

Removal of acid red-94 from aqueous solution using sugar cane dust: An agro-industry waste

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(Received 20 July 2010 • accepted 24 December 2010)

Abstract—The feasibility for the removal of Acid Red-94 by sugar cane dust, an agro-industry waste, has been investigated as an alternative for costly adsorbents. The effect of various experimental parameters (adsorbate concentration, solution pH and temperature) on removal of Acid Red-94 has been studied under batch mode of operation. Maximum removal upto 98.73% was achieved at a pH value of 2.0 and temperature 19 ± 0.5 °C in case of 10.0 mg/l initial dye concentration. Adsorption kinetics has been described by Lagergren equation and adsorption isotherms by classical Langmuir and Freundlich models. The kinetic studies suggest that the rate of uptake of Acid Red-94 on sugar cane dust was mainly diffusion controlled. Various thermodynamic parameters have been calculated and the temperature dependence indicates exothermic nature of adsorption process. The results indicate that sugar cane dust could be used as an eco-friendly and cost-effective adsorbent in the removal of Acid Red-94 from aqueous solution.

Key words: Acid Red-94, Sugar Cane Dust, Batch Mode Operation, Adsorption Kinetics, Isotherms and Thermodynamics

INTRODUCTION

Rapid industrialization in India has resulted in ever-increasing water pollution by discharging of effluents in natural water bodies. Among various industries, the carpet and textile industries in India use dyes and pigments to color their products and discharge a huge amount of waste water. The removal of color from these effluents is one of the growing concerns of environmental issues. The discharge of colored waste water to natural water bodies is not only aesthetically objectionable, but also because it prevents reoxygenation and reduces the penetration of sunlight through the water body. As a result, it disturbs the biological activity of aquatic life. The removal of synthetic dyes is of great concern, since some of the dyes and their degradation products or intermediates may be carcinogenic and toxic [1]. These compounds retard photosynthesis, inhibit the growth of aquatic biota and interfere with oxygen solubility in water body [2]. Carpet and textile dyes in general are non-biodegradable under aerobic conditions. Hence, decolorization of dye house effluent has become an urgent need of the time and important aspect of carpet and textile wastewater treatment. In recent years, much attention has been focused on treating such effluents prior to their discharge and developing an appropriate technology to check the growing impact of water pollution.

Recently, a number of conventional methods have been used for wastewater treatment, such as precipitation, ion exchange, electrochemical reduction, flocculation, electroflotation, irradiation, ozonation and katox treatment, but these methods involve large liquid surface area and long detention period. Adsorption has an edge over the above methods due to being sludge free and having ease of operation, low initial cost, simple design and insensitivity to toxic sub-

stances. Most widely used adsorbent, activated carbon, was first proposed by Watanabe and Ogawa [3] and later on used by many workers due to its large surface area and high adsorption capacity [4,5], but its high operating cost and expensive regeneration hamper its large scale application. This has led to further studies for cheaper and easily available substitutions with two-fold objectives: to replace activated carbon with cheaper alternatives and to utilize various waste products for the purpose. Various low-cost and waste materials, either directly or through carbonization, have been used for adsorptive scavenging of pollutants. Use of low cost materials such as fly ash and red mud [6], clay [7], ferrofluid-modified saw dust [8], orange peel [9], barley husk [10], coalchar [11] has been recently reported. Many workers have also prepared activated carbon from locally available waste materials and used them for wastewater treatment such as parthenium [12,13], coir pith [14], palm nut shells, cashew nut shells and broom sticks [15], silk cotton hull, coconut tree saw dust, sago waste, maize cob and banana pith [16], used tea leaves [17], mahogani saw dust [18], *Prsopis cineraria* saw dust [19], rice husk [20] and bagasse [21]. In the present study, sugar cane dust (SCD) produced by sugar mills was used as an adsorbent for removal of Acid Red-94 (AR-94) from aqueous solution. Not only is SCD available abundantly at no or very low cost but it also reduces the disposal problem of wastes. The experiments were conducted in batch mode to determine the factors (contact time, pH, initial dye concentration and temperature) affecting adsorption and kinetics of the process. The optimum operating conditions, equilibrium data and adsorption kinetics for removal of AR-94 using SCD were also obtained.

MATERIALS AND METHODS

All chemicals were purchased from E. Merck, India. Chemicals used for preparation of reagent solutions were of analytical reagent

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grade. The stock solution, reagent solutions and diluted samples were prepared using double-distilled water. Stock solution of dye (1,000 mg/l) was prepared by dissolving AR-94 in distilled water. The stock solution was then diluted with distilled water to obtain desired concentrations and analyzed spectrophotometrically (UV/Visible spectrophotometer-118, Systronics, Ahmedabad, India) at their respective λ_{max} (548 nm) carefully. The pH of the adsorbent-adsorbate system was adjusted by using 0.1 N HCl or 0.1 N NaOH. The pH of the solution was measured by using a pH meter (LI 120, Elico India). A thermostatic water bath shaker (REMI Equipments Ltd., Mumbai, India) for shaking the samples was used to do the batch adsorption experiments. An oven (S. M. Scientific Instruments Pvt. Ltd., New Delhi, India) was used for drying the adsorbent.

1. Adsorbent

The SCD was procured from The Kashi Co-operative Sugar Mill, Aurai, S.R.N. Bhadohi, U.P., India. It was washed with tap water followed by distilled water, dried under sunlight until all the moisture evaporated and finally placed in a hot air oven at 60 °C overnight and then ground to fine powder. The resulting material was passed through 74 μ m sieve and stored in a vacuum desiccator for further use.

2. Adsorbate

The commercial dye, AR-94 (C.I.-45440) from E. Merck, India was used as such without any treatment to prepare adsorbate solution. It is di-sodium salt of 4, 5, 6, 7-tetrachloro-2', 4', 5', 7'-tetraiodofluorescein and can be regarded as a dianionic dye. It has a molecular weight of 1,017.65.

3. Instruments Used for Adsorbent Characterization

Chemical analysis of SCD was performed by applying Indian standard methods of fired clay and silica refractory materials. Fourier transform infrared (FTIR) spectra of the adsorbent were recorded in KBr using Varian FTIR - 3100 spectrophotometer. X-ray diffractogram was obtained by Rigaku DMAX - III rotating diffractometer operating at 12 KW and 40 KV. The average particle size distribution was measured by HIAC - 320 model (ROYCO Instrument Div., USA). The surface area was determined by BET method using low temperature N_2 gas adsorption technique. The porosity and bulk density were determined by mercury porosimeter and densitometer or specific gravity bottles, respectively.

4. Adsorption Studies

Batch adsorption experiments were carried out by mixing 100 mg SCD with 50 ml of aqueous solution of AR-94 of desired initial concentration, temperature and pH in a series of 100 ml-Erlenmeyer flasks. The suspension was shaken at a fixed agitation speed of 175 rpm in a thermostatic water bath shaker. The progress of adsorption was determined at different time intervals until saturation was achieved. For this purpose, the samples were withdrawn from shaker at predetermined time intervals and the dye solution was separated from adsorbent by filtration followed by centrifugation (Centrifuge Machine, H32KS, Modern Appliances, Ambala, India) at 3,500 rpm for 10 min. The residual dye concentration was estimated spectrophotometrically by analyzing supernatant liquid at a corresponding λ_{max} (548 nm) and comparing with carefully prepared standard calibration curve of the dye. Blanks were also run without adsorbent under similar conditions of concentration, temperature and pH in all cases in order to find background adsorption, if any, and corrections were made accordingly. The extent of removal of dye has

been calculated by using the following equations:

$$\text{Percentage removal} = [(C_i - C_e)/C_i] \times 100 \quad (1)$$

$$\text{Amount adsorbed (q)} = X/m = (C_i - C_e)/m \quad (2)$$

Where, C_i = initial concentration of the dye [mg/l]

C_e = equilibrium concentration of the dye [mg/l]

X = amount of dye adsorbed [mg/l]

m = mass of adsorbent [g/l]

The effects of contact time (0-80 min), concentration (10-50 mg/l), initial pH of the solution (2-10), and temperature (19-50 °C with ± 0.5 °C) on removal of AR-94 from aqueous solution were studied. Adsorption kinetics and isotherms for removal of dye were also investigated at different temperatures. The precision of the analytical procedure, expressed as relative standard deviation, ranged from 3 to 5%. All experiments were carried out in duplicate and the mean values are reported.

5. Regeneration Experiments

The spent SCD must be regenerated in order to make the adsorbent efficient for repeated use in wastewater treatment process. To be economically feasible adsorbent, SCD was subjected to adsorption-desorption operation up to three cycles. For desorption, the dye-loaded SCD was contacted with 100 ml of 0.1 N NaOH as eluent for 2 h on the thermostatic water bath shaker at 175 rpm. The SCD after desorption was washed extensively with distilled water and used again for the next cycle.

RESULTS AND DISCUSSION

1. Characterization of Adsorbent

The SCD was found to be stable in water, dilute acids and bases. The mean particle diameter was found to be 70×10^{-6} m. The surface area obtained from the N_2 gas adsorption technique was calculated as 1,318.28 m²/g. The bulk density and apparent porosity were found to be 650 kg/m³ and 6.23, respectively. The composition of SCD was cellulose- 54.75%, lignin- 30.32%, SiO₂- 4.25%, Fe₂O₃- 0.45%, Al₂O₃- 0.05%, and moisture- 8.50% by weight (Table 1). The spectra of SCD were measured by an FTIR spectrometer in the range of wave number from 400 to 4,000 cm⁻¹. The important IR bands of SCD along with their possible assignments are presented in Table 2. From FTIR analysis, it was observed that functional groups like O-H, C-H, >C=O, Fe-O, Si-O, Al-O, and >C=C< were present on the SCD surface. The band 3,421 cm⁻¹ is generally attributed to the surface hydroxyl groups, while the band around 2,923 cm⁻¹ is due to C-H stretching vibrations of the cellulose. The

Table 1. Physicochemical properties of sugar cane dust

Constituents	Percentage	Parameter	Value
Moisture	08.50	pH	8.05
Cellulose	54.75	Particle size (μ m)	74
Lignin	30.32	Surface area (m ² /g)	1318.28
SiO ₂	04.25	Mean particle diameter (m)	70×10^{-6}
Fe ₂ O ₃	00.45	Bulk density (kg/m ³)	650
Al ₂ O ₃	00.05	Apparent porosity	6.23

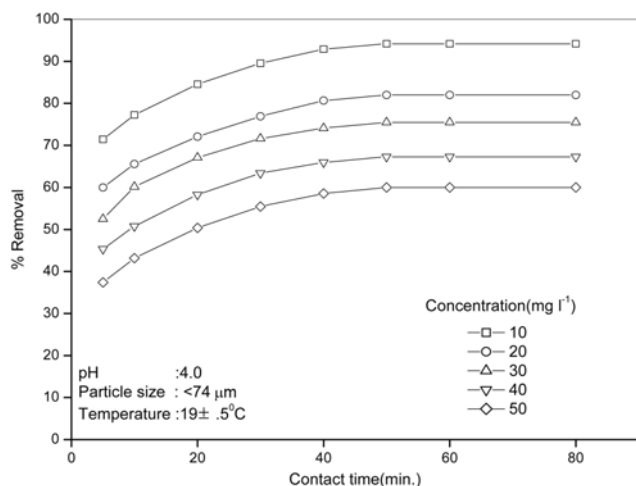
Table 2. Important IR bands of sugar cane dust along with their possible assignments

Band position (cm ⁻¹)	Assignment
3421	O-H
2923	C-H
1734	>C=O
1627	>C=C<
1109	Si-O
1053	Al-O
815	Fe-O

Table 3. 'd' values of sugar cane dust

d (Å)	Possible components
4.30	Cellulose
3.97	Cellulose
3.39	Cellulose
3.03	Cellulose
2.47	Cellulose
2.24	Quartz
1.54	Quartz
1.41	Quartz
1.49	Haematite

strong band 1,734 cm⁻¹ is due to C=O stretching vibrations in lignin and carboxyl groups. The band at around 1,627 cm⁻¹ is caused by C=C stretching vibrations and this is an indication of carbonyl containing group formation. The band at 1,109 cm⁻¹ is observed due to the Si-O vibrations. The bands around 1,053 and 815 cm⁻¹ are attributed due to the stretching of Al-O and Fe-O, respectively in quartz and haematite. It is expected that dye will be removed by C-H, carbonyl and carboxyl groups. It is also believed that oxide from surface hydroxyl compounds with dye gives positively or negatively charged surface. The presence of cellulose, lignin, quartz and haematite was indicated by the X-ray diffraction pattern of SCD d-spacing values (Table 3).

**Fig. 1. Time variation of adsorbent of Acid Red 94 on sugar cane dust at different initial concentrations.**

2. Effect of Contact Time and Concentration

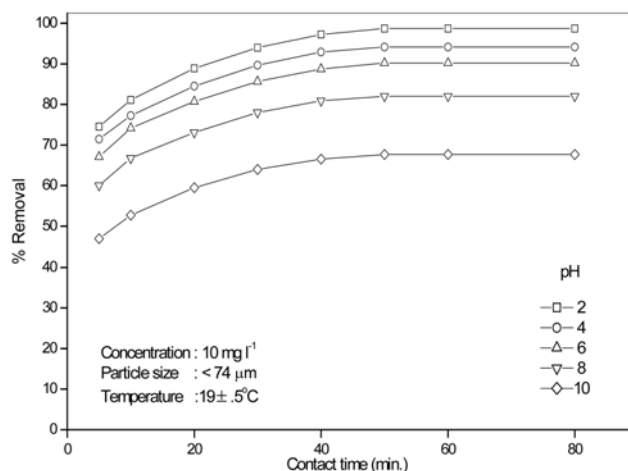
The experiments were performed as a function of time for a range of initial dye concentrations (10–50 mg/l) at a fixed adsorbent dose of 2.0 g/l at pH 4.0 and temperature of 19 ± 0.5 °C. The results are shown in Fig. 1, which clearly indicates that the removal of AR-94 by adsorption on SCD is rapid initially and attains a maximum value at 50 min and thereafter remains constant at 94.18%. It can be seen from Fig. 1 that the equilibrium time is independent of dye concentration but the uptake of dye is highly dependent on initial dye concentration. Lowering in percentage removal of dye with increase in concentration may be due to the lack of available active sites on adsorbent as well as the formation of monolayer of dye on the surface of adsorbent and also any further formation of layer is highly hindered at higher concentration. This finding is in good agreement with those reported earlier [6,22].

3. Effect of pH

The extent of adsorption is strongly dependent on the pH of medium. Therefore, the effect of pH was investigated by varying pH of the solution from 2–10 at constant temperature (19 ± 0.5 °C) and initial dye concentration of 10 mg/l. The removal decreases from 98.73 to 67.64% when the pH of medium increases from 2.0 to 10.0 (Fig. 2). The time-dependent adsorption curve was found single, smooth and continuous, i.e., curved near origin and becoming straight after equilibrium time (50 min). The decrease in adsorption with increase in pH may be due to surface hydroxylation, surface complexation and ion exchange. Another important factor is point of zero charge (pH_{ZPC}); the positive charge on the surface of adsorbent increases with decrease in pH below pH_{ZPC} of the adsorbent favoring an increase in adsorption of AR-94 (an anionic dye) from aqueous solution. Similar findings have been reported in the literature [7,21].

4. Effect of Temperature

The adsorption studies were carried out at three different temperatures, 19, 35 and 50 ± 0.5 °C, and the results are presented in Fig. 3. The removal of dye decreases from 94.18 to 77.09% as the temperature is increased from 19 to 50 ± 0.5 °C. The decrease in adsorption with rise in temperature indicates that the process is exothermic, which is due to weakening of adsorptive forces between

**Fig. 2. Time variation of adsorbent of Acid Red 94 on sugar cane dust at different pH values.**

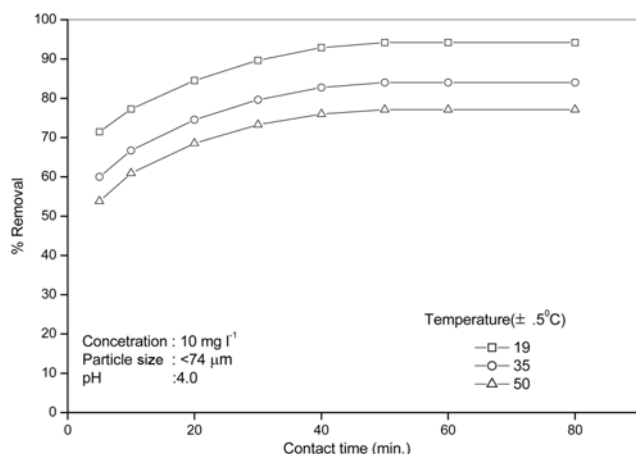


Fig. 3. Time variation of adsorbent of Acid Red 94 on sugar cane dust at different temperatures.

the active sites of adsorbate and adsorbent and also between the adjacent molecules of the adsorbed phase. Similar findings have been reported in the past [5,11].

5. Adsorption Dynamics

5-1. Adsorption Kinetics

The adsorption kinetics is quite important as it describes the solute uptake rate which in turn controls the residence time of solute uptake at the solid-liquid interface [23]. Temperature, adsorbent dose, concentration, shaking speed and pH of the medium were kept constant for all experiments. To determine the adsorption kinetics for AR-94 dye removal, the Lagergren kinetic model was tested. Pseudo first-order kinetic model of Lagergren can be expressed as [24]:

$$\log(q_e - q) = \log q_e - K_{fd} t / 2.303 \quad (3)$$

Where q_e and q (both in mg/g) are the amount of dye adsorbed at equilibrium and at any time, t , respectively, and K_{fd} is first-order adsorption rate constant (min^{-1}).

The pseudo second-order kinetic model of Lagergren can be expressed in simplified form:

$$t/q = 1/K_{sd} q_e^2 + t/q_e \quad (4)$$

Where K_{sd} is the second-order adsorption rate constant ($\text{g/mg} \cdot \text{min}$). The results for adsorption of AR-94 were fitted to Eqs. (3) and (4). The pseudo first-order kinetic model shows better correlation than the second-order kinetic model. The kinetic parameters calculated are presented in Table 4. The linear plots of $\log(q_e - q)$ vs. t in Fig. 4 also suggest the applicability of first-order kinetics of the process.

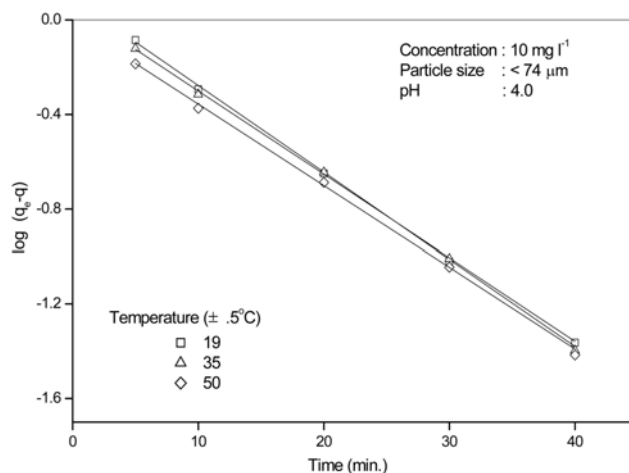


Fig. 4. Rate constant plot for adsorbent of Acid Red 94 on sugar cane dust at different temperatures.

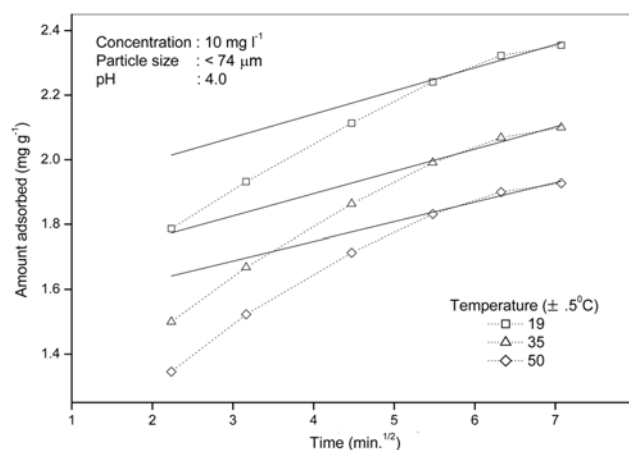


Fig. 5. Intraparticle diffusion plot for adsorbent of Acid Red 94 on sugar cane dust at different temperatures.

The rate of adsorption is highly dependent on porosity and surface area of the adsorbent. Therefore, the possibility of intraparticle diffusion cannot be overlooked during batch experiments. In the present work, the intraparticle diffusion was studied according to equation as follows [25]:

$$q = K_{id} t^{1/2} \quad (5)$$

Where, q is the amount (mg/g) of dye adsorbed at time, t and K_{id} is intraparticle diffusion rate constant ($\text{mg/g} \cdot \text{min}^{1/2}$). A plot of q vs. $t^{1/2}$ at different temperatures is shown in Fig. 5. The double nature

Table 4. Rate constant of adsorption, intraparticle rate constant and their regression coefficients for Acid Red-94 - Sugar cane dust at various temperatures

Concentration: 10 mg l ⁻¹ Particle size: <74 μm pH: 4.0						
Temperature (±0.5 °C)	First-order rate constant, K_{fd} (min ⁻¹)	Regression coefficient (R ²)	Second-order rate constant, K_{sd} (g/mg · min)	Regression coefficient (R ²)	Intraparticle rate constant, K_{id} (mg/g · min ^{1/2})	Regression coefficient (R ²)
19	0.0846	0.9797	0.3172	0.9027	0.1264	0.9725
35	0.0812	0.9784	0.3014	0.8724	0.1217	0.9631
50	0.0794	0.9678	0.2531	0.7652	0.1208	0.9806

of the plots may be due to varying extent of adsorption in initial and final stages. The initial curved portion of the plots is due to boundary layer diffusion effect, while the final linear portion is due to the intraparticle diffusion effect. The extrapolation of the linear part of the plot to the axis provides the intercept, which is proportional to the extent of boundary layer thickness: the larger the intercept, the greater is the boundary layer effect [4]. The values of K_{id} for different temperatures with R^2 values are presented in Table 4.

5-2. Adsorption Isotherm

Several equilibrium models have been developed to describe the adsorption isotherm relationships. To determine the sorption potential of adsorbent and binding energy of adsorption, the results obtained by the adsorption experiment were analyzed by Freundlich and Langmuir models.

The logarithmic form of the Freundlich isotherm can be expressed by following equation [26]:

$$\log q_e = \log K_f + 1/n \log C_e \quad (6)$$

Where, C_e is equilibrium concentration of adsorbate in mg/l, q_e is amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium and K_f , n are constants. The parameters K_f and n indicate adsorption capacity and intensity of adsorption, respectively. The Freundlich constants K_f and n were determined from the intercepts and slopes of linear plots of $\log q_e$ vs. $\log C_e$ and the results are shown in Table 5.

The Langmuir isotherm, based on monomolecular adsorbed layer at the surface of adsorbent, can be represented by the following equation [27]:

$$C_e/q_e = 1/Q^0 b + C_e/Q^0 \quad (7)$$

Where, C_e is equilibrium concentration of dye (mg/l), q_e is amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg/g), Q^0 and b are Langmuir constants indicating the sorption capacity and energy of adsorption, respectively. The values of Q^0 and b at different temperatures were determined from the slopes and intercepts of the linear plots of C_e/q_e vs. C_e . The validity of both the models was tested by the following equations:

$$m = \frac{n \sum x_i y_i - \sum x_i \sum y_i}{n \sum x_i^2 - (\sum x_i)^2} \quad (8)$$

$$c = \frac{1}{n} [\sum y_i - m \sum x_i] \quad (9)$$

Where, n is the number of pairs of x and y variables, m is slope and c is intercept. The values of m and c were determined and substituted in the straight line equation $y = mx + c$ to find the value of the Freundlich and Langmuir constants at 19, 35 and 50 °C, respec-

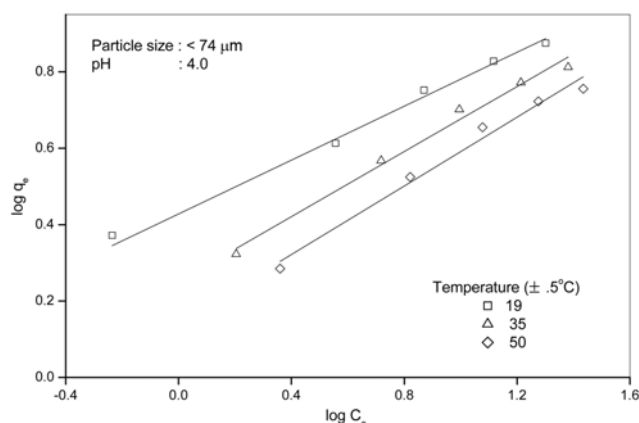


Fig. 6. Freundlich isotherm for adsorbent of Acid Red 94 on sugar cane dust at different temperatures.

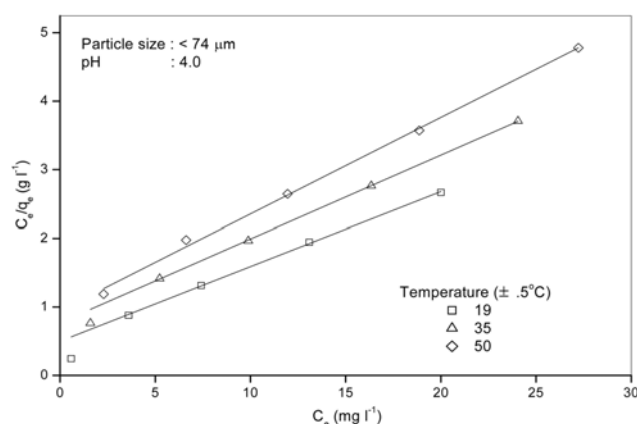


Fig. 7. Langmuir isotherm for adsorbent of Acid Red 94 on sugar cane dust at different temperatures.

tively. Both the isotherms are presented graphically in Figs. 6 and 7. The values of various constants are given in Tables 5 and 6 with their respective R^2 values. Another essential characteristic of the Langmuir model is the prediction of feasibility of the adsorption process, which is expressed in terms of dimensionless constant R_L [28]. The separation factor or equilibrium factor (R_L) can be defined by equation:

$$R_L = [1/(1 + bC_0)] \quad (10)$$

Where, b is the Langmuir constant and C_0 is the initial concentration of dye. In the present study the calculated value of R_L is found to be $0 < R_L < 1$, which indicates that sorption is favorable (Table 6). It is obvious from the Tables 5 and 6 that the values of all the con-

Table 5. Freundlich constants and their regression coefficients for Acid Red-94 - Sugar cane dust at different temperatures

Temperature (±0.5 °C)	Freundlich constants				Regression coefficient (R ²)
	K _F		n		
	Graphical value	Computer regression value	Graphical value	Computer regression value	
19	2.7930	2.7930	2.9856	2.9856	0.9957
35	1.7822	1.7822	2.3501	2.3501	0.9884
50	1.3852	1.3852	2.2234	2.2234	0.9837

Table 6. Langmuir constants, their regression coefficients and separation factors for Acid Red-94 - Sugar cane dust at different temperatures

Temperature (±0.5 °C)	Langmuir constants				Regression coefficient (R ²)	Separation factor (R _L)
	Q ^o (mg/g)		b (l/mg)			
	Graphical value	Computer regression value	Graphical value	Computer regression value		
19	8.3332	9.1707	0.3553	0.2186	0.9854	0.2196
35	7.7952	8.1920	0.1949	0.1823	0.9961	0.3391
50	7.0991	7.0991	0.1487	0.1487	0.9977	0.4021

Table 7. Changes in free energy, enthalpy, and entropy for Acid Red-94 - Sugar cane dust at various temperatures

Temperature (±0.5 °C)	ΔG ^o (kCal/mol)	ΔH ^o (kCal/mol)	ΔS ^o (kCal/mol)
19	-0.811		
35	-0.166	-9.5882	-0.0302
50	-0.120		

stants decrease with increase in temperature, indicating the exothermic nature of the process. Nearer the value of R² to unity showing the linear relationship between x and y variables confirms the applicability of both the models. However, the Langmuir model provides better correlation than the Freundlich model.

6. Thermodynamic Parameters

The effect of temperature on adsorption of AR-94 by SCD can be explained on the basis of thermodynamic parameters, such as change in standard free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o). Thermodynamic parameters are expressed by following equations [7]:

$$K_c = \frac{C_{Ae}}{C_{Fe}} \quad (11)$$

$$\Delta G^o = -RT \ln K_c \quad (12)$$

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (13)$$

Where, K_c is the equilibrium constant at temperature T, R is universal gas constant and C_{Ae}, C_{Fe} are the equilibrium concentrations of adsorbate on the adsorbent and solution, respectively. The values of thermodynamic parameters are given in Table 7. The negative values of ΔG^o indicate the feasibility of the process and spontaneous nature of the adsorption. The negative value of ΔH^o confirms the exothermic nature of the process. The negative value of ΔS^o corresponds to a decrease in degree of freedom of the adsorbed species owing to association, fixation or immobilization and suggests no significant change in the internal structure of SCD during the adsorption of AR-94.

CONCLUSION

The SCD obtained from the local sugar industry is an effective adsorbent for the removal of AR-94 from aqueous solutions. The carbonyl, carboxyl, C-H and hydroxyl are the major groups for adsorption of AR-94 on SCD from aqueous solutions. The adsorp-

tion of dye is highly dependent on temperature, pH and initial dye concentration. Isotherm data of AR-94 on SCD follows both the Freundlich and Langmuir models, but the Langmuir model has an edge over the Freundlich model. The adsorption kinetics fit to pseudo first order rate expression with the intraparticle diffusion as one of the rate determining steps. The adsorption process is exothermic with maximum removal of 98.73% at pH 2.0 and 10 mg/l initial dye concentration. Further research is needed for removal of other commercial dyes (i.e., AR-14, AR-66, AR-88, AR-114, etc.) by using the same adsorbent from industrial wastewaters.

ACKNOWLEDGEMENT

Authors thank K.N. Govt. P.G. College, Gyanpur and Banaras Hindu University, Varanasi, India for providing financial support to undertake the work.

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