



Use of cellulose-based wastes for adsorption of dyes from aqueous solutions

Gurusamy Annadurai^a, Ruey-Shin Juang^{b,*}, Duu-Jong Lee^a

^a Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan, ROC

^b Department of Chemical Engineering, Yuan Ze University, Chung-Li 320, Taiwan, ROC

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Abstract

Low-cost banana and orange peels were prepared as adsorbents for the adsorption of dyes from aqueous solutions. Dye concentration and pH were varied. The adsorption capacities for both peels decreased in the order methyl orange (MO) > methylene blue (MB) > Rhodamine B (RB) > Congo red (CR) > methyl violet (MV) > amido black 10B (AB). The isotherm data could be well described by the Freundlich and Langmuir equations in the concentration range of 10–120 mg/l. An alkaline pH was favorable for the adsorption of dyes. Based on the adsorption capacity, it was shown that banana peel was more effective than orange peel. Kinetic parameters of adsorption such as the Lagergren rate constant and the intraparticle diffusion rate constant were determined. For the present adsorption process intraparticle diffusion of dyes within the particle was identified to be rate limiting. Both peel wastes were shown to be promising materials for adsorption removal of dyes from aqueous solutions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption; Dyes; Banana and orange peels; Isotherms; Kinetics

1. Introduction

Many industries often use dyes and pigments to color their products. Most dyes are inert and non-toxic at the concentration discharged into the receiving water, however, they impart color undesirable to the water user. Color removal from textile effluents is a major environmental problem because of the difficulty to treating such streams by conventional physicochemical and biological treatment methods [1]. Liquid-phase adsorption has been shown to be an effective way for removing suspended solids, odors, organic matter, and oil from aqueous solutions. Nassar and El-Geundi [2] evaluated the cost of dye removal

* Corresponding author. Tel.: +886-3-4636800x555; fax: +886-3-4559373.

E-mail address: cejuang@ce.yzu.edu.tw (R.-S. Juang).

using natural clay, bagasse pith, and maize cob. While many physical and chemical methods including adsorption, coagulation, precipitation, filtration and oxidation have been used for the treatment of dye-containing effluent, adsorption appears to offer the best prospects over all the other treatments [3].

Activated carbon is the most widely used adsorbent for this purpose because it has a high capacity for adsorption of organic matter, but its use is limited because of its high cost [4–7]. This has led to search for cheaper substitutes. Coal, fly ash, wood, silica gel, clay materials (bentonite, montmorillonite, etc.), agricultural wastes (bagasse pith, maize cob, coconut shell, rice husk, etc.), and cotton wastes have been tried with varying success for color removal [5–9].

The purpose of this work was to test the possibility of using cellulose-based wastes, banana and orange peels, for adsorption removal of various dyes: methyl orange (MO), methylene blue (MB), Rhodamine B (RB), Congo red (CR), methyl violet (MV), and amido black 10B (AB) from water. The amounts of equilibrium adsorption were measured. The batch contact time method was used to measure the adsorption rate. Kinetic parameters were then evaluated and were finally correlated with process variables such as dye concentration and solution pH.

2. Materials and methods

2.1. Adsorbents and dyes

Banana and orange peels were obtained from a local fruit stall at Chung-Li, Taiwan. The peels were dried, crushed, and washed thoroughly with deionized water (Milli-Q, Millipore) to remove the adhering dirt. They were air dried in an oven at 100–120 °C for 24 h. After drying, the adsorbent was sieved through a 5 mm mesh size. The densities of banana and orange peels were 1.72 and 1.47 g/ml, respectively. The BET surface areas of both peels were in the range 20.6–23.5 m²/g obtained from N₂ adsorption isotherms by sorptiometer (Quantachrome Co., NOVA 2000). All dyes were obtained from Merck Co. The solution pH was adjusted by adding a small amount of 0.1 M HCl or NaOH.

2.2. Adsorption studies

Adsorption equilibrium experiments were carried out by adding the dried adsorbent (0.1 g) in 100 ml of dye solution with desired concentration and pH at 30 °C in a shaker at 180 rpm. After 24 h the suspension was filtered and the final concentration of dye in solution was measured using an UV–VIS spectrophotometer (Hitachi U-2000). The amount of dye adsorbed onto the peels, q_e (mg/g), was calculated by a mass balance relationship (Eq. (1)).

$$q_e = (C_0 - C_e) \frac{V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of dyes, respectively (mg/l), V the volume of the solution (L), and W the weight of the dry peel used (g).

The procedures of kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals, and the concentrations of dyes were similarly measured.

3. Results and discussion

3.1. Adsorption isotherms

Figs. 1 and 2 show the adsorption isotherms of different dyes (q_e versus C_e) using banana and orange peels, respectively. Two isotherm equations are tested in this work. One is the Langmuir equation (Eq. (2)), which has been successfully applied to many adsorption processes [10–15].

$$\frac{1}{q_e} = \left(\frac{1}{q_{\text{mon}}} \right) + \left(\frac{1}{K_L q_{\text{mon}}} \right) \left(\frac{1}{C_e} \right) \quad (2)$$

where K_L is the Langmuir constant and q_{mon} the amount of dye adsorbed when the saturation is attained. A plot of $1/q_e$ versus $1/C_e$ gives K_L and q_{mon} if the isotherm follows the Langmuir equation. Table 1 lists the parameters calculated. The present adsorption capacities (q_{mon}) are smaller than those obtained using activated carbons, mainly because their BET surface areas are significantly different (21–24 m²/g versus 600–1000 m²/g) [1,2].

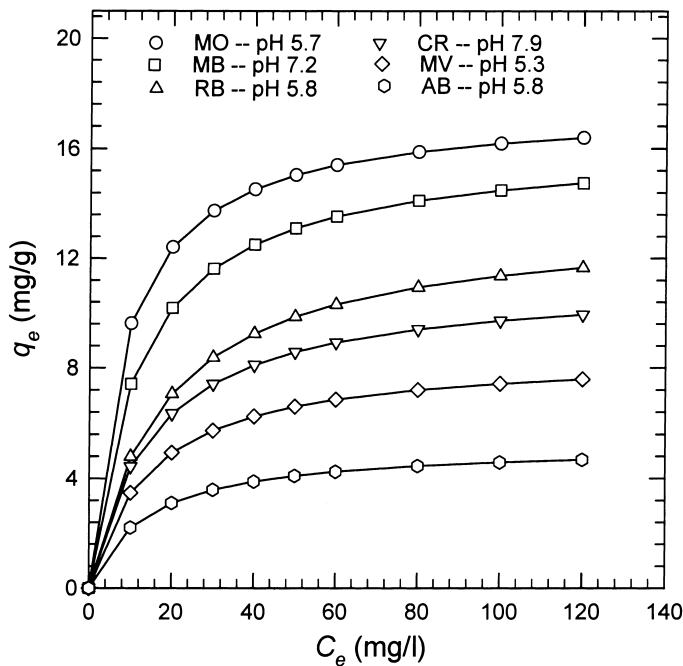


Fig. 1. Adsorption isotherms of dyes using banana peel.

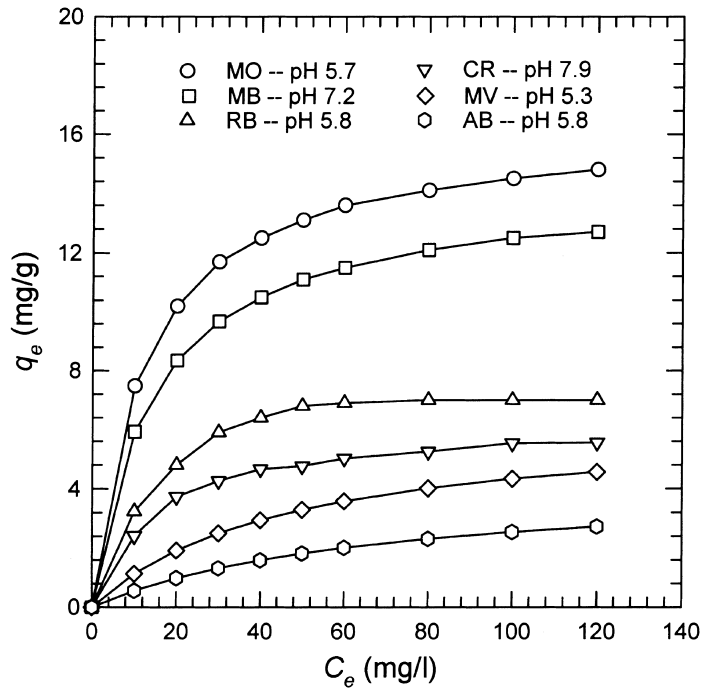


Fig. 2. Adsorption isotherms of dyes using orange peel.

The Freundlich equation [14,15], which is also often used for heterogeneous surface energy systems.

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (3)$$

The intercept K_F obtained from the plot of $\log q_e$ versus $\log C_e$ is roughly a measure of the sorption capacity and the slope ($1/n$) of the sorption intensity (Table 2). It was indicated by that magnitude of the term ($1/n$) gives an indication of the favorability and capacity of the adsorbent/adsorbate systems [15].

Table 1
Parameters obtained for the Langmuir equation

Dye	Banana peel			Orange peel		
	q_{mon} (mg/g)	K_L (l/mg)	R	q_{mon} (mg/g)	K_L (l/mg)	R
MO	21.0	11.4	0.9340	20.5	16.5	0.9541
MB	20.8	16.5	0.9524	18.6	19.9	0.9659
RB	20.6	32.6	0.9572	14.3	32.0	0.9377
CR	18.2	37.7	0.9480	14.0	46.8	0.9739
MV	12.2	29.1	0.9616	11.5	56.7	0.9794
AB	6.5	17.4	0.9632	7.9	59.2	0.9747

Table 2
Parameters obtained for the Freundlich equation^a

Dye	Banana peel			Orange peel		
	K_F	$1/n$	R	K_F	$1/n$	R
MO	1.73	0.26	0.9861	2.20	0.17	0.9401
MB	1.34	0.33	0.9851	1.75	0.26	0.9519
RB	0.39	0.47	0.9644	1.01	0.39	0.9399
CR	0.05	0.54	0.9589	0.65	0.44	0.9820
MV	1.08	0.73	0.9867	0.24	0.59	0.9566
AB	1.26	0.66	0.9687	0.65	0.99	0.9470

^a Unit of K_F was (mg/g)(mg/l)^{-1/n}.

Based on the correlation coefficient (R) shown in Tables 1 and 2, the adsorption isotherms with banana peel can be slightly better described by the Freundlich equation, and by the Langmuir equation in the case of organic peel. The fit of the data to the Freundlich equation may indicate the heterogeneity of the adsorbent surface.

3.2. Effect of solution pH on adsorption capacity

The effect of solution pH on the adsorption of dyes by banana and orange peels was shown in Figs. 3 and 4. For banana peel, the amount of adsorption increases when the pH

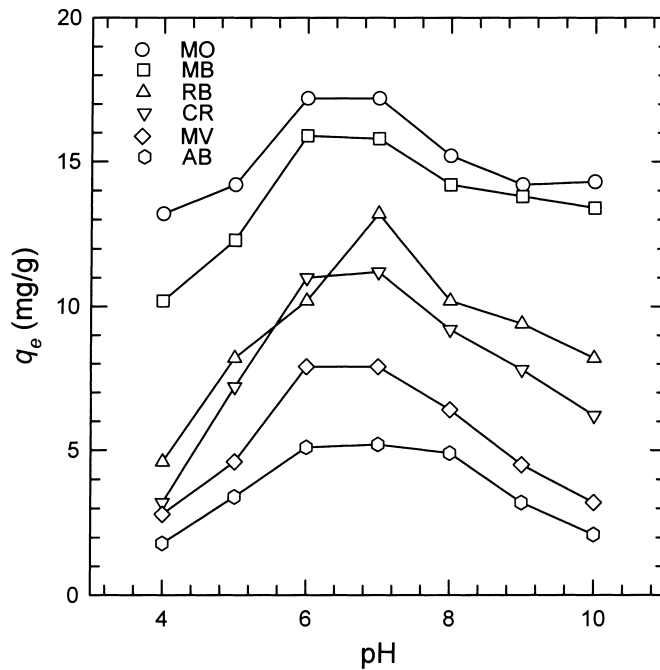


Fig. 3. Effect of pH on adsorption of dyes using banana peel ($C_0 = 100$ mg/l).

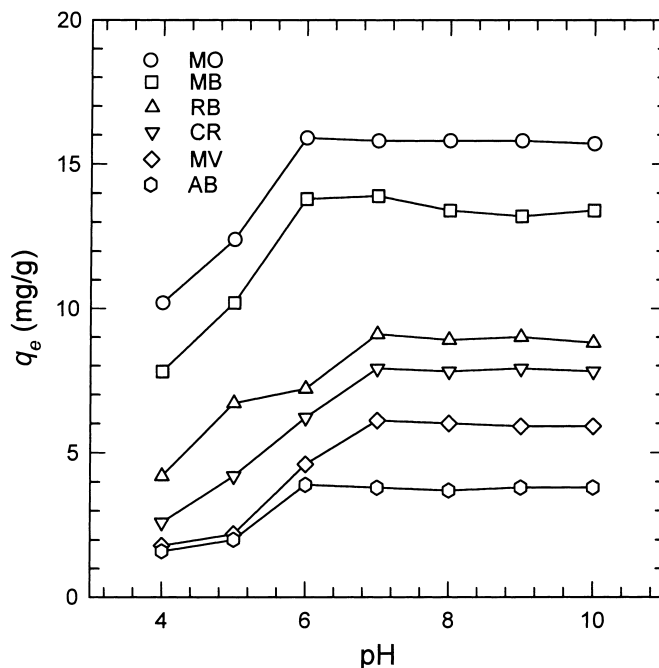


Fig. 4. Effect of pH on adsorption of dyes using orange peel ($C_0 = 100$ mg/l)

is increased. The adsorption capability reaches maximum at pH 6–7, but decreases when pH is increased further. Similar results of pH effect were also reported for the adsorption of dyes on banana peel [16] and biological waste slurry [17], and even of Ni^{2+} on orange peel [18]. In the case of orange peel (Fig. 4), however, the amount of dye adsorbed reaches a plateau at pH > 7. Under the conditions tested in Figs. 3 and 4, the highest amounts of adsorption are 17.2 (MO), 15.9 (MB), 13.2 (RB), 11.2 (CR), 7.9 (MV), and 7.9 (AB) mg/g using banana peel, as well as 15.8 (MO), 13.9 (MB), 9.1 (RB), 7.9 (CR), 6.1 (MV), and –3.8 (AB) mg/g using orange peel.

Solution pH would affect both aqueous chemistry and surface binding-sites of the adsorbents. At lower pH, H^+ may compete with dye ions for the adsorption sites of both peel wastes, thereby inhibiting the adsorption of dyes. Actually, the zeta potentials of the adsorbent suspensions were measured (Malvern Zetasizer 3000 system). From pH 2.0 to 8.0, the zeta potentials of original banana and orange peels decline from –8.2 to –62.4 mV and from –3.2 to –44.5 mV, respectively (not shown). The sharper change in zeta potential for banana peel than orange peel may explain their different pH trends of dye adsorption.

The SEM images of original banana and orange peels (Fig. 5a and b) show that the pores within the peel particles are highly heterogeneous. However, this is not the case after adsorption (Fig. 5c and d). After dye adsorption, a significant change is observed in structure of the peels. The peels appear to have a rough surface with crater-like pores because they are partially covered by dye molecules.

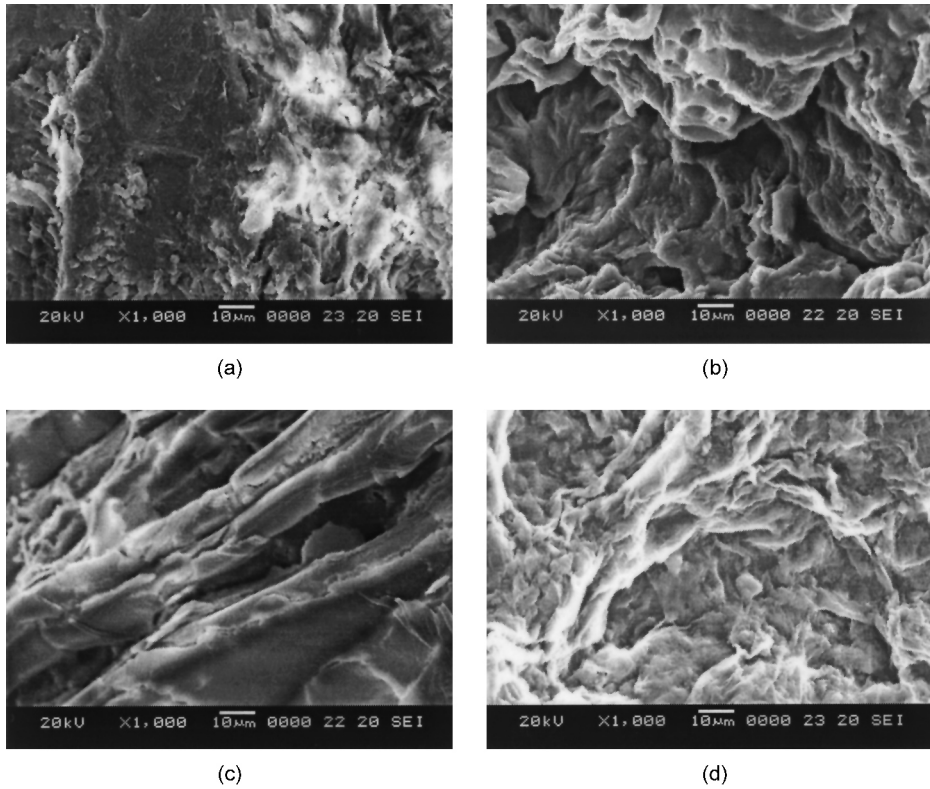


Fig. 5. SEM images for banana and orange peels: (a) original banana peel; (b) original orange peel; (c) banana peel after adsorption and (d) orange peel after adsorption.

3.3. Adsorption kinetics

Figs. 6 and 7 show that the amount of dye adsorption increases with time and it remains constant after a contact time of about 65 min (i.e. the equilibrium time). The equilibrium time is independent of initial dye concentration. The time profile of dye uptake is a single, smooth, and continuous curve leading to saturation, suggesting the possible monolayer coverage of dyes on the surface of the adsorbent. The Langergren equation, a pseudo-first-order equation, describes the kinetics of adsorption process as follows [4,19].

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t \quad (4)$$

where q_t is the amount of dye adsorbed (mg/g) at any time, and k_1 is the rate constant. The plot of $\log(q_e - q_t)$ versus t indicates that such first-order rate expression is not so valid to the present systems (not shown, correlation coefficient <0.91). However, the values of k_1 calculated are still listed in Table 3 for reference.

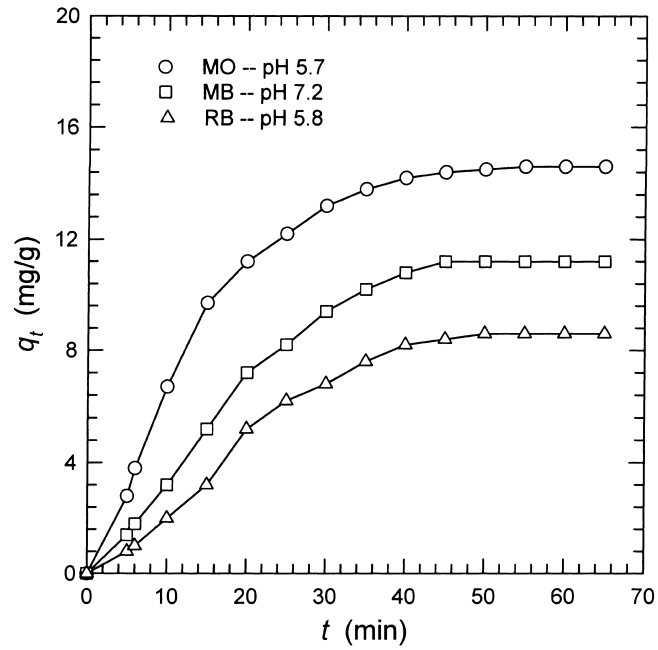


Fig. 6. Time profiles of solid-phase concentrations of dyes using banana peel ($C_0 = 50$ mg/l).

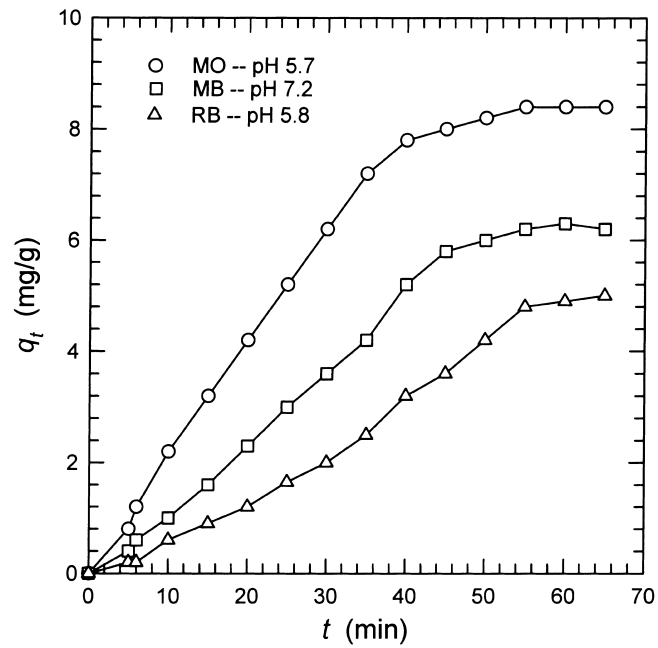


Fig. 7. Time profiles of solid-phase concentrations of dyes using orange peel ($C_0 = 50$ mg/l).

Table 3
Parameters obtained for different dyes

Dye	Banana peel		Orange peel	
	k_1 (min^{-1})	k_p ($\text{mg}/(\text{g min}^{1/2})$)	k_1 (min^{-1})	k_p ($\text{mg}/(\text{g min}^{1/2})$)
MO	0.39	2.42	0.40	1.68
MB	0.35	2.12	0.29	1.20
RB	0.19	1.70	0.21	0.81

The data of solid-phase dye concentrations against time at an initial dye concentration of 20 mg/l were further processed for testing the role of diffusion (as the rate controlling step) in the adsorption process. Adsorption process incorporates the transport of adsorbate from bulk solution to the interior surface of the pores [20]. There is a possibility that the transport of dyes from the solution into the pores of the adsorbent is rate controlling in batch experiments with rapid stirring. The rate parameters for intraparticle diffusion (k_p) for different dyes are determined using the following equation [21].

$$q_t = k_p t^{1/2} \quad (5)$$

where k_p is the intraparticle diffusion rate constant.

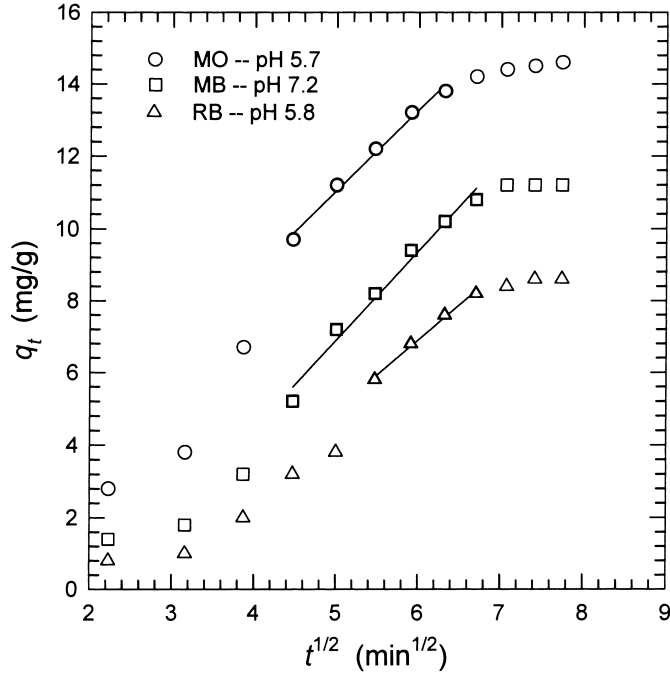


Fig. 8. Test of intraparticle diffusion model for adsorption of dyes using banana peel.

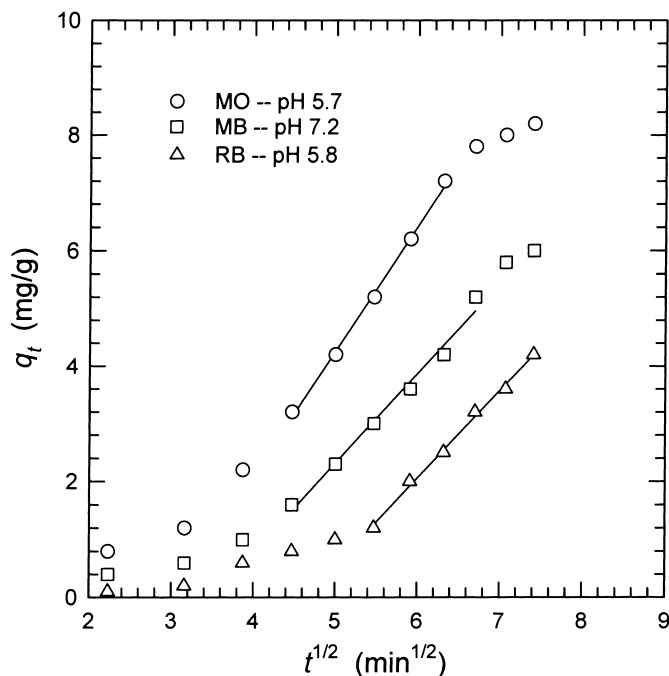


Fig. 9. Test of intraparticle diffusion model for adsorption of dyes using orange peel.

Due to mass transfer effects, the shape of q_t versus $t^{1/2}$ plot is curved at a small time limit [20]. All the plots have the same general features, initial curved portion followed by linear portion and a plateau. The initial curved portion is attributed to the bulk diffusion and the linear portion to the intraparticle diffusion. These phenomena have been reported for the adsorption of Cd^{2+} on waste Fe(III)/Cr(III) hydroxide [22] and on thermally activated electroplating sludge [23]. At a certain time limit (about 20 min), the curves reveal a linear characteristic that the intraparticle diffusion controls the adsorption process (Figs. 8 and 9). The values of k_p are obtained from the slope of the straight lines, and are listed in Table 3. According to the acceptable adsorption capacity (based on per specific surface area) and rate, the present low-cost peel wastes are expected to be attractive for adsorption removal of color from aqueous streams. Unlike activated carbons, however, thermal regeneration of the peel wastes is not feasible. Thus, the spent adsorbents may be post-treated with other solid wastes such as activated sludge.

4. Conclusion

Equilibrium and kinetic studies were made for the adsorption of dyes from aqueous solutions onto banana and orange peels in the concentration range 10–120 mg/l at 30 °C. The Freundlich equation showed a somewhat better fit than does the Langmuir equation for

adsorption of dyes using banana peel, but exactly reversed using orange peels. Under the conditions tested ($C_0 = 100$ mg/l, dosage of adsorbent 1 g/l), the amounts of adsorption were maximized at pH 6–7 up to 17.2 (MO), 15.9 (MB), 13.2 (RB), 11.2 (CR), 7.9 (MV), and 7.9 (AB) mg/g using banana peel, and at pH > 7 up to 15.8 (MO), 13.9 (MB), 9.1 (RB), 7.9 (CR), 6.1 (MV), and –3.8 (AB) mg/g using orange peel. The intraparticle diffusion of dye molecules within the particles was found to be rate controlling in these adsorption processes after 20 min contact. The present work revealed that the waste banana and orange peels were the promising materials for the removal of dyes from aqueous solutions.

Acknowledgements

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