Korean J. Chem. Eng., **26**(1), 102-107 (2009)

Studies on auramine dye adsorption on psidium guava leaves

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(*Received 10 February 2008 • accepted 13 June 2008*)

Abstract−Removal of auramine dye from aqueous waste solutions was investigated by using very cheap and biosorbent, withered guava tree leaves and activated carbon. Guava leaves are readily available in the western and northern parts of India throughout the year, and hence form a cost effective alternative for removal of dyes from waste waters. The optimum contact time was found to be 120 min. in a pH range of 8-9 for 92-94% removal of the dye from aqueous solutions containing 150 mg/L of auramine dye using 2 g of the adsorbent. The effect of pH, dye concentration, sorbent dosage, temperature and contact time on the dye removal efficiency has been studied. Experimental results were found to fit both Freundlich and Langmuir models. Since the dye contains a cationic species, the removal efficiency was highest in a pH range of 8-9. Continuous adsorption studies in a packed column showed 100% removal efficiency for a flow rate of 10 ml·min^{-1}. When compared with the activated carbon, it was also found that adsorbent derived from guava leaves is more efficient in removal of dye.

Key words: Auramine Dye Removal, Guava Leaves, Adsorption Isotherms, Adsorption Kinetics, Breakthrough Curve

INTRODUCTION

Various industries such as textile, paper, carpet and printing discharge their dye-containing effluents into the natural water resources leading to increase in toxicity and COD (chemical oxygen demand) and substantial reduction in the light penetration causing adverse effect on photosynthesis. Color being a visible pollutant, its presence in minute quantities also makes the water undesirable for consumption. In recent years, stringent government regulations have made it mandatory to stop such effluents, unless they are treated properly; hence, the removal of color from the effluent discharge has become environmentally important [1,2]. Among various physicochemical methods [3-6], removal of color by adsorption is gaining importance commercially due to its cost effectiveness, easy availability, simple design, high efficiency and ability to treat water with high concentration of dyes [2,7]. Activated carbon is the most appropriate choice as an adsorbent due to its high adsorption capacity for several organic molecules; however, its higher cost may be prohibitive in some cases [8-10]. Therefore, efforts are being made to investigate low-cost, biodegradable adsorbents of natural origin [11-13] for removal of dyes from waste water. In the present work, the use of withered leaves of the guava tree have been successfully demonstrated for the removal of auramine (Basic Yellow 2, see Fig. 1) dye from an aqueous solution. Auramine dye was selected because of its highly hazardous nature as indicated by its interference with the oxygen-carrying ability of blood that can cause weakness, shortness of breath and bluish color to the fingernails, nose and lips. Mere contact with auramine can irritate and may damage the eyes [6]; it is also a probable carcinogen in humans. There may be no safe level of exposure to a carcinogen, so all contact should be reduced to the lowest possible limit [14]. One of our objectives was to study the effect of various process parameters such as contact time, pH, dosage, temperature and initial concentration of auramine on the adsorption capacity of guava leaves. Also, the sorption kinetics of auramine at solid liquid interfaces has been studied under equilibrium conditions.

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EXPERIMENTAL

The naturally withered guava leaves were procured locally from the Maharashtra state (India). These were first washed to remove dirt and then dried, powdered and sieved through a 200-250 mesh. The powdered tree leaves were again heated on a hot plate for about 15 minutes at 60-70 °C for thorough drying. The characteristics of Psium Guava leaves powder are given in Table 1. Basic Yellow 2 dyes (auramine) as well as other chemicals were purchased from Merck India. The chemical structure of this dye is shown in Fig. 1.

The activated carbon granular LR grade was supplied by SD Fine-Chem (Boisar, India) in the size range 2-5 mm. It was manufac-

Table 1. Physical characteristics of psium guava leaf powder

Sr. no.	Characteristics	Value
1	Bulk density, gm·ml^{-1}	0.333
2	Surface area, m^2·gm^{-1}	1.70
3	Average particle size, microns	200
4	Matter soluble in water, %	Nil
5	Matter soluble in 1 M HCl, %	Nil
6	Matter soluble in 0.001 M NaOH, %	Nil
7	pH	6.2

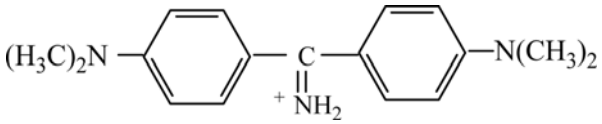

Fig. 1. Chemical structure of basic yellow 2 (auramine).

Table 2. Characteristics of granular activated carbon

Physical characteristics	
BET surface area m^2/g	579.23
Specific gravity	0.92
Bulk density g/ml	0.977
Hardness	Less than 1 (in Mohr's hardness scale)
Porosity	24.43%
Chemical compositions (wt%)	
Carbon	95.50
SiO_2	0.47
Al_2O_3	0.06
K_2O	0.51
Na_2O	0.06
CaO	1.54
MgO	0.08
Fe_2O_3	0.07
H_2O	1.20

tured from coconut shells and was treated with acid wash before delivery. These were subsequently pulverized and sieved through 18 to 44 BS mesh to get the activated carbon particles of the desired size range. The uniform-sized particles as retained on different sieves were mixed, and the average diameter was estimated to be 0.536 mm. To remove any fines attached to these particles and any leachable matter, this was further washed a number of times with distilled water. The activated carbon was considered fit for use when the distilled water obtained after washing was visibly clear. After washing the activated carbon, it was dried in an oven at 105 °C for 72 h. This time was sufficient to drive off the moisture. After drying, this was stored in a glass bottle until use. Table 3 shows the physical and chemical characteristics of activated carbon.

1. Adsorption Studies

Batch sorption studies were carried out by shaking 50 ml aqueous dye solution having concentrations in the range of 50-150 mg/*l* with various amounts of adsorbents in a glass-stoppered conical flask. The extent of color removal was monitored by change of absorbance after every 30 minutes. At the end of the desired time the solution was filtered through whatman 45 filter paper and the filtered solution was taken for analysis of the residual dye present in the solution. The absorbance measurements were made with a UV spectrophotometer (Bausch and Lomb Spectonic 20) at λ_{max}=432 nm. Sorption tests were performed in the temperature range 303 K-313 K. Effect of pH was studied in the pH range from 2 to 11.

2. Fixed Bed Adsorption Column Studies

Adsorption studies were also conducted in a continuous down-flow manner by using a glass column (60 cm×0.8 cm). The experimental set up is shown in Fig. 2. The 2 gm of guava sorbent was

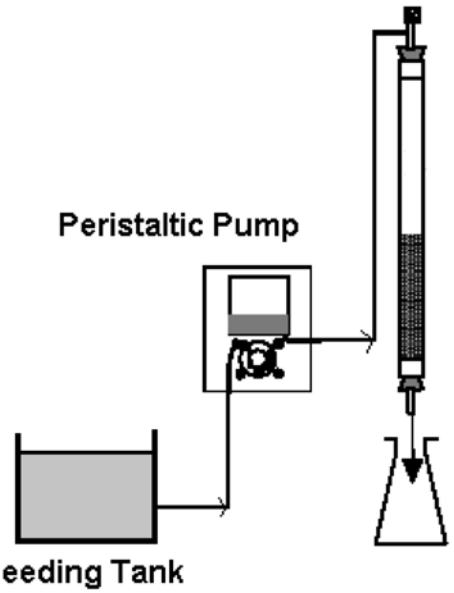

Fig. 2. The experimental setup.

suspended in distilled water for about 10 minutes and was then used for column studies; glass wool was kept at the bottom of the column to avoid the losses of sorbent with the flow of dye solution. Then the sorbent was transferred onto the glass wool in the column. Dye solution was fed into the column at a flow rate of 10 ml/min with a peristaltic pump. To determine exhaustive capacity, 50-ml fractions of the effluent were collected from the bottom of the column. The process was continued until the amount of dye in the effluent was the same as that in the feed.

RESULTS AND DISCUSSION

1. Adsorption Studies

The adsorption efficiency of auramine dye on guava leaves was evaluated by determining the percentage decrease of the absorbance at 432 nm by using the following relation (Eq. (1)).

$$\% \text{ dye removal} = \frac{A_i - A_f}{A_i} \times 100 \quad (1)$$

where A_i is the initial absorbance and A_f is the final absorbance of the dye solution.

The effect of initial concentration of dye on the percentage dye removal efficiency was studied, and the results are presented in Fig. 3(a), (b), (c). Sorption capacity was found to increase with an increase in dye concentration. Adsorption rate was very rapid during the initial period of contact, and about 81% of sorption was achieved within the first 30 minutes. However, equilibrium was attained within

Table 3. Linearized isotherm coefficients for basic yellow 2, dye

Adsorbent	Langmuir constants 30 °C		Langmuir equilibrium parameter	Freundlich constants 30 °C	
	θ^0 mg/gm mg·gm^{-1}	b L/mg L·mg^{-1}	R	K_f	1/n
Psium guava leaves	7.76	0.26	0.99	7	0.3
Activated carbon	16.66	0.14	0.98	4.75	0.34

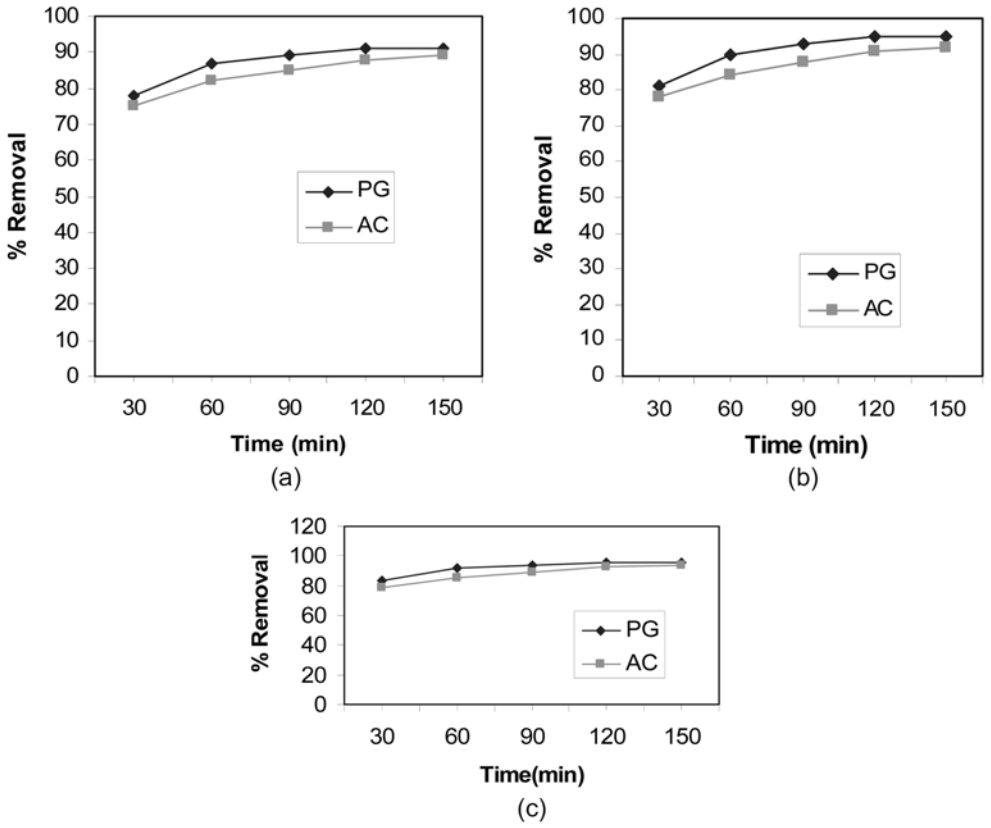

Fig. 3. (a) Effect of time and concentration on auramine dye (50 mg/lit) removal on guava. (b) Effect of time and concentration on auramine dye (100 mg/lit) removal on guava leaves. (c) Effect of time and concentration on auramine dye (150 mg/lit) removal on guava leaves.

120 minutes contact time. It was observed that adsorption was greater in guava than activated carbon.

2. Adsorption Isotherms

Adsorption is defined as the material at the interface between solid and liquid phases. The adsorption isotherm is an equilibrium relationship of adsorbent and adsorbate given by the ratio of the quantity of material adsorbed to that remaining in the solution at a constant temperature. The observed adsorption data can be fitted into one of the isotherm models that can be later used for scale up purposes [15].

The sorption data of the present work was represented by attempting both Langmuir and Freundlich isotherms. The Langmuir model can be given by the following equation.

$$1/q_e=(1/\theta^0 b)\ 1/C_e+1/\theta^0 \quad (2)$$

where,

θ_e=amount of dye adsorbed per unit weight of sorbent (mg/g)

C_e=equilibrium concentration of dye in aqueous solution (mg/L)

θ^0=maximum adsorption capacity (mg/g)

b=constant (L/mg)

The linear plots of $1/q_e$ vs $1/C_e$ at different temperatures, as shown in Fig. 4(a) and Fig. 4(b), confirmed the applicability of the Langmuir model for the system under investigation [16-19]. The applicability of the Langmuir isotherm indicates the monolayer coverage of the dye on the surface of the guava leaves. The values of θ^0 and b were determined from the plot and are given in Table 3. The essential characteristic of the Langmuir isotherm may be expressed in terms of dimensionless equilibrium parameter, R, using the following equation [20].

$$R=1/(1+bC_0) \quad (3)$$

Where b is the Langmuir constant and C_0 is the initial dye concentration (mg/L). The type of isotherm depends on the values of R, and in our case since R lies between 0 and 1, the adsorption is favorable (see Table 3) [21].

The sorption data was also fitted to the linear form of the Freundlich isotherm as represented by the following equation [22].

$$\text{Log } q_e=\log K_f+1/n \log C_e \quad (4)$$

where K_f is the adsorption capacity (unit concentrations) and 1/n adsorption intensity respectively.

Fig. 5(a) and 5(b) show a linear plot of log q_e vs. log C_e for auramine dye adsorption on guava leaves and activated carbon at room temperature. As can be seen from Table 3, the values of 1/n lie between 0.9-0.95, indicating appreciable adsorption potential of the guava leaves as an adsorbent.

3. Effect of pH

The % dye removal by adsorption on guava leaves was studied in a wide range of pH between 2-11 and the results are shown in Fig. 6. The removal of the dye was more favorable in basic medium as compared to that of acidic medium. It was observed that the sorp-

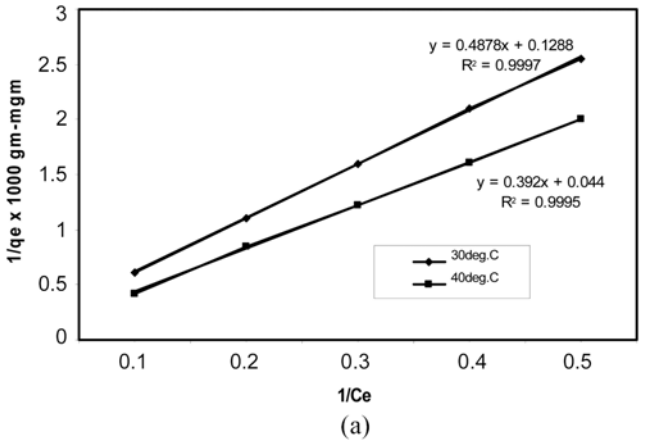

Fig. 4. (a) Langmuir adsorption isotherm of auramine dye using guava leaves. (b) Langmuir adsorption isotherm of auramine dye using activated carbon.

Table 4. Thermodynamic parameters at different temperatures

Sr. no.	Temperature, K	Auramine dye	
		−ΔG KJ/mol	ΔS J/mol
1	303	9854.9	52.00
2	313	9705.73	49.87

tion capacity of the dye increases from 59% removal at pH 2 to 92% removal at pH 9. As shown in Fig. 1, auramine dye has a cationic species ($^{+}NH_2$) which will have greater electrostatic attraction towards the negatively charged surface of the adsorbent at basic pH [23].

4. Adsorption Kinetics

A kinetic equation based on the Lagergren model was proposed to represent the observed data of auramine dye adsorption on guava leaves [24,25]. A linear form of the pseudo-first order Lagergren model is given below.

$$\log(q_e - q_t) = \log q_e - \left(\frac{K}{2.303}\right)t \quad (5)$$

where q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and at time t, respectively, and K is the pseudo-first order equilibrium adsorption constant (min^{-1}). A straight line plot of $\log(q_e - q_t)$ vs. time t for the sorption of auramine is shown in Fig. 7, confirming the first order kinetics for the adsorption of auramine dye on

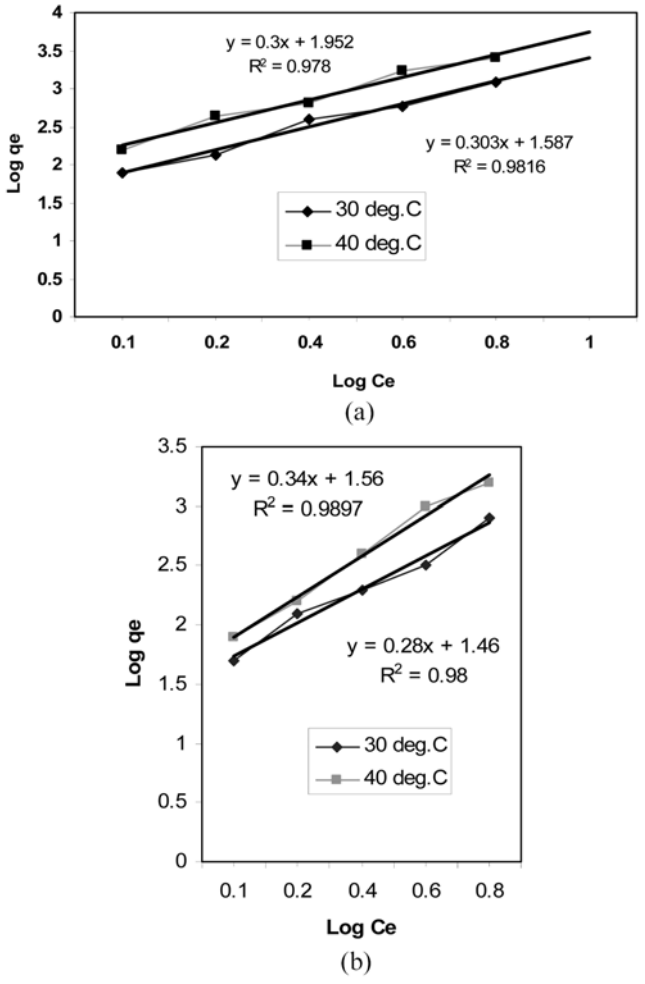

Fig. 5. (a) Freundlich adsorption isotherm for auramine dye using guava leaves. (b) Freundlich adsorption isotherm for auramine dye using activated carbon.

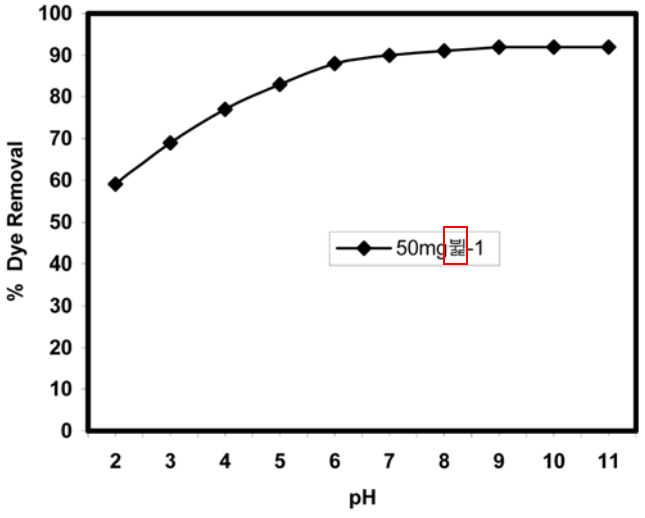

Fig. 6. Effect of pH on the adsorption of auramine dye on guava leaves.

guava leaves. The adsorption constant K calculated from this data was found to be 26.8×10^{-3} min^{-1}.

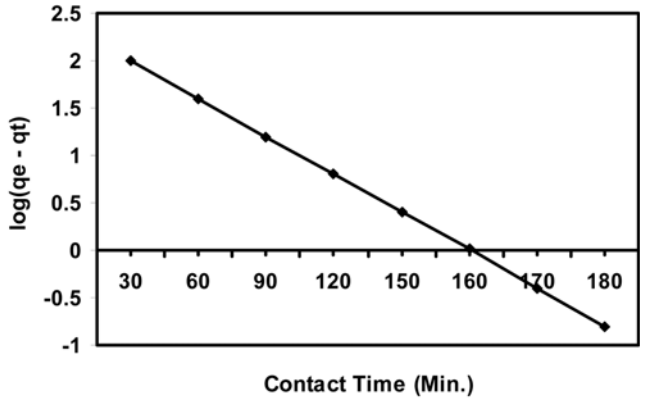

Fig. 7. Lagergren model fitting for auramine dye removal using guava leaves.

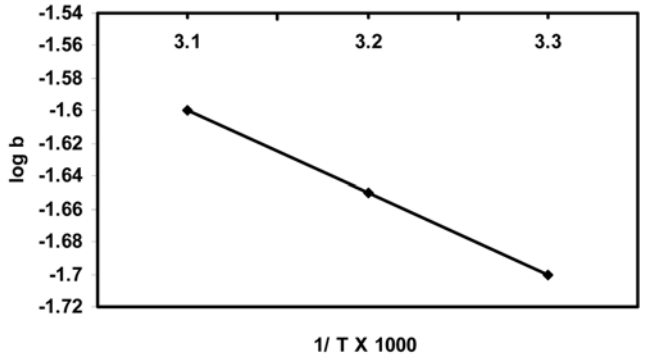

Fig. 8. Arrhenius plot for auramine dye adsorption on guava leaves.

5. Effect of Temperature

The sorption capacity of the guava leaves increased with an increase in temperature, indicating the process to be endothermic. The increase in the uptake of the dye with temperature may be due to increase in the porosity of sorbent. Also, a plot of log b vs. 1/T, as shown in Fig. 8, gave a positive ΔH confirming the endothermic nature of the process and suggested the possibility of strong binding between sorbate and sorbent. Negative values of ΔH indicate the process to be feasible and spontaneous [26], and positive values of entropy reflect the affinity of the sorbent material for the auramine dye. The change in enthalpy (ΔH), free energy (ΔG) and entropy (ΔS) of the adsorption were calculated from the following thermodynamic equations [27].

$$\ln b = \frac{\ln b - \Delta H}{RT} \tag{6}$$

$$\ln \frac{1}{b} = \frac{\Delta H}{RT} \tag{7}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{8}$$

The values of ΔG and ΔS at different temperatures are listed in Table 4.

6. Continuous Adsorption

To test the feasibility of guava leaves as an adsorbent for the removal of auramine dye for an industrial application, a continuous mode of adsorption was studied in a glass column.

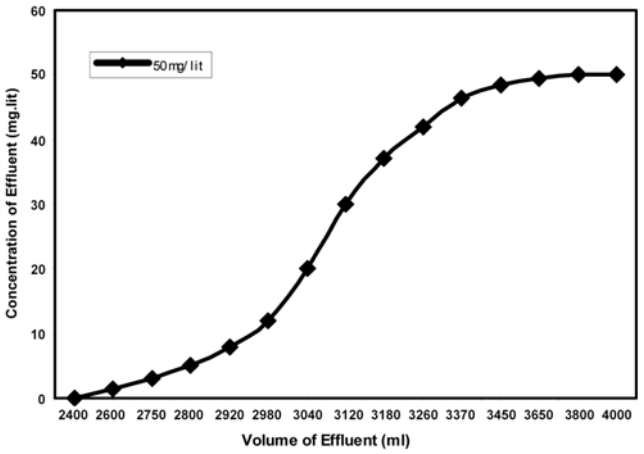

Fig. 9. Breakthrough curve for auramine dye removal on guava leaves.

For the column test runs, a pyrex tube of 0.8 cm inner diameter and 60 cm height was used. The experimental set up is shown in Fig. 2. The column was maintained at constant room temperature, i.e., 30 °C for all test runs. 25 g of psidium guava powder was randomly packed in the column. The stock auramine dye solution with an initial concentration of 50 mg/L was fed to the top of the adsorption column by a feed pump at a desired rate between 5 mL/min. Samples were taken periodically at the bottom of the column for auramine concentration measurement by using the standard methods (American Public Health Association 1992). At the beginning of a test run, the exit auramine concentration was initially nil, and after a certain time had elapsed, it began to rise. The run continued until the exit auramine concentration became close to the inlet concentration.

The breakthrough curve shown in the Fig. 9 reveals that 2,600 ml of auramine dye solution can be passed through the column of the sorbent without any trace of the dye being detected in the effluent. The exhaustive capacity of the sorbent is 8 mg/gm, which is higher in case of continuous adsorption process than that for the batch process, which was 7 mg/gm. This is due to a continuously renewed liquid solid interface for adsorption in a column, while the concentration gradient decreases with time in a batch process [28].

CONCLUSION

The results of the present work showed the adsorption is high at a pH of 9, indicating the use of guava leaves as a suitable adsorbent for removal of auramine dye from the waste water. The experimental adsorption results were fitted to both Langmuir and Freundlich models and the coefficients showed a better fit for the Langmuir isotherm. Experimental results also showed a pseudo-first order kinetics for the adsorption of auramine dye on guava leaves, giving a value of K as 26.8×10^{-3} min^{-1}. The rapid adsorption kinetics was also validated by carrying out a continuous flow process for the removal of auramine dye in the present work.

In this study, psidium guava leaves have been shown to be more effective for the removal of auramine dye from aqueous solutions than activated carbon. The adsorption in these systems is highly de-

pendent on pH. For the psidium guava-dye interaction, the adsorption takes place between pH values of about 2-10, and it would appear that the adsorption reaction occurs in the dye removal with the psidium guava. The experiments show that dye was adsorbed at pH 3.0 and maximum adsorption was attained at around pH of solution 9. Between pH values 2 and 3, the sorption of dye was negligible. The adsorption isotherm was obtained and the data in the linear form of Langmuir equation gave satisfactory correlation coefficients and concentration ranges. The adsorption capacities are 8 mg/g for the continuous and 7 mg/g for the batch process.

ACKNOWLEDGMENT

Authors are thankful to Prof. Dhirendra, Principal, Pravara Rural Engineering College, Loni for providing necessary facilities and support.

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