultural wastes and byproducts of cellulosic origin have been studied in the literature for their capacity to remove dyes from aqueous solutions such as barley husks, sugar cane dust, wheat straw, tree ferns, wood chips, and corn-cob shreds.<sup>14–22</sup>

In this paper, we attempt to use an agricultural byproduct, coconut husk (CH), as an adsorbent, which is a very cheap and easily available waste material for the removal of tartrazine from aqueous solution. The dye "tartrazine" chosen as a model compound for the present study finds vast applications. Tartrazine is an acidic azo dye with a sulfonic group as an auxochrome that is highly water-soluble and polar. It is widely used to dye sweets, chewing gum, jellies, puddings, juices, jams, mustard, sodas, drugs, and cosmetics.<sup>23</sup> Tartrazine has been implicated as the food additive most often responsible for allergic reactions, having thus been targeted by the scientific community. Although urticaria, asthma, purpura, and eczema have been described, chiefly affecting individuals' allergy to aspirin, the underlying immunologic mechanism has proved elusive. Some authors have studied the carcinogenetic and mutogenetic effects of tartrazine with variable results.<sup>24-27</sup> Because of the large degree of organics present and stability of tartrazine dye, conventional physicochemical and biological treatment methods are ineffective for their removal. This led to the study of other effective methods. The adsorption process is one of the efficient methods to remove dyes from solution.<sup>28</sup> The process of adsorption has an edge over other methods due to its sludge free clean operation and complete removal of dyes even from dilute solutions.

The objective of this work is to evaluate and compare the adsorptive efficiency of CH for the removal of the toxic dye

<sup>\*</sup> Corresponding author. Address: Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India. E-mail: vinodfcy@gmail.com; vinodfcy@iitr.ernet.in. Tel.: +91-1332-285043. Fax: +91-1332-273560.

<sup>&</sup>lt;sup>‡</sup> King Fahd University of Petroleum and Minerals.

tartrazine with that of an AC. Currently 1.81 million hectares of land are under coconut cultivation in India, and annually around 6908 kg of CH are available per hectare. The CHs are at present used as a fuel for coconut processing, as a domestic fuel, and as a source of fiber for ropes, mats, and coir. Conversion of CHs into AC will serve a double purpose. First, unwanted agricultural waste is converted to useful, value-added adsorbents, and second, the use of agricultural byproducts represents a potential source of adsorbents which will contribute to solving part of the wastewater treatment problem in India. Various studies have been carried out on CH based AC. Some of them are the adsorption of arsenic on copper-impregnated CH carbon,<sup>29</sup> preparation of AC from digested sewage sludge with ZnCl<sub>2</sub> as activating agent,<sup>30</sup> production of AC from coconut fibers for removal of phenol, Acid Red 27 dye, and Cu<sup>2</sup> ions,<sup>31</sup> and preparation of AC from CH for adsorption of a basic dye.<sup>32</sup>

#### 2. Materials and Methods

For the present investigation water-soluble tartrazine dye [A] (4,5-dihydro-5-oxo-1-(4-sulfophenyl)-4-[(4-sulfophenyl)azo]-1*H*-pyrazole-3-carboxylic acid trisodium salt; molecular formula  $C_{16}H_9N_4Na_3O_9S_2$ , molecular weight 534.37 g·mol<sup>-1</sup>) was obtained from Merck, and a 0.01 M stock solution was prepared in double-distilled water.

To prepare various solutions at desired concentrations from the stock solution, double-distilled water was used for necessary dilutions. All reagents used in the present work were of analytical grade.

Adsorbent AC was also purchased from Merck and used as received. All pH metric measurements were carried out with a decibel DB 1011 digital pH meter, fitted with a glass electrode. A chemical oxygen demand (COD) digestion apparatus (Spectra Lab-2015 S) was used for determining the COD of the solutions. Absorbance measurements were recorded on a Spectronic 20D+ thermospectronic spectrophotometer over the wavelength range (200 to 800) nm.



**2.1.** *Material Development.* The CH obtained was cleaned, thoroughly washed with distilled water, and then dried in an oven. This dried material was then treated with hydrogen peroxide solution for 24 h to oxidize adhering organic impurities and dried at 110 °C for 1 h in a vacuum oven. The material was grounded and sieved to desired particle sizes such as > 0.15, (0.12 to 0.15), (0.089 to 0.12), (0.075 to 0.089), (0.066 to 0.075), (0.053 to 0.066), and < 0.053 mm. Finally, granules of CH thus obtained were stored in separate vacuum desiccators until required. However, the procured AC was separated to obtain similar particle sizes and also kept in desiccators.

**2.2.** Adsorption Studies. To obtain rate and equilibrium data, adsorption studies of the adsorbents AC and CH were performed by a batch technique at (30, 40, and 50) °C. For every adsorption isotherm study, a series of volumetric flasks containing equal volumes (30 mL) of adsorbate solutions at varying concentrations were employed at the desired pH. The pH of the solution was kept constant by adding 0.1 M NaOH or 0.1 M HNO<sub>3</sub>.

The concentrations were decided after considerable preliminary investigations. An optimized amount of adsorbent of particle size < 0.15 mm was then added into each flask that were intermittently agitated. Water samples were drawn from each flask after regular intervals to calculate the progress of adsorption. When the equilibrium was thought to be established, the supernatant was carefully filtered through Whatmann filter paper (No. 41) and analyzed by a Spectronic 20 D+ thermospectronic spectrophotometer at  $\lambda_{max}$  429 nm. The experiments were repeated three times, and average values were reported. Standard deviations were found to be  $\pm$  1.4 %. Further, error bars for the figures were so small as to be smaller than the symbols used to plot the graphs and, hence, are not shown. The dye uptake  $q_e$  (mol·g<sup>-1</sup>) was determined as follows:

$$q_{\rm e} = (C_0 - C)V/W$$
 (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 mass of adsorbent (g).

**2.3.** *Quality Assurance/Quality Control.* To establish the accuracy, reliability, and reproducibility of the collected data, all of the batch isotherm tests were replicated thrice, and the experimental blanks were run in parallel. Check standards and blanks were also run. Multiple sources of National Institute of Standard and Technology (NIST) traceable standards were used for instrument calibration and standard verification. All jars, conical flasks, and containers used in the study were prepared by soaking in 5 % HNO<sub>3</sub> solution for a period of 3 days before being doubly rinsed with distilled, deionized water, and ovendried. In different experiments, blanks were run, and corrections made wherever necessary. All observations were recorded in triplicate, and average values were reported.

#### 3. Results and Discussion

**3.1.** Characterization of Adsorbent Material. The AC and CH were characterized by scanning electron microscopy (SEM) and are shown in Figure 1. SEM is widely used to study the morphological features and surface characteristics of the adsorbent materials. In the present study, scanning electron micrographs (Figure 1) of tartrazine before and after adsorption reveals surface texture and porosity.

3.2. Effect of Adsorbent Dose. The effect of adsorbent dose on the removal of tartrazine was studied by varying the dose of adsorbent from (0.06 to 0.46)  $g \cdot L^{-1}$  for AC and (1.66 to 11.6)  $g \cdot L^{-1}$  for CH. The experiment was carried out at a fixed pH of 2.5,  $6 \cdot 10^{-5}$  M initial dye concentration, and at three different temperatures (30, 40, and 50) °C. From Figure 2a,b, it is apparent that initially the rate of increase in the percentage of dye removal has been found to be rapid from (0.06 to 0.4)  $g \cdot L^{-1}$ which then slowed down as the dose increased from (0.4 to 0.46)  $g \cdot L^{-1}$  for AC, while in case of CH, dye removal increases as the dose of adsorbent increases from (1.66 to 10)  $g \cdot L^{-1}$ , which then decreases as the dose increased from (10 to 11.6)  $g \cdot L^{-1}$ . 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 intraparticle diffusion taking place simultaneously with the dominance of adsorption. With a rise in adsorbent dose, there is a less commensurate increase in adsorption resulting from lower adsorptive capacity utilization of the adsorbent.<sup>33,34</sup>

**3.3.** Effect of Initial Dye Concentration. There is a direct relationship between initial dye concentration and removal rate.



**Figure 1.** SEM micrographs: (a) SEM of AC and (1b) SEM of CH.



Figure 2. Plots of adsorbent dose vs amount adsorbed for tartrazine (a) AC and (b) CH, at different temperatures.

The adsorption experiments were carried out in concentration ranges from  $(1 \cdot 10^{-5} \text{ to } 8 \cdot 10^{-5})$  M. The results are given in Figure 3. The figure indicates that the adsorption of the total amount of dye increases with an increase in the dye concentration from  $(1 \cdot 10^{-5} \text{ to } 6 \cdot 10^{-5})$  M in the solution, for both the



(Ib)



Figure 3. Plots of concentration of adsorbate vs amount adsorbed for tartrazine over AC and CH, at 30  $^{\circ}$ C.

adsorbents. It shows that the removal of dye is dependent upon the concentration of dye in solution. As a whole, the percentage removal decreases from (98 to 48) % for AC and (75 to 39) % for CH with the increase in dye concentration as observed in the plot. The initial rate of adsorption was greater for a higher initial dye concentration because, as resistance to dye uptake decreased, the mass transfer driving force increased. This will suit the findings which had been quoted by the other researchers.<sup>35–37</sup>

**3.4.** Effect of pH. The pH of the aqueous solution is an important controlling parameter in the adsorption process.<sup>38,39</sup> The effect of pH on the adsorption of tartrazine has been studied by varying the pH of the medium from 2.5 to 9.1 at a fixed dose of 0.3 g·L<sup>-1</sup> for AC and 3.33 g·L<sup>-1</sup> for CH and a concentration of  $6 \cdot 10^{-5}$  M. It is apparent from Figure 4 that the percent color removal of tartrazine decreases with an increase in pH from 2.5 to 5.1, and thereafter it becomes almost constant with an increase in pH from 6.2 to 9.1. At acidic pH, the positively charged species start dominating, and the surface tends



Figure 4. Plots of pH vs % color removal for tartrazine over AC and CH, at 30 °C.



Figure 5. Plots of particle size vs amount adsorbed for tartrazine over AC and CH, at 30  $^{\circ}$ C.

to acquire a positive charge, while the adsorbate species are still negatively charged. As the adsorbent surface is positively charged, the increasing electrostatic attraction between negatively charged adsorbate species and positively charged adsorbent particles would lead to an increased adsorption of the tartrazine dye. The maximum removal of the tartrazine dye with AC and CH was hence observed at pH 2.5.

3.5. Effect of Particle Size. The rate of adsorption of tartrazine was studied at different particle sizes of AC and CH, namely, (> 0.15), (0.12 to 0.15), (0.089 to 0.12), (0.075 to 0.15)0.089), (0.066 to 0.075), (0.053 to 0.066), and (< 0.053) mm. The maximum adsorption (76.8 %) occurs for AC, and 65.9 % adsorption occurs for CH at size > 0.15 mm and then decreases up to (0.053 to 0.066) mm size. Beyond this it remains constant up to < 0.053 mm size for both cases (Figure 5). From the figure it is clear that the removal rate improved as the particle size decreased. This is because the small particles have more surface area and access to the particle pores is facilitated when their size is small. It is also believed that the breaking up of large particles to form smaller particles opens some tiny scaled channels, which might then become available for adsorption, and so the sorption by smaller particles is higher than that by large particles.40

**3.6.** Effect of Contact Time. The adsorption experiments were also carried out for different contact times with a fixed adsorbent dose of 0.3 g·L<sup>-1</sup> for AC and 3.33 g·L<sup>-1</sup> for CH with an initial concentration of  $6 \cdot 10^{-5}$  M at pH 2.5 and temperature 30 °C. It is apparent from Figure 6 that the adsorption gradually increases with an increase in contact time with both adsorbents. The time required to attain the equilibrium was 40 min for AC and 210 min for CH.



Figure 6. Effect of contact time on the adsorption of tartrazine over AC and CH, at 30  $^{\circ}$ C.



Figure 7. Effect of temperature on the adsorption of tartrazine on (a) AC and (b) CH.

**3.7.** *Effect of Temperature.* Adsorption studies were carried out at (30, 40, and 50) °C for AC and CH. Figure 7a,b shows that for AC, the rate of dye uptake increases rapidly with a rising temperature from (30 to 50) °C at a 0.33 g  $\cdot$ L<sup>-1</sup> dose in 10 min from a 6  $\cdot$ 10<sup>-5</sup> M dye solution, since the adsorption rate increases as the diffusion coefficient rises with temperature; hence, the process is endothermic in nature, whereas in the case of CH the rate of dye uptake decreased with an increase in temperature from (30 to 50) °C with a 3.33 g  $\cdot$ L<sup>-1</sup> dose in 60 min from a 6  $\cdot$ 10<sup>-5</sup> M dye solution, indicating that the process is exothermic in nature. This may be due to the tendency of dye molecules to escape from the solid phase to bulk phase with an increase in temperature of the solution.

**3.8.** Adsorption Isotherms. The analysis of adsorption data is important to develop an equation which accurately represents the results and which could be used for design purposes. The distribution of dye between the liquid phase and the adsorbent



**Figure 8.** Freundlich adsorption isotherms for the (a) tartrazine-AC and (b) tartrazine-CH adsorption systems, at different temperatures.

is a measure of the position of equilibrium in the adsorption process and can be generally expressed by two of the most popular isotherm theories, namely, the Freundlich and the Langmuir adsorption isotherms. In this work, attempts have been made to analyze adsorption by these two models. Linear regression was used to determine the best fitting model.

**3.8.1.** *Freundlich Isotherm.* The equilibrium data obtained at varying adsorbent dosage and fixed initial dye concentration conform to the Freundlich isotherm model<sup>41</sup> expressed by the equation

$$\log q_{\rm e} = \log K_{\rm f} + 1/n \log C_{\rm e} \tag{2}$$

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>), and  $K_f$  and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

When log  $q_e$  is plotted against log  $C_e$  at three different temperatures, (30, 40, and 50) °C, straight lines with slope 1/nare obtained (Figures 8a and b). Correlation coefficients ranged from 0.93 to 0.969 for the AC-tartrazine system and 0.90 to 0.97 for the CH-tartrazine system, which clearly specifies that the adsorption of tartrazine over both the adsorbents follows the Freundlich isotherm. From these plots, the Freundlich constants  $K_f$  and n are calculated, and the values of these at different temperatures are also presented in Table 1.

**3.8.2.** Langmuir Isotherm. To evaluate the thermodynamic parameters associated with the dye adsorption over AC and CH, sorption data of tartrazine by AC and CH have been correlated with the Langmuir model.<sup>42</sup> The experimental values of the Langmuir constants were evaluated at temperatures of (30, 40, and 50) °C using the well-known linear form of the Langmuir adsorption isotherm equation,

$$1/q_{\rm e} = 1/Q^{\rm o} + 1/(bQ^{\rm o}C_{\rm e})$$
 (3)

where  $q_e$  is the amount of tartrazine adsorbed (mol·g<sup>-1</sup>),  $C_e$  is the equilibrium concentration of the tartrazine (mol·L<sup>-1</sup>), and  $Q^\circ$  and *b* are Langmuir constants related to the maximum adsorption capacity and energy of adsorption, respectively. When  $1/q_e$  is plotted against  $1/C_e$  at the three different temperatures, straight lines with slope  $1/(bQ^\circ)$  and intercept  $1/Q^\circ$ are obtained, and correlation coefficients ranged from 0.87 to 0.92 for the AC-tartrazine system and 0.93 to 0.97 for the CHtartrazine system, which shows that the adsorption of tartrazine follows the Langmuir isotherm, (Figures 9a,b) for both adsorbents. Langmuir constants are calculated, and the values of these constants at (30, 40, and 50) °C are given in Table 2.

The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor for equilibrium parameter,  $R_L$ ,<sup>43,44</sup> defined as follows:

$$R_{\rm L} = 1/(1 + bC_0) \tag{4}$$

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, irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ), or unfavorable ( $R_L > 1$ ), and values of the separation factor for both adsorbents are presented in Table 3. It is clear from the Table that all of the values of  $R_L$  are less than unity, confirming thereby the favorable adsorption process in both cases.

**3.9.** Thermodynamic Parameters. The thermodynamic parameters obtained for both adsorption systems were also calculated using the following equations.

$$\Delta G^{\circ} = -RT \ln b \tag{5}$$

$$\Delta H^{\circ} = -R(T_2T_1)/(T_2 - T_1) \ln b_2/b_1$$
 (6)

$$\Delta S^{\circ} = \Delta H^{\circ} - \Delta G^{\circ}/T \tag{7}$$

 $\Delta G^{\circ}$  is the change in Gibbs energy,  $\Delta H^{\circ}$  is the change in enthalpy, and  $\Delta S^{\circ}$  is the change in entropy; *b*, *b*<sub>1</sub>, and *b*<sub>2</sub> are Langmuir constants at (30, 40, and 50) °C, respectively, and were obtained from the slopes of the Langmuir isotherms. The negative Gibbs energy values indicate the feasibility of the process and its spontaneous nature in both cases. The change in enthalpy  $\Delta H^{\circ}$  for tartrazine adsorption on AC was found to be positive, which confirms the endothermic nature of adsorption, while on CH was found to be negative, which confirms the exothermic nature of adsorption. The positive value of entropy shows the increased randomness at the AC/tartrazine interface and good affinity of AC toward the dye, while the negative value of entropy shows the decreased randomness at the CH/tartrazine interface, reflects the affinity of CH toward the dye, and also suggests the probability of favorable adsorp-

 Table 1. Freundlich Constants for the Removal of Tartrazine over

 Activated Carbon and Coconut Husk

	AC			СН		
	$K_{\mathrm{f}}$			$K_{ m f}$		
temperature	$(\operatorname{mol} \cdot g^{-1}) \cdot L \cdot \operatorname{mol}^{-1/n}$	п	$R^2$	$(\operatorname{mol} \cdot g^{-1}) \cdot L \cdot \operatorname{mol}^{-1/n}$	п	$R^2$
30 °C	71.779	2.346	0.9435	20.864	1.171	0.9085
40 °C	115.39	2.717	0.9699	8.302	1.050	0.9798
50 °C	98.764	2.645	0.9324	27.726	1.172	0.9378



**Figure 9.** Langmuir adsorption isotherm for the (a) tartrazine-AC and (b) tartrazine-activated CH adsorption systems at different temperatures.

 Table 2. Langmuir Constants for the Removal of Tartrazine over

 Activated Carbon and Coconut Husk

	AC			СН		
	b	$Q^{\circ}$		b	$Q^{\circ}$	
temperature	$L \cdot mol^{-1}$	$mol \cdot g^{-1}$	$R^2$	$\overline{L \cdot mol^{-1}}$	$mol \cdot g^{-1}$	$R^2$
30 °C 40 °C 50 °C	64.142 91.737 52.008	$\begin{array}{c} 25.60 \cdot 10^{3} \\ 25.77 \cdot 10^{3} \\ 34.77 \cdot 10^{3} \end{array}$	0.9232 0.8764 0.9042	6.198 3.423 8.556	$\begin{array}{c} 4.312 \cdot 10^{3} \\ 6.390 \cdot 10^{3} \\ 2.460 \cdot 10^{3} \end{array}$	0.9435 0.9699 0.9324

Table 3.  $R_{\rm L}$  Values Obtained at Different Temperatures for Tartrazine Activated Carbon and Coconut Husk

	$R_{\rm L}$ values			
adsorbent	30 °C	40 °C	50 °C	
AC	0.9511	0.7989	0.8243	
CH	0.9992	0.9989	0.9970	

	$-\Delta G^{\circ} (\text{kJ} \cdot \text{mol}^{-1})$			$\Delta H^{\circ}$ (kJ·mol <sup>-1</sup> )	$\Delta S^{\circ}$ (J·K <sup>-1</sup> ·mol)
adsorbent	30 °C	40 °C	50 °C	(30 °C)	(30 °C)
AC	$3.81 \cdot 10^3$	$7.62 \cdot 10^3$	$7.42 \cdot 10^3$	$13.89 \cdot 10^{3}$	$0.155 \cdot 10^3$
CH	$1.17 \cdot 10^{3}$	$0.642 \cdot 10^3$	$0.845 \cdot 10^3$	$-5.67 \cdot 10^{3}$	$-22.60 \cdot 10^{3}$

tion. The values of  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$ , and  $\Delta S^{\circ}$  are consistent with the results presented in Table 4.

**3.10.** Adsorption Kinetics. The successful application of an adsorption technique demands the development of inexpensive, nontoxic, readily available adsorbents of known kinetic parameters and sorption characteristics. Therefore, kinetic studies were carried out at three different temperatures of (30, 40, and 50) °C for both adsorbents wherein the extent of adsorption was analyzed at regular time intervals. To determine the specific rate constant of tartrazine-AC and



**Figure 10.** Lagergren plots for (a) tartrazine-AC and (b) tartrazine-activated CH adsorption system at different temperatures.

Table 5. Rate Constants  $k_{\rm ad}$  for the Removal of Tartrazine over Activated Carbon and Coconut Husk

	$k_{\rm ad} \ ({\rm min}^{-1})$		$k_{ad} (min^{-1})$	
temperature	(AC)	$R^2$	(CH)	$R^2$
30 °C	$12.85 \cdot 10^{-2}$	0.9824	$1.42 \cdot 10^{-2}$	0.9148
40 °C	$10.68 \cdot 10^{-2}$	0.9851	$1.22 \cdot 10^{-2}$	0.8786
50 °C	$7.55 \cdot 10^{-2}$	0.9368	$1.28 \cdot 10^{-2}$	0.9760

tartrazine-CH systems, the well-known Lagergren first-order rate equation was employed.

$$\log(q_{\rm e} - q_{\rm f}) = \log q_{\rm e} - k_{\rm ad} t/2.303 \tag{8}$$

where  $q_e$  and  $q_t$  signify the amount adsorbed at equilibrium and at time *t*, respectively. For both systems, the graphs 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 with high correlation coefficients (> 0.98) (Figure 10 part a for AC and part b for CH). The  $k_{ad}$ values evaluated and correlation coefficients for each system from the respective Lagergren plots are presented in Table 5.

#### 4. Desorption Studies

Regeneration and recycling is the most significant aspect of the adsorption study for an economical technology. After determining the adsorption profile, the possibility of recycling the adsorbent is investigated. An adsorption column chromatography method<sup>45</sup> was adopted. A portion of 400 mg of AC and CH was packed in the column separately. The length of the packing in the column was set up to 4.5 cm. Three different concentrations of NaOH, that is, (1.0, 0.1, and 0.01) M as eluent,



Figure 11. Desorption of tartrazine dye from (a) AC and (b) CH using different concentrations of NaOH.

were used, 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 Figure 11a,b that the maximum dye (99 %) desorbed from AC and 92 % of dye desorbed from CH with 1.0 M NaOH.

#### 5. Chemical Oxygen Demand

After adsorption treatment, both colored and treated solutions were subjected to measure the pollution strength of the wastewater. These compounds have very high COD values along with intense color. Therefore, initial and final COD tests were necessary to get an idea of the pollution strength. A 2 h open reflux method<sup>46</sup> was applied for the COD determination, and it was found that for the dye solutions COD values show that a significant decrease from (1380 to 156) mg·L<sup>-1</sup> and 205 mg·L<sup>-1</sup> when adsorbed over AC and CH, respectively, was observed, indicating less toxicity of the treated products in comparison to the original dye.

#### 6. Summary

The results revealed that the CH waste material was efficiently utilized as an adsorbent for the removal of the dye tartrazine. Langmuir and Freundlich isotherms fitted very well both the adsorbents within the temperature and concentration ranges studied. The suitability of the kinetic models for the adsorption of dye on AC and CH was also discussed. It was clear that the adsorption kinetics of the dye to AC and CH obeyed pseudo first-order adsorption kinetics. The reduction of the COD of the wastewater suggests a lower toxicity of dye with color removal. Thermodynamic parameters obtained confirm the feasibility of the process. The reduction of the COD of the wastewater suggests the lower toxicity of dye with color removal. Results clearly indicate that activated CH can act as an excellent adsorbent which is quite economic and commercially available and thus can act as a better replacement for AC. As a waste product, the use of CH as adsorbent would also solve their disposal problem.

### Literature Cited

- Weber, E.; Wolfe, N. L. Kinetic Studies of reduction of aromatic azo compounds in anaerobic sediment/water system. *Environ. Technol. Chem.* 1987, 6, 911–920.
- (2) Sivraj, R.; Namasivayam, C.; Kadirvelu, K. Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions. *Waste Manage*. 2001, 21, 105–110.
- (3) Chen, K. C.; Wu, J. Y.; Huang, C. C.; Liang, Y. M.; Hwang, S. C. J. Decolorisation of azo dye using PVA-immobilized microorganisms. *J. Biotechnol.* 2003, 101, 241–252.
- (4) Gupta, V. K.; Mittal, A.; Jain, R.; Mathur, M.; Sikarwar, S. Adsorption of Safranine-T from waste water using waste materials-activated carbon and activated rice husks. J. Colloid Interface Sci. 2006, 303, 80–86.
- (5) Jain, A. K.; Gupta, V. K.; Bhatnagar, A.; Jain, S.; Suhas. A comparative assessment of adsorbents prepared from industrial wastes for the removal of cationic dye. *J. Indian Chem. Soc.* **2003**, *80*, 267–270.
- (6) Gupta, V. K.; Mittal, A.; Jain, R.; Mathur, M.; Sikarwar, S. Adsorption of Safranine-T from waste water using waste materials-activated carbon and activated rice husks. J. Colloid Interface Sci. 2006, 303, 80–86.
- (7) Gupta, V. K.; Ali, I.; Suhas; Saini, V. K. Adsorption of 2, 4 D and carbofuran pesticides using fertilizer and steel industry wastes. J. Colloid Interface Sci. 2006, 299, 556–563.
- (8) Gupta, V. K.; Jain, R.; Varshney, S. Removal of reactofix golden yellow 3RFN from aqueous solution using wheat husk- An agricultural waste. J. Hazard. Mater. 2007, 142, 443–448.
- (9) Gupta, V. K.; Ali, I.; Saini, V. K. Adsorption studies on the removal of Vertigo Blue 49 and Orange DNA 13 from aqueous solutions using carbon slurry developed from a waste material. *J. Colloid Interface Sci.* 2007, *315* (1), 87–93.
- (10) Ali, I.; Gupta, V. K. Advances in water treatment by adsorption technology. *Nat. Protocols* **2007**, *1*, 2661–2667.
- (11) Gupta, V. K.; Mittal, A.; Jain, R.; Mathur, M.; Sikarwar, S. Photochemical degradation of the hazardous dye Safranin-T using TiO<sub>2</sub> catalyst. J. Colloid Interface Sci. 2007, 309, 460–465.
- (12) Gupta, V. K.; Mittal, A.; Kurup, L.; Mittal, J. Adsorption of basic fuchsin using waste materials—bottom ash and deoiled soya—as adsorbents. J. Colloid Interface Sci. 2008, 319 (1), 30–39.
- (13) Gupta, V. K.; Mittal, A.; Gajbe, V. Adsorption and desorption studies of a water soluble dye, Quinoline Yellow, using waste materials. J. Colloid Interface Sci. 2004, 284, 89–98.
- (14) Nigam, P.; Armour, G.; Banat, I. M.; Singh, D.; Marchant, R. Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues. *Bioresour. Technol.* 2000, 72, 219– 226.
- (15) Chandran, C. B.; Singh, D.; Nigam, P. Remediation of Textile Effluent Using Agricultural Residues. *Appl. Biochem. Biotechnol.* 2002, 102, 207–212.
- (16) Ho, Y. S.; Chiang, T. H.; Hsueh, Y. M. Removal of basic dye from aqueous solution using tree fern as a biosorbent. *Process Biochem.* 2005, 40, 119–124.
- (17) Ho, Y. S.; Chiu, W. T.; Wang, C. C. Regression analysis for the sorption isotherms of basic dyes on sugarcane dust. *Environ Int.* 2005, 96, 1285–1291.
- (18) Sekar, M.; Sakthi, V.; Rengaraj, S. Kinetics and equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell. *J. Colloid Interface Sci.* 2004, 279, 307–313.
- (19) Stephen, B. I.; Sulochana, N. Basic dye adsorption on a low cost carbonaceous sorbent — kinetic and equilibrium studies. *Indian* J. Chem. Technol. 2002, 9, 201–208.
- (20) Stephen, B. I.; Sulochana, N. Use of jackfruit peel carbon (JPC) for adsorption of rhodamine- B, a basic dye from aqueous solution. *Indian J. Chem. Technol.* 2006, *13*, 17–23.
- (21) Kumar, K. V.; Sivanesan, S.; Ramamurthi, V. Adsorption of malachite green onto pithophora sp., a fresh water algae: equilibrium and kinetic modelling. *Process Biochem.* 2005, 40, 2865–2872.
- (22) Kumar, K. V.; Kumaran, A. Removal of methylene blue by mango seed kernel powder. J. Biochem. Eng. 2005, 27, 83–93.
- (23) Moutinho, I. L. D.; Bertges, L. C. Prolonged use of the food dye tartrazine (FD&C yellow no. 5) and its effects on the gastric mucosa of Wistar rats. *Braz. J. Biol.* 2007, 67, 141–145.

- (24) Borzelleca, J. F.; Hollazan, J. B. Chronic toxicity/carcinogenicity studies of FD & C yellow no. 5 (tartrazine) in rats. *Food Chem. Toxicol.* **1988**, 26, 175–190.
- (25) Collins, T. F. X.; Black, T. N.; Brown, L. H.; Bulhack, P. Study of the teratogenic potential of FD & C Yellow no. 5 when given by gavage to rats. *Food Chem. Toxicol.* **1990**, *28*, 821–827.
- (26) Collins, T. F. X.; Black, T. N.; Bulhack, P.; O'Donnell, M. W. Study of the teratogenic potencial of FD & C Yellow no. 5 when given in drinking-water. *Food Chem. Toxicol.* **1992**, *30*, 263–268.
- (27) Sasaki, Y. U. F.; Kawaguchi, S.; Kamaya, A.; Ohshita, M.; Kabasawa, K.; Iwama, K.; Taniguchi, K.; Tsuda, S. The comet assay with 8 mouse organs: results with 39 currently used food additives. *Mutat. Res.* 2002, *519*, 103–119.
- (28) Nigam, P.; Banut, L. M.; Singh, A. D.; Marchant, R. Microbial process for the decolorization of textile effluent containing azo, diazo and reactive dyes. *Process Biochem.* **1996**, *31*, 435–442.
- (29) Manju, G. N.; Raji, C.; Anirudhan, T. S. Evaluation of coconut husk carbon for the removal of arsenic from water. *Water Res.* 1998, 32 (10), 3062–3070.
- (30) Tay, J. H.; Chen, X. G.; Jayaseelam, S.; Graham, N. Optimising the preparation of activated carbon from digested sewage sludge and coconut husk. *Chemosphere* 2001, 44, 45–51.
- (31) Phan, N. H.; Rio, S.; Faur, C.; Coq, L. L.; Cloivec, P. L.; Nguyen, T. H. Production of fibrous activated carbon from natural cellulose (jute, coconut) fibres for water treatment application. *Carbon* 2006, 44, 2569–2577.
- (32) Tan, I. A. W.; Hameed, B. H.; Ahmad, A. L. Optimisation of preparation conditions for activated carbon from coconut husk using response surface methodology. *Chem. Eng. J.* 2008, 137, 462–470.
- (33) Raghuvanshi, S. P.; Singh, R.; Kaushik, C. P.; Raghav, A. K. Kinetics study of methylene blue dye bioadsorption on baggase. *Int. J. Appl. Ecol. Environ. Res.* 2004, 2, 35–43.
- (34) Jain, A. K.; Gupta, V. K.; Bhatnagar, A.; Suhas. A comparative study of adsorbents prepared from industrial wastes for removal of dyes. *Sep. Sci. Technol.* 2003, *38*, 463–481.
- (35) Gupta, V. K.; Mittal, A.; Krishnan, L.; Mittal, J. 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.* **2006**, *45*, 446–1453.

- (36) Gupta, V. K.; Mittal, A.; Krishnan, L.; Mittal, J. Adsorption treatment and recovery of the hazardous dye, Brilliant Blue FCF, over bottom ash and de-oiled soya. J. Colloid Interface Sci. 2006, 293 (1), 16–26.
- (37) Wang, S.; Boyjoo, Y.; Choueib, A.; Zhu, Z. H. Removal of dyes from aqueous solution using fly ash and red mud. *Water Res.* 2005, *39*, 129–138.
- (38) Ajmal, A.; Rao, R. A. K.; Ahmad, R. Adsorption studies on citrus reticulate (fruit peel of orange): removal of Ni(II) from electroplating wastewater. J. Hazard. Mater. 2000, B79, 117–131.
- (39) Nuhoglu, Y.; Oguz, E. Removal of Cu(II) from aqueous solutions by biosorption on the cone biomass of Thuja Orientalis. *Process Biochem.* 2003, 38, 1627–1631.
- (40) Gupta, V. K. Suhas; Application of low cost adsorbents for dye removal- A review. J. Environ. Manage. 2009, 90, 2313–2342.
- (41) Freundlich, H. M. F. Ueber die adsorption in lö sungen. Z. Phys. Chem. (Leipzig) 1906, 57A, 385–470.
- (42) Langmuir, I. The constitution and fundamental properties of solids and liquids. Part I. solids. J. Am. Chem. Soc. 1916, 38, 2221–2295.
- (43) Gupta, V. K.; Rastogi, A. Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: kinetics and equilibrium studies. *J. Hazard. Mater.* **2008**, *152* (1), 407–414.
- (44) Jain, A. K.; Gupta, V. K.; Bhatnagar, A.; Suhas. Utilization of industrial waste products as adsorbents for the removal of dyes. *J. Hazard. Mater.* 2003, 50, 517–528.
- (45) Gupta, V. K.; Mohan, D.; Sharma, S.; Park, K. T. Removal of Chromium (VI) from Electroplating Industry Wastewater Using Bagasse fly ash - A sugar Industry waste material. *The Environmentalist* **1999**, *19* (2), 129–136.
- (46) APHA. Standard methods for water and wastewater examination, 19th ed.; American Public Health Association: Washington, DC, 1995.

Received for review June 13, 2010. Accepted July 24, 2010. One of the authors (A.N.) is thankful to the Ministry of Human Resource Development (MHRD), New Delhi, India, for financial support.

JE100649H