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Quaternized Wood as Sorbent for Reactive Dyes

KUN-SHE LOW,* CHNOONG-KHENG LEE,
AND BEE-FOONG TAN

Chemistry Department,
Faculty of Science and Environmental Studies,
Universiti Putra Malaysia, UPM 43400 Serdang, Selangor, Malaysia,
E-mail: kslow@fsas.upm.edu.my

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Abstract

Various species of local wood modified with *N*-(3-chloro-2-hydroxypropyl)-trimethylammonium chloride showed sorption enhancement for hydrolyzed Reactive Blue 2 (HRB) compared to the untreated samples. The enthalpy of sorption of HRB on Simpoh (*Dillenia suffruticosa*) was found to be endothermic. Maximum sorption capacity calculated from the Langmuir isotherm was 250.0 mg/g. Under continuous flow conditions HRB could be successfully removed. Dye removal was a function of bed depth and flow rate. However, the bed depth service time model of Bohart and Adams was not applicable in the HRB–quaternized wood system. The modified wood was applied to a sample of industrial textile effluent, and it was found to be able to remove the color successfully under batch conditions.

Index Entries: Wood; chemical modification; biosorption; reactive dyes.

Introduction

Dye wastewater from various industries poses a serious environmental problem because the dyes are generally resistant to aerobic digestion and stable to light and oxidizing agents. Dye wastewater is easily recognizable and is perceived to be a pollution indicator even though it is present in very minute quantities. One of the most mentioned sources of dye discharge is textile waste. Various waste treatments exist, and the most commonly employed method is sorption via activated carbon. The advantages of using activated carbon over other conventional methods include smaller

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*Author to whom all correspondence and reprint requests should be addressed.

land area, greater tolerance to daily changes in waste, and more efficient uptake of organic contaminants *(1)*. The high cost of using activated carbon has prompted the search for a cheaper alternative. Various low-cost biological materials have been studied as substitutes for activated carbon, including maize cob *(2)*, peat *(3)*, and linseed cake *(4)*. Negatively charged groups such as carboxylate, hydroxyl, phosphate, amine, and amide, which are present in these materials, are the binding sites for the basic dye molecules. However, they are not effective in removing reactive dyes that are negatively charged in solution.

Because reactive dyes are becoming more commonly used in textile industries, there is a need to investigate suitable low-cost sorbents for their removal from textile wastewater. Currently, reactive dyes represent about 20–30% of the total market for dyes. A large fraction, typically about 30%, of the reactive dyes is wasted because of dye hydrolysis in the alkaline dye bath. As a result, the textile waste contains a large amount of the dye. Conventional methods (sorption and aerobic biodegradation) have a low removal efficiency for reactive and other anionic soluble dyes *(5)*. In this article, we report on the use of a chemically modified wood as sorbent for the removal of hydrolyzed Reactive Blue 2 (HRB) from aqueous solution.

Materials and Methods

Materials

Six wood samples obtained from a plywood factory situated in Mentakab, Pahang, Malaysia, were ground to pass through a 1-mm sieve. It was boiled with 0.5 *M* NaOH solution for 2 h and washed with distilled water until the filtrate was near neutral. It was dried and labeled as hydrolyzed wood. It was necessary to pretreat the wood with NaOH because experiments carried out in alkaline conditions would induce leaching of organic substances that rendered the solution brownish. The species of wood investigated were Simpoh (*Dillenia suffruticosa*), Meranti Pipit (*Shorea acuminata*), Keruing (*Dipterocarpus costulatus*), Mesawa (*Anisoptera marginata*), Kedondong (*Burseraceas* spp.), and Meranti Bukit (*Shorea* spp.).

Each species of hydrolyzed wood was quaternized with *N*-(3-chloro-2-hydroxypropyl)-trimethylammonium chloride according to the method reported by Laszlo *(6)*. The wood was labeled as quaternized wood. Reactive Blue 2 (C.I. [color index] 61211, 60% purity; Sigma, St. Louis, MO) was used without further purification. The hydrolyzed dye was prepared by dissolving 10 g of dye solution in 2000 mL of 5% Na_2CO_3 solution at 50°C. The pH of the solution was adjusted to 11.0 *(7)*. The solution was labeled as HRB.

Analysis

The concentration of dye in the solution was determined with a Shimadzu 160 double-beam ultraviolet spectrophotometer using a 1.0-cm light path cuvet at a wavelength of 607 nm for HRB. All measurements were made at 28 ± 2°C. Dilution was carried out when measurement exceeded the linearity of the calibration curve. The percentage of uptake of dye by the sorbent is defined as $(C_o - C_t)/C_o \times 100$ in which C_o and C_t are the concentrations of the dye at time 0 and t, respectively. Errors were calculated to be <8% obtained from duplicate experiments under batch conditions.

Batch Experiments

All the experiments were conducted at room temperature (28 ± 2°C) unless otherwise stated. Sorption was measured by equilibrating 0.1 g of sorbate with 20 mL of dye solution at an agitation rate of 150 rpm for 6 h. A control without sorbent was simultaneously used to ascertain that the wall of the container did not contribute to the sorption process. At the end of the contact time, the sorption mixture was centrifuged at 2000*g* for 5 min, and the supernatant was analyzed for its dye content.

The rate of dye uptake by quaternized wood was determined by agitating the sorption mixture at different predetermined intervals and analyzing its dye content. Dye concentrations of 1000, 1500, and 2000 mg/L were investigated. Sorption isotherms were obtained by agitating samples of the sorbent using dye concentrations of 1000–4000 mg/L. The effect of temperature on dye sorption was studied by varying the temperature from 30 to 70°C.

A comparative study on the sorption of HRB by various commonly available sorbents was also conducted. These were granular activated carbon (Sigma), Amberlyst A-26 (Sigma), powdered activated carbon (BDH), chrome sludge (obtained from a local electroplating plant), water hyacinth roots, and various quaternized biological materials.

To establish the usefulness of the present sorption system, a sample of industrial textile wastewater was treated with quaternized wood.

Column Studies

Column experiments were conducted using a glass column of internal diameter of 1.0 cm and the column was packed with 1.0, 1.5, and 2.0 g of quaternized wood corresponding to 6-, 10-, and 14-cm bed depths, respectively. A total of 3000 mL of 100 mg/L of HRB solution was passed through the column. Flow rates were adjusted by means of a peristaltic pump, and fractions of 100 mL of solution were collected and analyzed for dye content.

Results and Discussion

Preliminary investigation had shown that all the species of hydrolyzed wood had very little affinity for HRB (Table 1) with <1% sorption. The reason for low sorption was the coulombic repulsion between the anionic colored component in aqueous solution and the negatively charged surface of the hydrolyzed wood surface. However, all the quaternized wood except Meranti Bukit had sorption >70%. The reason for the low sorption of Meranti Bukit is not clear. It could be because of the constituents of the

Table 1
Uptake of HRB by Hydrolyzed and Quaternized Woods[a]

	Uptake (%)	
Wood species	Hydrolyzed	Quaternized
Simpoh (*D. suffruticosa*)	0.24	84.10
Meranti Pipit (*S. acuminata*)	0.66	83.43
Keruing (*D. costulatus*)	0.50	78.67
Mesawa (*A. marginata*)	0.48	77.95
Kedondong (*Burseraceas* spp.)	0.74	71.62
Meranti Bukit (*Shorea* spp.)	0.41	19.83

[a] Conditions: 0.1 g of sorbent in 20 mL of 1000 mg/L of HRB solution at pH 11.0.

Table 2
Comparative Sorption of Hydrolyzed Dyes
by Hydrolyzed and Modified Simpoh[a]

	Uptake (%)	
Dyes (hydrolyzed)	Hydrolyzed wood	Quaternized wood
Reactive Blue 2	0.98	54.31
Reactive Yellow 2	0.98	77.34
Reactive Orange 16	2.60	91.24

[a] Conditions: 0.1 g of wood in 20 mL of 1500 mg/L of dye solution at 150 rpm for 6 h.

wood. The sorption enhancement was owing to the positively charged nitrogen in the quaternized material. A likely sorption mechanism is as follows:

$$\mathrm{WS{-}CO_2CH_2CH(OH)CH_2N^+(CH_3)_3Cl^- + Dye^- \rightarrow}$$
$$\mathrm{WS{-}CO_2CH_2CH(OH)CH_2N^+(CH_3)_3Dye^- + Cl^-}$$

All experiments were conducted under basic conditions because this reflects more accurately on the textile wastewater conditions. Table 2 shows the ability of modified Simpoh to sorb other reactive dyes. Because Simpoh showed the greatest uptake for HRB, all subsequent experiments were performed using such a species.

Rates of Sorption

Figure 1 shows the rates of HRB sorption by quaternized wood at three different initial concentrations of HRB. The results show that the time taken to reach equilibrium was independent of the initial dye concentration. A very rapid uptake was followed by a more gradual process. Poots et al. *(3)* reported that the initial concentration of dyes had only a small influence on the time of contact necessary to reach equilibrium in the sorption study of Telon Blue by peat. The fractional uptake increased with decreasing concentration. Various sorption kinetic models have been used to describe the

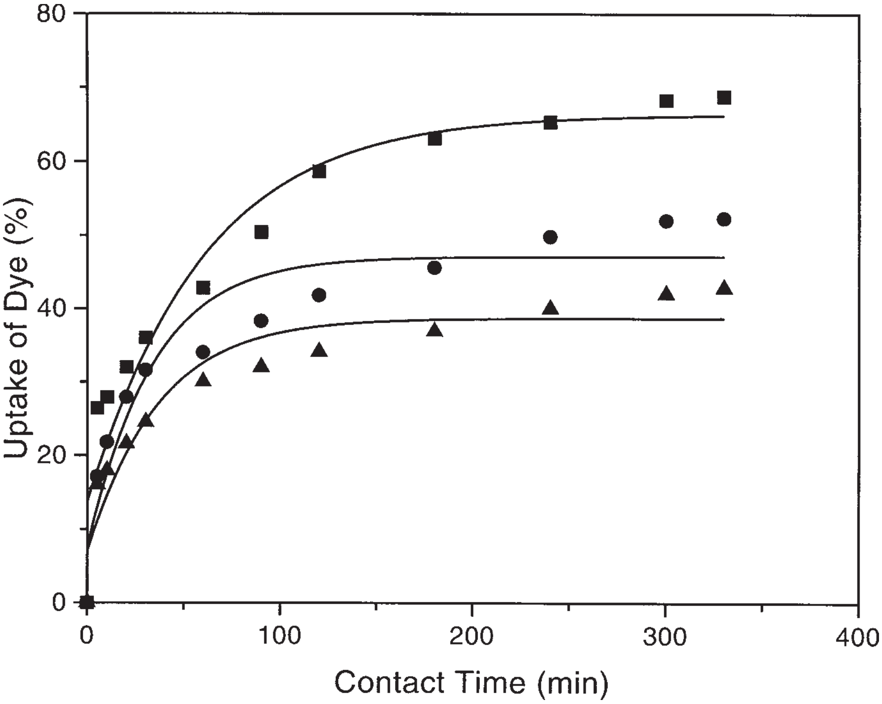

Fig. 1. The rates of uptake of HRB by quaternized Simpoh at various initial concentrations: ■, 1000; ●, 1500; and ▲, 2000 mg/L.

uptake of dyes. The first-order kinetics process has been used for reversible reaction with an equilibrium being established between liquid and solid phases. The pseudo-first-order rate equation by Lagergren has also been widely used. Recently Ho and McKay *(8)* reported that most of the sorption systems followed a pseudo-second-order kinetics model that can be expressed as follows:

$$t/q_t = 1/\mathrm{k} + t/q_e$$

in which t is the contact time (minutes); q_t and q_e are the quantities of sorbate sorbed at time t and at equilibrium (milligrams/gram); and k is the rate constant (grams/[milligrams · minute]). Plots of t/q_t vs t for the HRB–quaternized wood system are given in Fig. 2, which shows that the sorption process for dye on quaternized wood followed the pseudo-second-order kinetics model.

Agitation Rate

Figure 3 shows the influence of agitation rate on the uptake of HRB. The uptake was found to depend on the agitation rate: a higher agitation gave a higher uptake of dye. The increase in dye uptake with increasing agitation may be attributed to the decrease in the diffusion layer surrounding the sorbent particles. Similar observations were also reported by Asfour et al. *(9)* in their study of uptake of basic dyes by hardwood sawdust, and

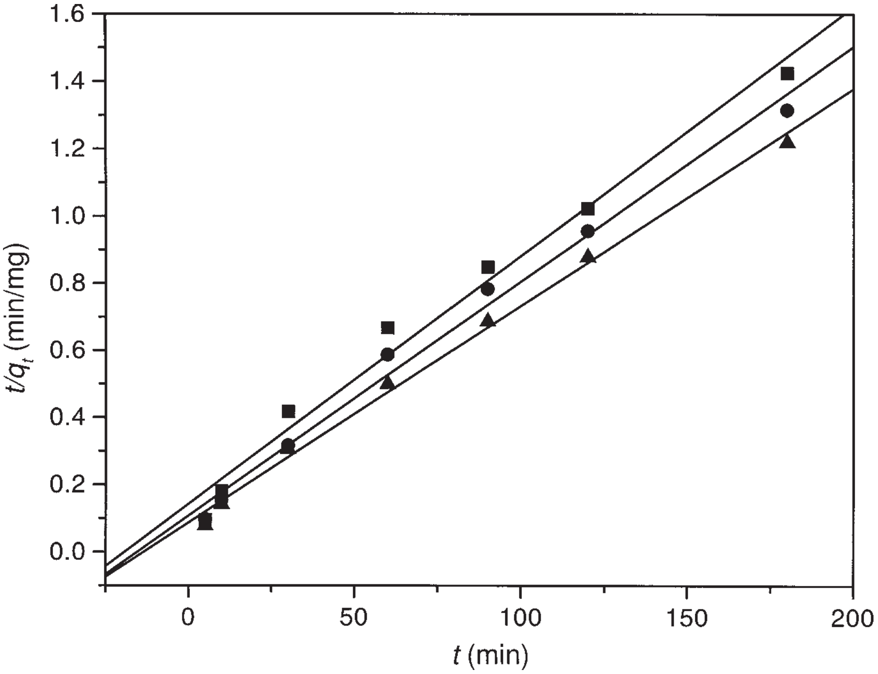

Fig. 2. Pseudo-second-order kinetics of HRB on quaternized Simpoh at different concentrations: ■, 1000; ●, 1500; and ▲, 2000 mg/L.

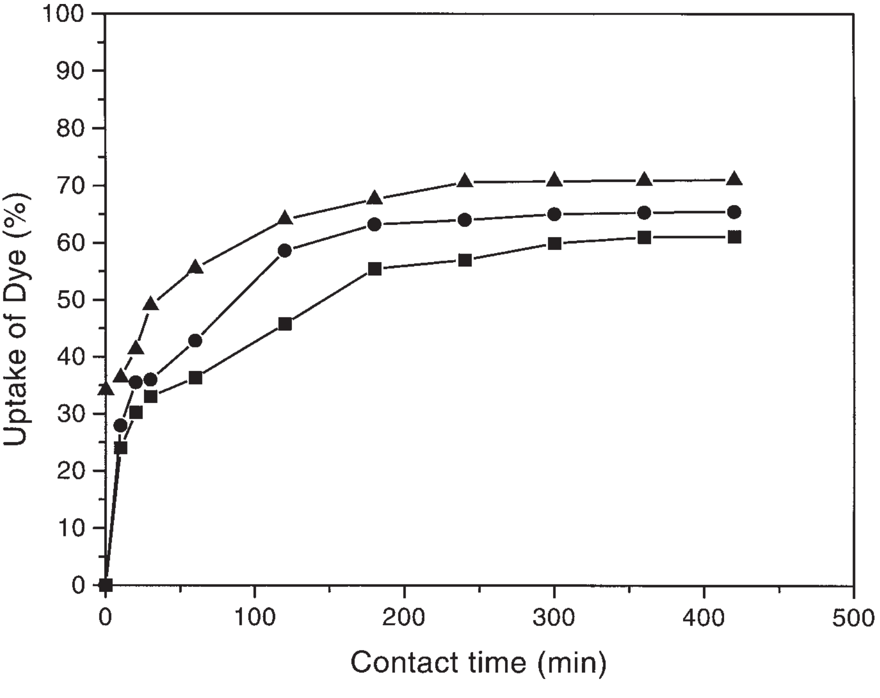

Fig. 3. Effect of agitation rate on the uptake of HRB by quaternized Simpoh: ■, 50; ●, 100; and ▲, 150 rpm.

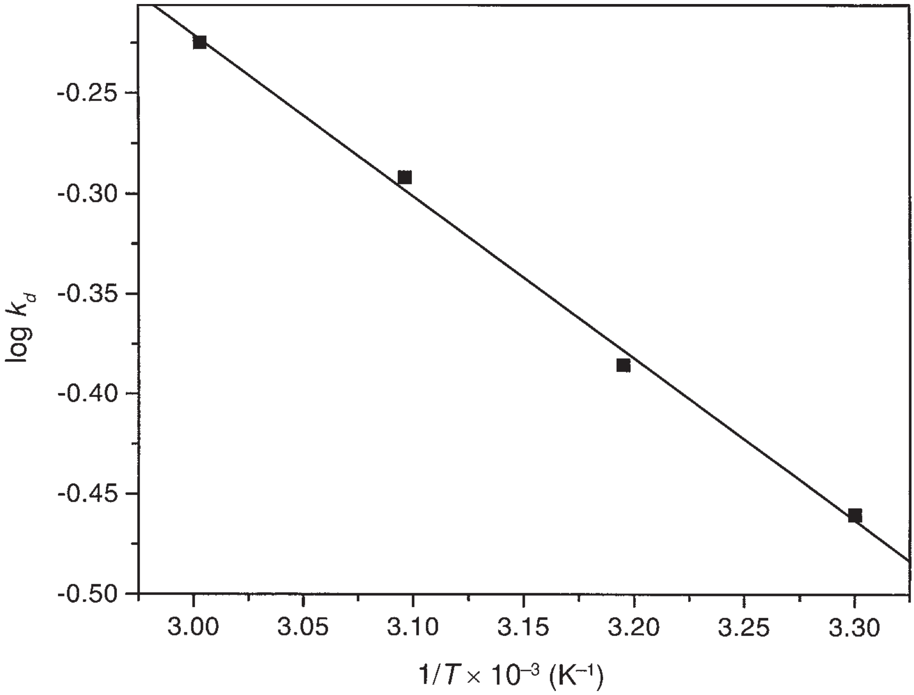

Fig. 4. van't Hoff plot of log k_d vs $1/T$ for the HRB-quaternized Simpoh system.

by McKay and Poots *(10)* in their study of adsorption of dyestuffs in aqueous solutions with activated carbon.

Effect of Temperature

The effect of temperature on the sorption was also investigated in the range of 30–60°C (303–333 K). There was an increase in uptake from 63.9 to 75.5% in the temperature range investigated. The increase in sorption could be due to changes in pore size, an increase in kinetic energy of the dye molecules, and the enhanced rate of intraparticle diffusion of sorbate *(11)*. The results can be plotted using the van't Hoff equation of the following form:

$$\log k_d = \Delta S°/2.303 \quad -\Delta H°/2.303RT$$

in which k_d is the distribution coefficient (q_e/C_e). A plot of log k_d vs $1/T$ is shown in Fig. 4, which gives a straight line of $y = 2.20 - 0.808x$. The coefficient of correlation (R^2) is 0.998. The sorption process of HRB–quaternized wood was endothermic. The values of $\Delta H°$ and $\Delta S°$ determined from the slope and intercept of the plot are 15.59 kJ/mol and 42.59 kJ/mol·K, respectively.

Langmuir Isotherm

To establish the maximum dye sorption capacity, the Langmuir equation was applied to the sorption equilibria at different initial concentra-

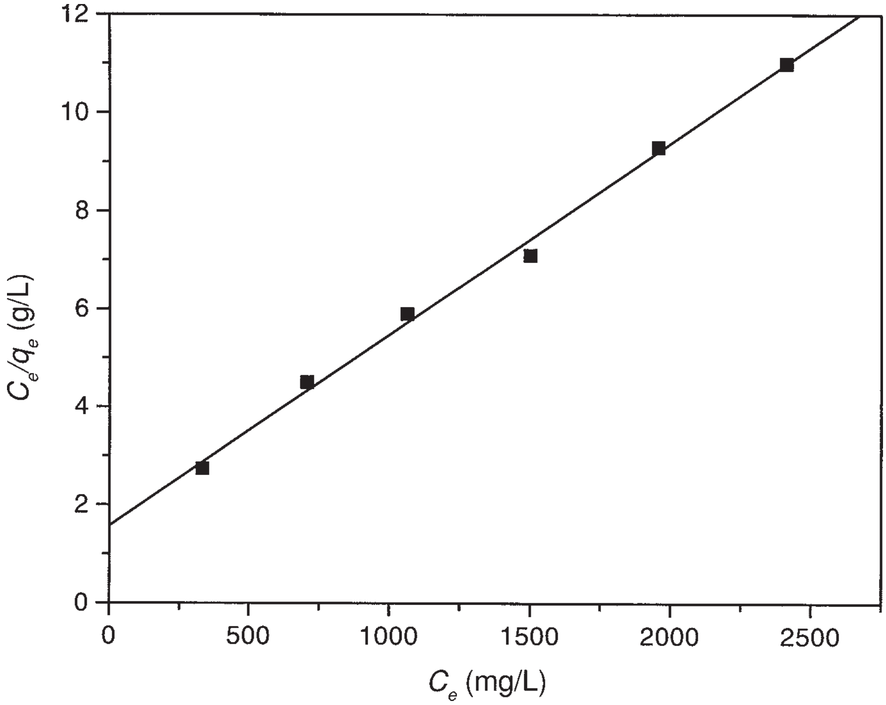

Fig. 5. Langmuir isotherm for HRB-quaternized Simpoh system at 28 ± 2°C.

tions. The Langmuir isotherm assumes monolayer coverage of the surface, uniform energies of sorption, and no transmigration of sorbate in the plane of the surface. It can be represented by the following expression:

$$C_e/q_e = 1/Q_0 b + C_e/Q_0$$

in which C_e is the equilibrium concentration of the dye (milligrams/liter); q_e is the amount of dye sorbed (milligrams/gram); Q_0 is the maximum sorption capacity of the sorbent; and b is a constant related to the energy of sorption. Although it could not be ascertained that the surface of quaternized wood is homogeneous, the application of such a model to the dye–quaternized wood provides useful information on its practical limiting sorption capacity. Figure 5 shows the result of such an application. Maximum sorption is calculated to be 250 mg/g, which compared favorably with that of quaternized rice hulls, which showed a maximum sorption of HRB of 130 mg/g *(12)*.

Comparative Study of HRB by Various Sorbents

The sorptive potential of quaternized wood for HRB was compared with that of a commercial activated carbon (powdered and granular), an anion exchanger (A-26), and some other sorbents we have investigated; Table 3 gives the results. The order of sorptive capacity is quaternized wood > powdered activated carbon > anion exchanger > quaternized rice

Table 3
Comparative Sorption Capacities
of HRB by Various Sorbents[a]

Sorbent	Uptake (%)
Quaternized Simpoh	68.8
Activated carbon (powdered)	53.6
Resin A-26	48.4
Quaternized rice husk	34.5
Quaternized peanut hull	32.8
Activated carbon (granular)	24.9
Chrome sludge	19.1
Water hyacinth roots	3.3

[a] Conditions: 0.1 g of sorbent in 20 mL of 1500 mg/L of HRB at 150 rpm.

husks > quaternized peanut hulls > granular activated carbon > chrome sludge > water hyacinth roots. It is evident that quaternized wood possesses great potential as a sorbent for the removal of reactive dyes.

Column Studies

Sorption isotherms have been used traditionally for preliminary tests before running more costly column tests. The sorption isotherms obtained from the batch system are useful in providing information on the efficiency of the dye uptake under equilibrium conditions. However, they do not give accurate scale-up data under continuous flow conditions. Consequently, it is necessary to carry out flow tests using columns prior to obtaining design models. Figure 6 shows the breakthrough curves of quaternized wood for HRB at different bed depths at a constant flow rate of 10 mL/min. Breakthroughs at $C_t/C_o = 0.5$ occurred at 973, 1279, and 2245 mL of dye solution for bed depths of 6, 10, and 14 cm, respectively. An increase in treatable volume of dye solution with increasing bed depth is attributed to the increasing binding sites on the sorbent.

Because the efficiency of the column depends also on the flow rate, experiments involving constant bed depth (14 cm) but different flow rates were also investigated. Figure 7 presents the results and shows that reducing the flow rate increased the breakthrough volume for a fixed bed depth. Various models exist that allow the prediction of the time of running a column before regeneration or replacement becomes necessary. The data obtained from such a study were applied to a bed depth service time (BDST) model that was proposed by Bohart and Adams *(13)* and later modified by Hutchins *(14)* of the following form:

$$t = N_o \nu / C_o [h - (1/kN_o) \ln(C_o/C_t - 1)]$$

in which t is the service time of breakthrough; N_o is the sorption capacity; C_o is the initial dye concentration; C_t is the eluent concentration; ν is the linear flow rate; h is the bed depth; and k is the rate constant of sorption.

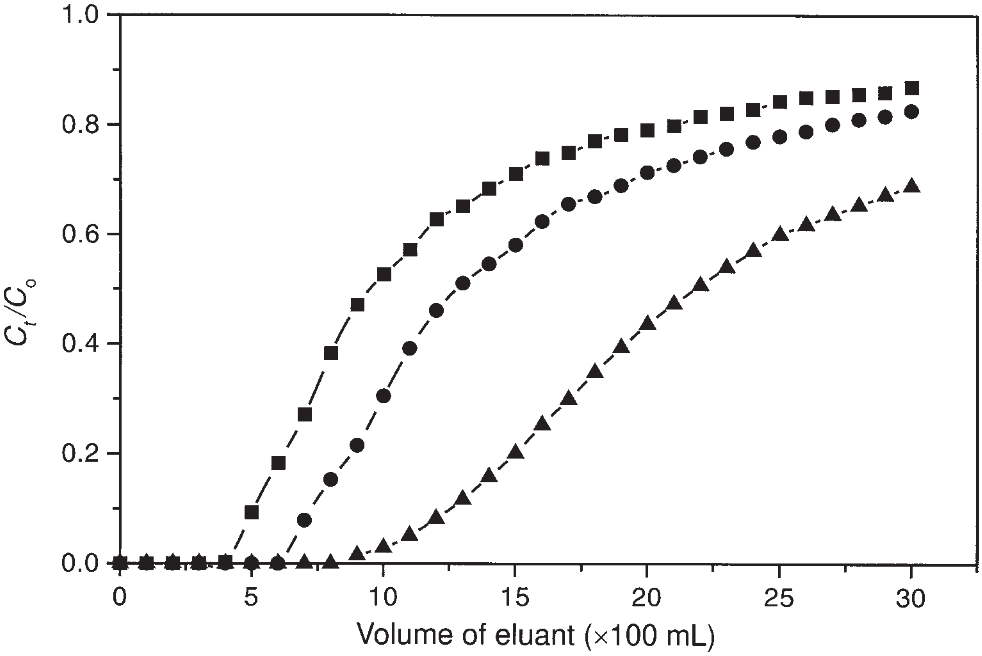

Fig. 6. Breakthrough curves of HRB (C_o = 100 mg/L) on quaternized Simpoh for different bed depths at constant flow rate of 10 mL/min: ■, 6; ●, 10; and ▲, 14 cm.

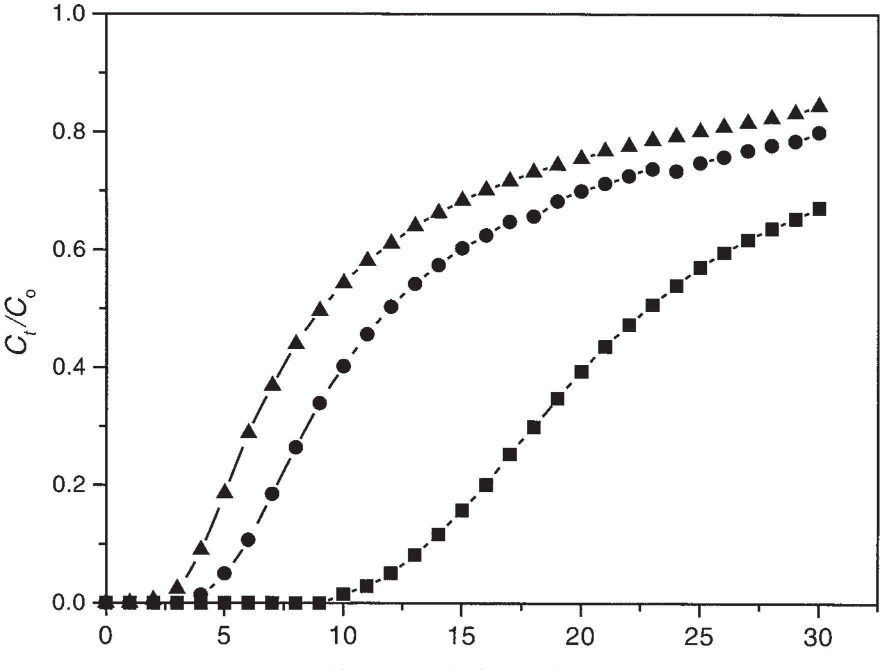

Fig. 7. Breakthrough curves of HRB (C_o = 100 mg/L) on quaternized Simpoh for different flow rates at constant bed depth of 14 cm: ■, 10; ●, 25; and ▲, 50 mL/min.

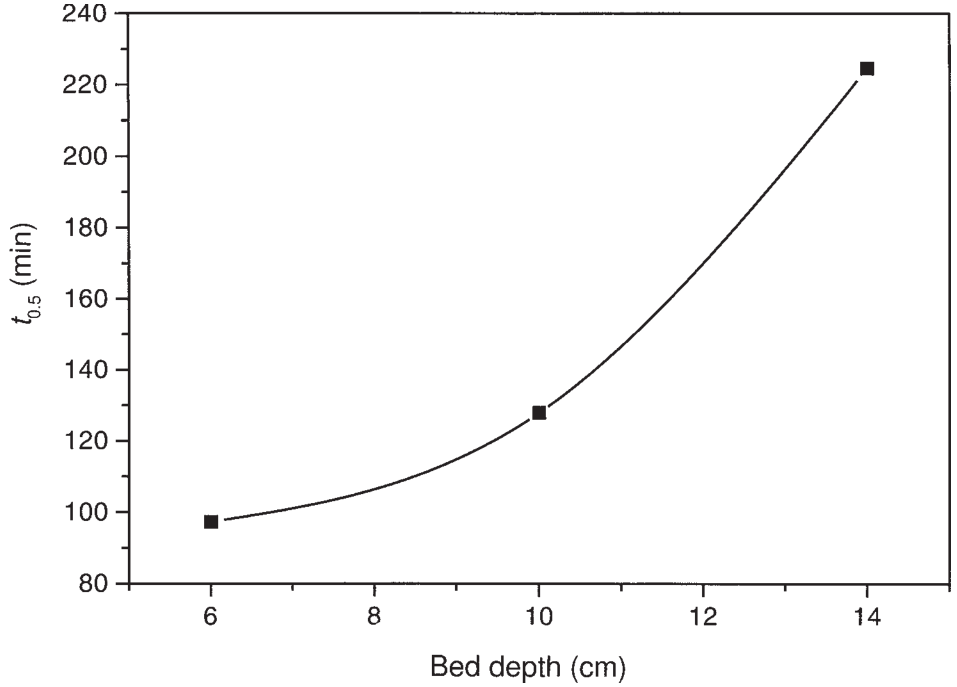

Fig. 8. Plot of bed depth vs service time at 50% breakthrough for HRB –quaternized Simpoh column at a flow rate of 10 mL/min.

Table 4
Product of Flow Rate and Treated Volume
at 50% Breakthrough at Constant Bed Depth of 10 cm

Flow rate (ν) (mL/min)	Treated volume (*V*) (mL)	ν*V*
10	2305	23,050
25	1291	32,275
50	907	45,350

At $C_o/C_t = 2$ (50% breakthrough), and $t = t_{0.5}$, the equation is reduced to $t_{0.5} = N_o \nu h/C_o$ or $t_{0.5} = \text{constant} \times h$.

Thus, a plot of BDST at 50% breakthrough against bed depth should be a straight line passing through the origin. The results of such a plot of the HRB–quaternized wood system are shown in Fig. 8 and clearly indicate that such a BDST model could not be applied to the present system. The BDST model also predicts that at 50% breakthrough, the product of flow rate (ν) and volume treated (*V*) should be a constant. From Table 4 it can be seen that such a prediction does not hold true.

The BDST model failed because the breakthrough curves should assume an "S" pattern, implying that a 0–50% breakthrough should be similar to a 50–100% breakthrough. However, this was not the case in the

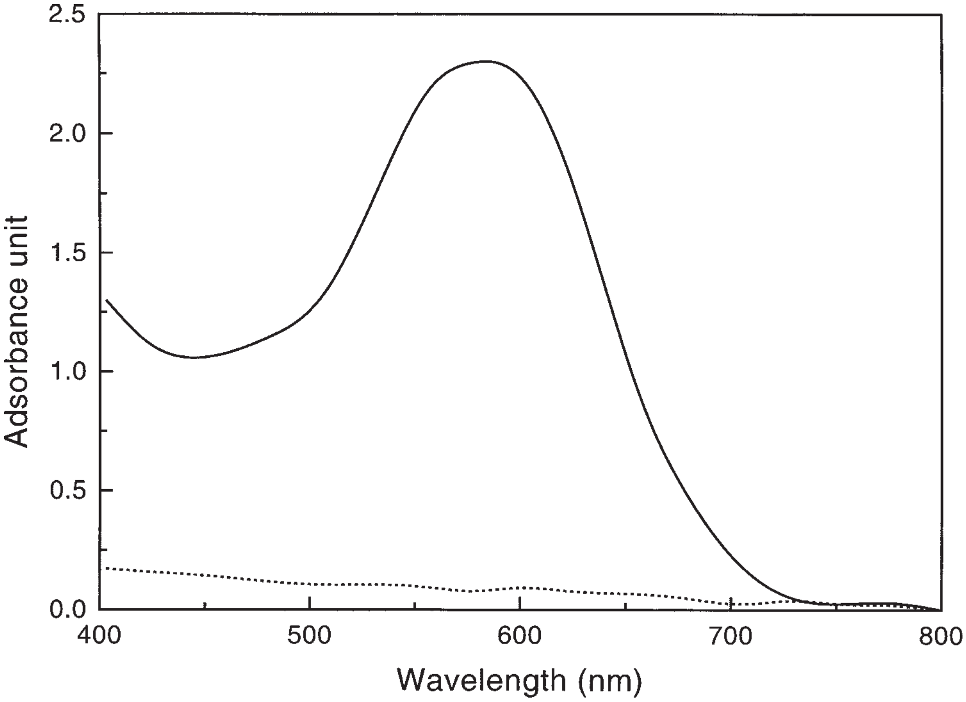

Fig. 9. Visible spectra of a textile waste before (——) and after (– – – –) 30 min of treatment.

present study. A similar observation was reported by McKay et al. *(15)* in the study of removal of Acid Blue 25 by peat. It was concluded that the sorption process in the column was complex and probably involved two or more rate-determining steps. A similar phenomenon could well occur in our study.

Color Removal from Textile Wastewater

Although quaternized wood could remove HRB quite efficiently under controlled laboratory conditions, the ultimate test of its usefulness is its application to a sample of industrial textile wastewater. Such a study was carried out by treating quaternized wood with an untreated textile waste consisting of a variety of reactive, disperse, direct, and sulfur-vat dyes and pigments. The pH of the waste was 10.4. Figure 9 presents the result of its color removal. Almost all the dyes were removed after a 30-min treatment, indicating that quaternized wood could be a suitable sorbent in the treatment of textile wastewater under batch conditions.

Conclusion

Various species of quaternized wood have been demonstrated to be able to sorb HRB. Equilibrium studies showed that quaternized Simpoh had a maximum sorption capacity, based on the Langmuir isotherm model, of 250 mg/g for HRB. In column experiments, the removal of the dye was a function of both bed depth and flow rate. The BDST model of Bohart and Adams *(13)* could not adequately correlate breakthrough service time with flow rate. A sample of textile waste containing a complex mixture of dyes was treated efficiently by quaternized Simpoh under batch conditions.

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