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The Possible Mechanism and Factors Affecting Synthetic Reactive Dye Removal by Treated Flute Reed

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Abstract

This study investigated the ability of treated flute-reed to adsorb synthetic reactive dye solution in a batch system. The effects of particle size, contact time and adsorption isotherms at various particle sizes and temperatures were investigated. Desorption was studied to confirm the mechanism of adsorption. The results showed that the adsorption capacity increased as the particle size decreased. The smaller particle size required less contact time to reach equilibrium because it had a higher rate of adsorption. Adsorption isotherms at various particle sizes indicated that the equilibrium data fitted well with the Langmuir isotherm. The maximum adsorption capacity (q_{max}) of particle size ranges of: less than 420, 420-1190, 1190-2000 and 2000-2800 μm, was 7.58, 4.42, 3.83 and 3.12 mg/g, respectively. For adsorption isotherms at various temperatures, the amounts of adsorption increased with increasing temperature. This is because the kinetic energy probably increased at higher temperatures resulting in increasing reactive dye removal. The results from the desorption studies confirmed that the adsorption of reactive dye by treated flute-reed was due to ion exchange and the adsorption mechanism was mainly chemical adsorption.

Keywords: Treated flute-reed; adsorption; adsorption isotherm; reactive dye; desorption

1. Introduction

Color is one of the indicators for water pollution. The effluents from dyeing and printing processes are highly colored. The discharge of color wastes into streams and rivers causes severe problems. Because of its toxicity and reduction of light penetration (Namasivayam *et al*., 2001), it negatively affects the aesthetic of the water environment, the photosynthetic activities of aquatic plants, and the activity of aquatic animals. In addition, it can cause water-transmitted disorders, for example, nausea, haemorrhage, ulceration of skin and mucous membrane, dermatitis, perforation of the nasal septum and severe irritation of the respiratory tract (Liversidge *et al*., 1997). Therefore, it is necessary to treat textile wastewater before it is discharged into receiving waters.

There are several methods used to decolorize textile wastewater, such as ozonation (Radetski *et al*., 2002) coagulation (Chu, 2001) membrane filtration (Ciadelli *et al*., 2003), ion exchange (Lin and Chen, 1997) and activated carbon adsorption (Walker and Weatherley, 1999). These methods are costly and require skillful operations and high maintenance. Nowadays, adsorption processes using agricultural residues are very attractive alternative methods for the decoloration of textile wastewater. A variety of adsorbents for this purpose have been reported in the literature, such aseucalyptus bark (Morais *et al*., 2000), coir pith (Namasivayam *et al*., 2001) and orange peel (Sivaraj *et al*., 2001).

The aim of this research is to study the use of treated flute-reed as an adsorbent for color removal in a batch system. The effects of particle size, contact time and adsorption isotherms at various particle sizes and temperatures were investigated. Desorption was studied to confirm the mechanism of adsorption.

2. Materials and Methods

2.1. Preparation of treated flute-reed

Flute-reed was obtained from Mahidol University (Salaya), Thailand. It was sliced into pieces of less than 1 inch, sun dried for 3 days and ground in a disk mill. After grinding, the flute-reed was treated by soaking with 0.2 N H_2SO_4 for 1 hour, the solution being replaced every hour until color was no longer leaching from the weed. After that, it was dried in a hot air oven at 80^{o}C for 12 hours and then separated into different particle sizes through a sieve and the particle size distribution was determined in % by weight as shown in Table 1.

Table 1. The particle size distribution of treated flute-reed

Particle size (μm)	% by weight
< 420	46.28
420-1190	32.35
1190-2000	14.13
2000-2800	4.04
2800-4000	2.46
> 4000	0.74

2.2. Preparation of synthetic reactive dye solution

The reactive dye used in this study was Procion Red H-E7B (C.I. Reactive Red 141, RR 141). This dye was obtained from Dystar Thai Ltd., of which the structure is shown in Fig. 1. The wavelength of maximum absorbance (λ_{max}) for RR 141 was 543 nm. RR 141 had a molecular weight and solubility of 1,774 and 50 g/L, respectively. A stock dye solution of 30 mg/L was prepared by mixing 0.03 g of dried dye with 1000 cm^3 distilled water. The desired initial concentration was obtained from diluting this stock solution.

2.3. Effect of particle size on color removal

Five different particle size ranges of treated flute-reed: <420, 420-1190, 1190-2000, 2000-2800 and 2800-4000 μm, were tested at 30°C in a system pH of 3.0±0.2. An amount of 0.3 g of each particle size of treated flute-reed was added to 15 ml of 30 mg/L of synthetic reactive dye solution in 30 ml sealed glass bottles and shaken in a shaker at 140 rpm for 18 hours. After that, the samples were centrifuged at 5,000 rpm for 10 minutes and analyzed for the remaining dye concentration by a spectrophotometer at a wavelength of 543 nm.

2.4. Effect of contact time

In order to study the effect of contact time, the same procedure as described for the particle size was performed with selected particle sizes. The samples were collected every hour for dye concentration measurements until equilibrium was reached.

2.5. Adsorption isotherms

Adsorption isotherms for various particle sizes were conducted by using the selected particle size ranges. The procedure was the same as described for the particle size except the initial dye concentrations were varied from 20 to 140 mg/L. All bottles were shaken for 24 hours and the equilibrium reactive dye concentrations (C_e) were measured and calculated for the amounts of dyes adsorbed per unit weight of treated flute-reed (q_e).

For the adsorption isotherms at various temperatures, the treated flute-reed particle size range of less than 420 μm was tested at the same conditions as the adsorption isotherms for the various particle sizes studied, except the temperature was varied at 20°C, 30°C and 40°C.

2.6. Desorption studies

In the desorption studies, 0.3 g of dye-adsorbed treated flute-reed, which had a particle size range of 420-1190 μm, was agitated with 15 ml of distilled water in 30 ml sealed glass bottles at 30°C. The system was adjusted to different pH values of 2, 4, 6, 8 and 10 with 0.2 N H_2SO_4 or 0.2 NaOH. After that, the same procedure as described for the particle size was repeated but the bottles were shaken in a shaker for 6 hours.

3. Results and discussion

3.1. Effect of particle size on color removal

Five different particle size ranges of treated flute-reed, <420, 420-1190, 1190-2000, 2000-2800 and 2800-4000 μm, were studied for their efficiency of color removal from a 30 mg/L synthetic reactive dye solution at 30°C at a system pH of 3.0±0.2. As shown in Fig. 2, the adsorption capacity of the treated flute-reed increased as the particle size range decreased. This is because the total surface area of the smaller particle size range available for adsorption of reactive dye was greater than that of the larger particle size ranges (Sun and Xu , 1997, Al-Qodah, 2000).

However, the efficiency of synthetic reactive dye

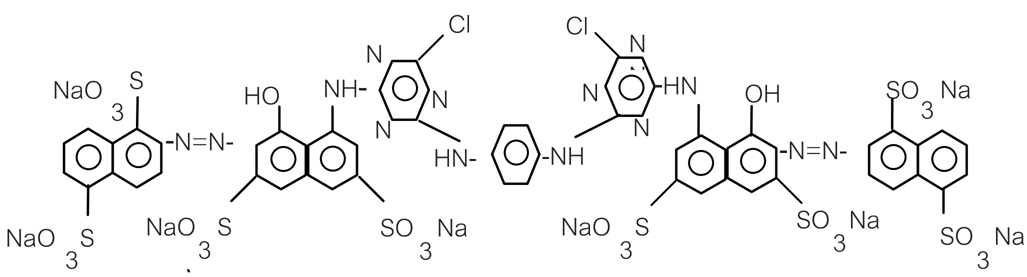

Figure 1. Chemical structure of Procion Red H-E7B (diazo C.I. Reactive Red 141, RR 141)

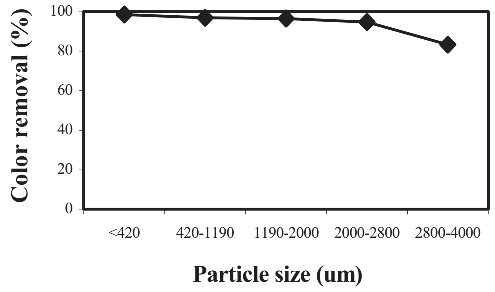

Figure 2. Effect of particle size range of treated flute reed on color removal

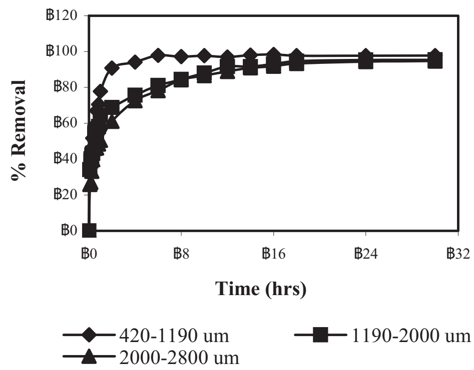

Figure 3. Effect of contact time on the adsorption of reactive dye solution by treated flute-reed

removal for the particle size ranges of <420, 420-1190, 1190-2000 and 2000-2800 μm was not significantly different. From the data, the smallest particle size range (<420 μm) had the highest efficiency of color removal at 98%, while the particle size ranges of 420-1190, 1190-2000 and 2000-2800 μm removed 97%, 96% and 95% of the dye, respectively.

3.2. Effect of contact time

The effect of contact time on the adsorption of 30 mg/L synthetic reactive dye solutions by treated flute-reed at the particle size ranges of 420-1190, 1190-2000 and 2000-2800 μm at 30°C under a system pH of 3.0±0.2 is shown in Fig. 3. The adsorption by the smaller particle size reached equilibrium faster than the larger particle sizes. The particle size range of

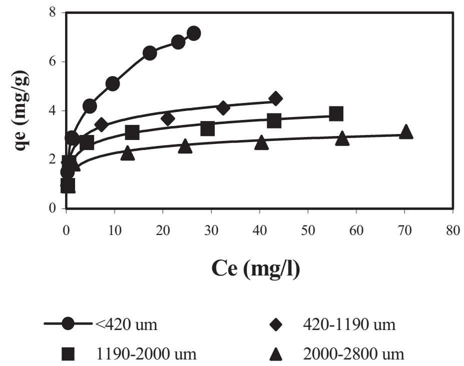

Figure 4. Langmuir isotherm fit of the non-linearized experimental data on the adsorption of reactive dye for various particle size ranges of treated flute-reed

420-1190 μm reached equilibrium in 6 hours and had a color removal efficiency of 98%. For the 1190-2000 and 2000-2800 μm size ranges, the adsorption reached equilibrium in 18 hours and a color removal of 95% and 93% was achieved, respectively. The smaller particle size required less contact time to reach equilibrium since it had a higher rate of adsorption (Alley, 2000). The particle diameter influences the rate of adsorption. Smaller diameter particles had a shorter diffusion path resulting in more rapid adsorption (Alley, 2000).

3.3. Adsorption isotherms at various particle sizes

Adsorption processes are usually explained by equilibrium isotherms. The fit of the Langmuir adsorption isotherm on the non-linearized and linearized experimental data for four different particle size ranges of treated flute-reed is shown in Figs. 4-5, respectively. The constants q_{max} and b obtained from the slope and intercept of the Langmuir fit of the linearized data along with the coefficient of correlation of the fit (R^2) are shown in Table 2. The adsorption isotherms of synthetic reactive dye solution for four different particle size ranges of treated flute-reed fit well with the Langmuir isotherm, as indicated by the high R^2 (>0.98). The values of the maximum adsorption capacity (q_{max}) ranged from 3.12

Table 2. Constants in the Langmuir and Freundlich isotherm for the adsorption of synthetic reactive dye for various particle size ranges of treated flute-reed

Particle size (μm)	Langmuir constants			Freundlich constants		
	q_{max} (mg/g)	b (L/mg)	R^2	n	K (L/g)	R^2
<420	7.58	0.366	0.9847	3.04	2.46	0.9902
420-1190	4.42	0.672	0.9914	4.27	1.95	0.8747
1190-2000	3.83	0.499	0.9929	4.46	1.64	0.8698
2000-2800	3.12	0.316	0.9908	4.91	1.32	0.9030

to 7.58 mg/g. The smallest particle size range had the highest adsorption capacity of all particle size ranges. This is because of the larger surface area made available by the smaller treated flute-reed particles when the mass of the treated flute-reed was constant (Gupta *et al*., 1992, Sankar *et al*., 1999). The affinity between the reactive dye and binding sites of treated flute-reed (*b*) decreased when the particle size ranges increased. This is because the number of binding sites on the adsorbent surface decreased when the larger particle sizes were used at the same dosage (Netpradit *et al*., 2003). The fit of the Freundlich adsorption isotherm on the linearized experimental data for four different particle size ranges of treated flute-reed is shown in Fig. 6. The constants *n* and *K* obtained from the slope and intercept, as well as the coefficient of correlation of the fit (R^2) are shown in Table 2. The adsorption isotherms of synthetic reactive dye solution for the various particle size ranges of treated flute-reed did not fit well with the Freundlich isotherm, except for that of the particle size range of <420 μm, as indicated by the coefficient of correlation of the fit (R^2), which ranged from 0.87 to 0.90 (Table 2). When compared with the R^2 value of the Langmuir isotherm, it was lower than the Langmuir fit. This indicates that the Langmuir isotherm could better explain the adsorption of various particle sizes of treated flute-reed than the Freundlich isotherm and the adsorption therefore tended to follow the ideal monolayer model. The constant *n* in the Freundlich isotherm was a function of the strength of the adsorption. It increased with increasing particle size ranges. The adsorption capacity (*K*) increased from 1.32 to 2.46 L/g when the particle size decreased from 2000-2800 to <420 μm. The obtained results agree with the value of q_{max} obtained from the Langmuir isotherm, indicating that the adsorption capacity of treated flute-reed increased as the particle size decreased.

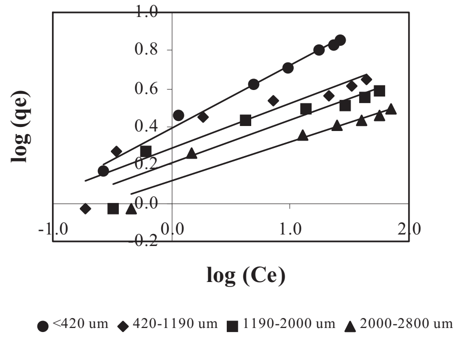

Figure 6. Freundlich isotherm fit of the linearized experimental data on the adsorption of reactive dye for various particle size ranges of treated flute-reed

3.4. Adsorption isotherms at various temperatures

Langmuir adsorption isotherms at three different temperatures, which represent the non-linearized and linearized experimental data are shown in Figs. 7-8, respectively. The constants in the Langmuir equation, as well as the enthalpy change (ΔH) and correlation coefficient (R^2), are shown at various temperatures in Table 3. The adsorption of reactive dye by treated flute-reed at various temperatures fitted well with the Langmuir equation ($R^2>0.98$). The amount of adsorption increased with increasing temperature. This is because the kinetic energy probably increased at higher temperatures and hence increased the mobility of the adsorbate resulting in the increasing reactive dye removal. This indicated that the adsorption process was endothermic (Gupta, 1998). The value of *b* indicated the adsorption affinity between the dyes and the binding sites of the adsorbent. The higher *b* values indicated higher adsorption affinity. From the results, the value of *b* at 40°C was higher than at 20°C. Therefore, the adsorption affinity at the higher temperature was higher than at the lower temperature. This confirmed that the adsorption process

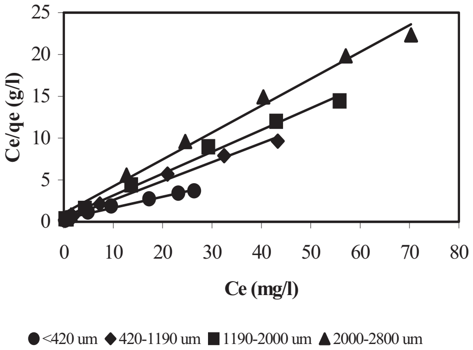

Figure 5. Langmuir isotherm fit of the linearized experimental data on the adsorption of reactive dye for varoius particle size ranges of treated flute-reed

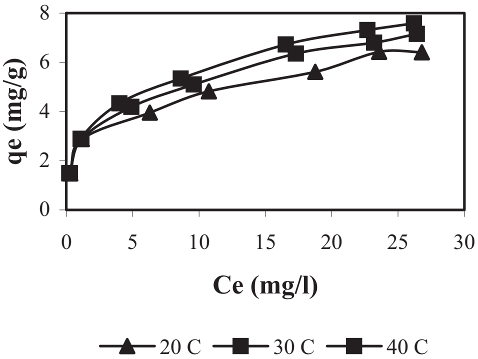

Figure 7. Langmuir isotherm fit of the non-linearized experimental data on the adsorption of reactive dye at various temperatures of treated flute-reed

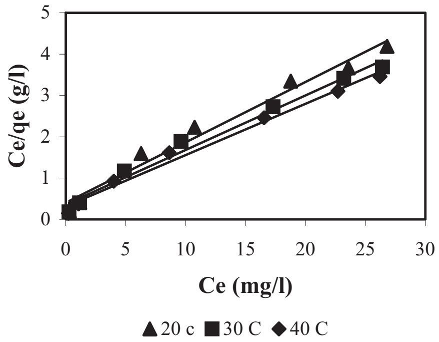

Figure 8. Langmuir isotherm fit of the linearized experimental data on the adsorption of reactive dye at various temperatures of treated flute-reed

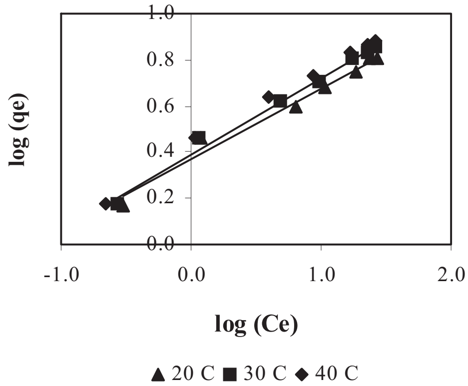

Figure 9. Freundlich isotherm fit of the linearized experimental data on the adsorption of reactive dye at various temperatures of treated flute-reed

was an endothermic reaction (Walker, 1999).

In addition, the value of ΔH of the treated flute-reed for three different temperatures was calculated from the slope of the plot of ln *b* and 1/T. This value could be used to confirm the process of adsorption, that is, a positive ΔH value indicated an endothermic adsorption (Gupta, 1998). Therefore, the adsorption by treated flute-reed at various temperatures was an endothermic reaction.

Moreover, the adsorption isotherm could be described by the Freundlich equation; the fit of the Freundlich adsorption isotherm on the linearized experimental data for three different temperatures is shown in Fig. 9. The constants *n* and *K* obtained from the slope and intercept, as well as the coefficient of correlation of the fit (R^2), are shown in Table 3.

As with the Langmuir isotherm, the data fitted well with the Freundlich isotherm Langmuir. The constant K in the Freundlich isotherm is related to the capacity of the adsorbent for the adsorbate. In this study, the adsorption capacity increased as the temperature increased. The results obtained agree with the value of q_{max} obtained from the Langmuir isotherm. Therefore, this confirms that the adsorption capacity of treated flute-reed increased with increasing temperature. The constant *n* decreased with increasing temperature and it was in the range 2 to 10, which represented good adsorption (Choi and Cho, 1996). Therefore, the adsorption of reactive dye by treated flute-reed was favorable.

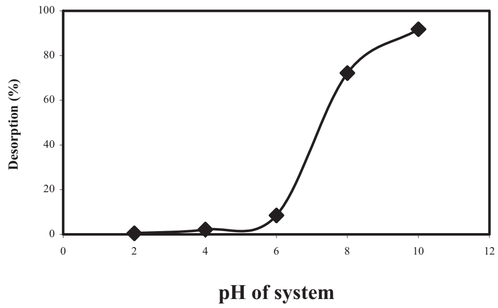

Figure 10. Effect of pH of system on the desorption of reactive dye solution by treated flute-reed

3.5. Desorption studies

The effect of pH on the desorption of synthetic reactive dye solution by treated flute-reed is shown in Fig. 10. The results show that the percentage of desorption increased with increasing in the pH of the system. When the pH of the system was increased from 2 to 10, the percentages of desorption increased from 1% to 92%. Increasing the system pH from 6 to 8, the percentages of desorption increased rapidly from 9% to 72%. This is due to the surface of adsorbed treated flute-reed containing a positive charge. Under basic conditions, the negative ions of OH^- increased and the SO_3^- ions from dyes were replaced by OH^- ions. Thus, the SO_3^- ions from dyes were released into the solution.

Table 3. Constants in the Langmuir and Freundlich isotherm for the adsorption of synthetic reactive dye at different temperatures of treated flute-reed

Temperature (^oC)	Langmuir constants				Freundlich constants		
	q_{max} (mg/g)	*b* (L/mg)	ΔH^o (kJ/mol)	R^2	*n*	*K* (L/g)	R^2
20	6.84	0.365		0.9789	3.25	2.35	0.9782
30	7.58	0.366	2493.20	0.9847	3.04	2.46	0.9902
40	8.06	0.390		0.9875	3.00	2.62	0.9946

This phenomenon indicates that ion exchange occurred. In addition, the amount of desorbed dye was very small at lower system pH values. The percentages of desorption were 1%, 2% and 9% at system pH values of 2, 4 and 6, respectively, while the desorption increased to nearly 100% at alkaline pH. This suggests that treated flute-reed had a tendency for ion exchange adsorption of sulfonated azo reactive dyes. Therefore, the major part of the adsorption mechanism was chemical adsorption. From this result, the percentages of desorption at system pH values of 8 and 10 were 72% and 92%, respectively. Therefore, these values were selected for further desorption studies in order to confirm the mechanism of adsorption. The results obtained are shown in Table 4. From this table, complete desorption occurred at system pH≥8. This confirms that the adsorption process was chemical adsorption. The results obtained were correlated with the results from the isotherm study, which found that the value of q_{max} increased with increasing temperature. Therefore, this confirms that the mechanism of adsorption of reactive dye on treated flute-reed was chemical adsorption.

4. Conclusion

Although treated flute-reed had low adsorption capacity of reactive dye, it is very cheap and available abundance. Therefore, treated flute-reed can be an alternative adsorbent for the removal of reactive dye. The dye adsorption capacity of treated flute-reed increased with decreasing particle size and increasing contact time and temperature. The adsorption isotherm fitted well with the Langmuir isotherm for various particle sizes and fitted well with the Langmuir isotherm and Freundlich isotherm for various temperatures. The desorption studies confirmed that the treated flute-reed had a tendency for ion exchange and chemical adsorption for synthetic reactive dye removal. It meaned that dye-adsorbed adsorbent will be hardly leached and contaminated environment.

Table 4. Desorption of Reactive Red 141 by multiple cycles of distilled water adjusted system pH to 8 and 10

No. of cycles	% Desorption	
	pH 8	**pH 10**
I	72.21	91.77
II	17.81	8.28
III	9.98	-
Total	100.00	100.05

Acknowledgements

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References

Al-Qodah Z. Adsorption of dyes using shale oil ash. Water Research 2000; 34(17): 4295-303.

Alley ER. Water Quality Control Handbook. McGraw-Hill; 2000

Choi YS, Cho JH. Color removal from dye wastewater using Vermiculite. Environmental Technology 1996; 17: 1169-80.

Chu W. Dye removal from textile dye wastewater using recycled alum sludge. Water Research 2001; 35(13): 3147-52.

Ciadelli G, Corsi L, Marcucci M. Membrane separation for wastewater reuse in the textile industry. Resources Conservation and Recycling 2003; 3, 189-97.

Gupta GS, Shukla SP, Prasad G, Singh VN. China clay as an adsorbent for dye house wastewaters. Environmental Technology, 1992; 13: 925- 36.

Gupta VK. Equilibrium uptake, sorption dynamics, process development, and column operations for the removal of copper and nickel from aqueous solution and wastewater using activated slag, a low-cost adsorbent. Industrial & Engineering Chemistry Research 1998; 37: 192-202.

Lin SH, Chen ML. Treatment of textile wastewater by chemical methods for reuse. Water Research 1997; 31(4): 868-76.

Liversidge RM, Lloyd GJ, Wase DAJ, Forster CF. Removal of Basic Blue 41 dye from aqueous solution by linseed cake. Process Biochemistry. 1997; 32(6): 473-77.

Morais LC, Goncalves EP,Vasconcelos LT, Gozalez Beca CG. Reactive dyes removal from wastewaters by adsorption on eucalyptus bark-adsorption equilibria. Environment Technology 2000; 2: 577-83.

Namasivayam C, Radhika R, Suba S. Uptake of dyes by a promising locally available agricultural solid waste: coir pith. Journal of Waste Management 2001; 2: 381-87.

Netpradit S, Thiravetyan P, Towprayoon S. Application of 'Waste' metal hydroxide sludge for adsorption of azo reactive dyes. Water Research 2003; 37: 763-72.

Radetski CM, Rosa SMC, Rosa EVC, Sierra MMD, Simionatto EL. Ozonation of textile wastewater: physicochemical and phytotoxic aspects. Environmental Technology 2002; 23: 537-45.

Sankar M, Sekaran G, Sadulla S, Ramasami T. Removal of diazo and triphenylmethane dyes from aqueous solutions through an adsorption process. Journal of Chemistry Technology 1999; 74: 337-44.

Sivaraj R, Namasivayam C, Kadirvelu K. Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions. Journal of Waste Management 2001; 21: 105-10.

Sun G, Xu X. Sunflower stalks as adsorbents for color removal from textile wastewater. Industrial & Engineering Chemistry Research 1997; 36: 808-12.
Walker GM, Weatherley LR. Kinetics of acid dye adsorption on GAC. Water Research 1999; 33(8): 1895-99.

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NOMENCLATURE

C_e = equilibrium dye concentration (mg/L)
C_o = initial dye concentration (mg/L)
q_e = amount of dyes adsorbed per unit weight of adsorbent at equilibrium (mg dye/g adsorbent)
q_{max} = maximum adsorption capacity (mg dye/g adsorbent)
b = Langmuir isotherm constant related to the affinity between the sorbent and sorbate (L/mg)
ΔH = Enthalpy change (kJ/mol)
K = Freundlich isotherm constant related to the capacity of adsorbent for adsorbate (L/g)
n = Freundlich isotherm constant related to a function of the strength of adsorbent (dimensionless)