

Removal of Color from Effluents Using Polyamide–Epichlorohydrin-Cellulose Polymer.

II. Use in Acid Dye Removal

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SYNOPSIS

The ability of polyamide–epichlorohydrin-cellulose (PAE-cell) to remove various acid dyes from aqueous solutions was investigated. The classes of acid dyes included the milling type, levelling type, and metal-complex type. Operational conditions such as PAE-cell type, dye type, PAE-cell particle size, dye bath flow rate, filling density in the column, initial dye concentration, pH of solution, and adsorbent mass were studied. The results show that these PAE-cell polymers exhibit better capacity for acid dye removal than some commercial activated carbons. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

A novel series of adsorbents prepared from the reaction of polyamide–epichlorohydrin resin and cellulose (PAE-cell) was reported in Part I of this series.¹ These PAE-cell polymers have been found to exhibit excellent ability in the adsorption of direct dyes in a fixed bed column system. These capacities for direct dye removal from solution have been found better than those of some commercial activated carbons. Acid dyes, the other popular anionic dyes, have been widely employed in dyeing various substrates such as wool, silk, nylon, and leather.² Because of the popularity of acid dye usage, a number of studies have been reported with respect to the adsorption equilibria and kinetics of the acid dye removal process using various adsorbents. Available adsorbents are activated carbon,^{3–9} wood,^{4,10–13} peat,^{4,14–16} chitin,^{17–22} chitosan,²³ chitosan fiber,²⁴ pith,²⁵ and several low-cost materials (teakwood bark, bentonite clay, etc.).²⁶ However only limited information is available in the literature regarding the use of polymeric adsorbents in removing acid dyes from aqueous solution. The ability of PAE-cell to adsorb

12 acid dyes from aqueous solution under several experimental conditions was studied in this work. The adsorption effect of PAE-cell on acid dyes indicates its potential as a removing agent for acid dyes.

EXPERIMENTAL

Materials

Polyamide–epichlorohydrin-cellulose polymers used in this study were prepared by the reaction of adipic acid, diethylenetriamine, epichlorohydrin and α -cellulose. The preparation of these adsorbents was described in Part I of this series.¹ The structure and analyses of these adsorbents are shown in Table I.

Table I Appearance and Nitrogen Content of PAE-Cell Compounds

	α -Cellulose Weight (%)	Appearance	Nitrogen (%)
PAE	0	Yellow ochre	12.08
PAE-cell-1	10	Yellow ochre	10.63
PAE-cell-2	20	Chrome yellow	8.51
PAE-cell-3	25	Chrome yellow	7.56
PAE-cell-4	30	White yellow	6.89

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Table II Acid Dyes Used

Molecular Structure	Trade Name	λ_{\max} (nm)	Color Index No.
	Everacid Mill. Yellow MR (C.I. Acid Yellow 42)	410	22910
	Everacid Mill. Cyanine (C.I. Acid Blue 113)	565	26360
	Everacid Mill. Red PG (C.I. Acid Red 85)	510	22245
	Everacid Mill. Red RS (C.I. Acid Red 114)	520	23635
	Everacid Orange II (C.I. Acid Orange 7)	480	15510
	Best Acid Blue 3R (C.I. Acid Blue 92)	572	13390
	Everacid Light Yellow GC (C.I. Acid Yellow 17)	400	18965

The activated carbons supplied by Germany FERAK, Japan Daiyo, and Sigma Ltd., were sieved into discrete particle size range (150–106 μm). The acid dyes used in the adsorption experiments are Yellow 42, Blue 113, Red 85, Red 114, Orange 7, and

Yellow 17 as supplied by Taiwan Everlight Chem. Co.; Blue 92 and Brown 14 as supplied by Taiwan Oriental Giant Dyes & Chem. Ind. Co.; Blue 158, Red 183, Blue 193, and Yellow 99 as supplied by BASF Co. Their molecular structure, trade name,

Table II (Continued from the previous page)

Molecular Structure	Trade Name	λ_{\max} (nm)	Color Index No.
	Best Acid Brown R (C.I. Acid Brown 14)	465	20195
	Palatin Fast Blue GGN (C.I. Acid Blue 158)	592	14880
	Palatin Fast Red GREN (C.I. Acid Red 183)	490	18800
	Acidol Dark Blue M-TR (C.I. Acid Blue 193)	577	15707
	Palatin Fast Yellow GRN (C.I. Acid Yellow 99)	443	13900

λ_{\max} , and Color Index number are shown Table II. They were used in the form of commercial salts.

Method

The acid dye was adsorbed on 2 g PAE-cell or activated carbon using the fixed bed column system described in Part I of this series.¹ Then, the treated dye bath was collected into a glass tube on a fraction collector (each tube contained 10 mL of treated dye bath). The initial dye concentration (C_0) and residual dye concentration (C_t) were measured using a Shimadzu model UV-240 spectrophotometer at a wavelength, λ_{\max} (corresponding to the maximum wavelength of adsorbance). These wavelengths were determined for each dyestuff and shown in Table II. The adsorption experiment was stopped when C_t

approached C_0 . The adsorption experiment conditions are shown in Table III.

RESULTS AND DISCUSSION

Effect of PAE-Cell Polymer Type

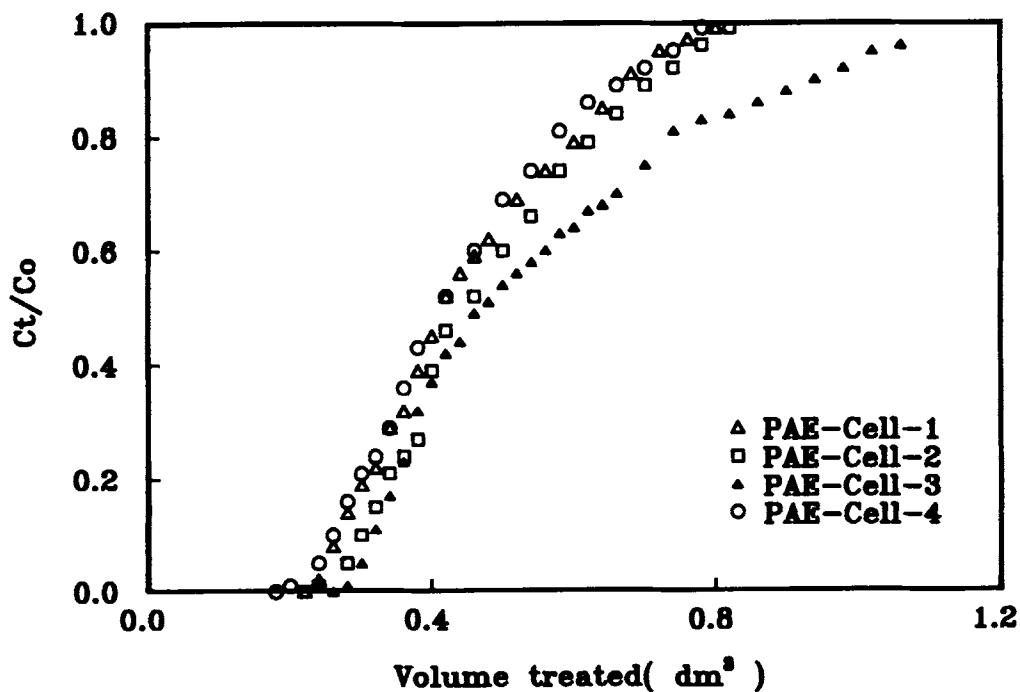
The PAE-cell polymers are classified as 10, 20, 25, and 30%, based on the α -cellulose weight ratio. The experiment used 2 g of PAE-cell to adsorb C.I. Acid Blue 113 of initial dye concentration 2000 mg dm^{-3} . Figure 1 shows the adsorption effectiveness of PAE-cell. The adsorption capacity of the PAE-cell is generally found better with an α -cellulose content of 25%. The difference in the adsorption capacity of PAE-cell and activated carbon is shown in Figure

Table III Experimental Conditions of Fixed Bed Adsorption System

	General Condition	Alternate Conditions
PAE-cell type (α -cellulose wt %)	25% (PAE-Cell-3)	10% (PAE-cell-1) 20% (PAE-cell-2) 30% (PAE-cell-4)
Acid dye type	Bule 113	Other acid dyes
PAE-cell particle range (μm)	150-106	300-150 600-300 710-600
Dye bath flow rate (mL min^{-1})	5	2, 8
PAE-cell filling density (g cm^{-3})	0.283	0.226, 0.189
Initial dye conc. (mg dm^{-3})	2000	1000, 1500
Dye bath pH value	7	3, 5, 9
Adsorbent mass (g)	2	0.5, 1, 3
Activated carbon		AC-1: Germany FERAK activated carbon AC-2: Japan Daiyo activated carbon AC-3: Sigma activated carbon

2, which shows that PAE-cell has better ability to absorb Acid Blue 113 than activated carbon does. One possible reason is the sulfonic acid groups of the dye, which make the dye very water soluble and polar; therefore, it is not readily adsorbable on activated carbon, which is nonpolar. The other reason

is probably the anionic repulsion at the surface of the carbon, since acid dyes are anionic in water. On the other hand, the PAE-cell has an amide group and hydroxyl group;¹ therefore, the PAE-cell has higher adsorption capacity for Blue 113 than activated carbon does.

**Figure 1** Breakthrough curves for C.I. Acid Blue 113. Effect of PAE-cell compounds.

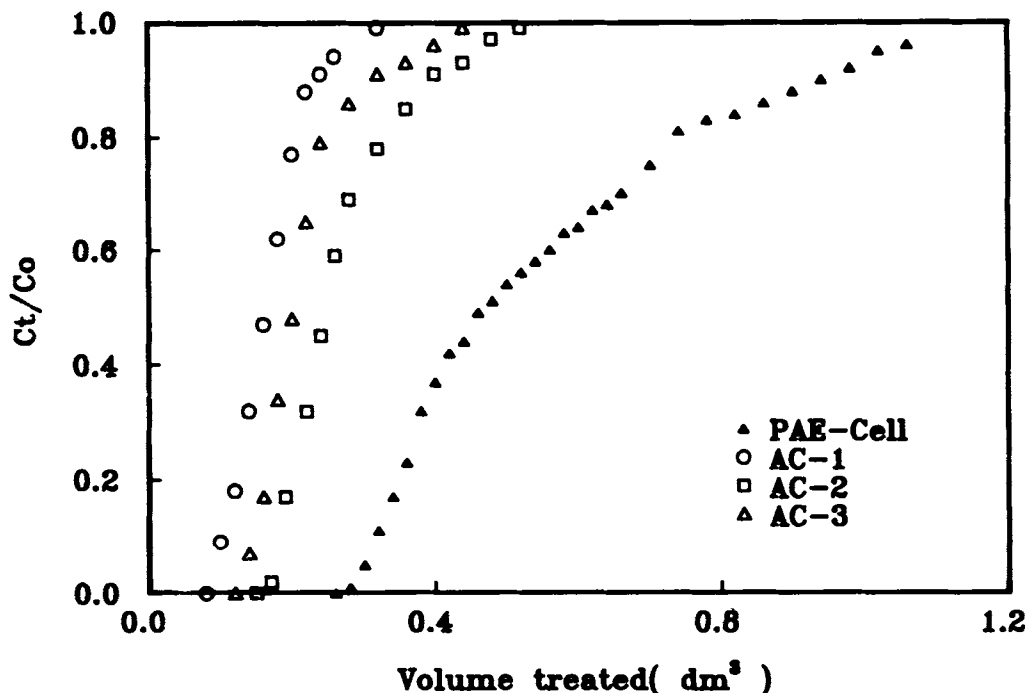


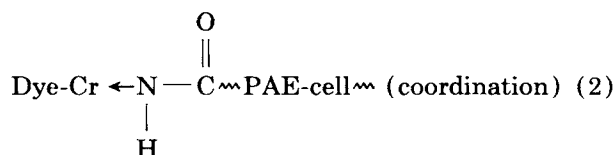
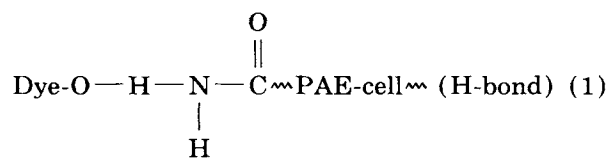
Figure 2 Breakthrough curves for C.I. Acid Blue 113. Effect of PAE-cell and activated carbon.

Effect of Acid Dye Type

Acid dyes are classified broadly into the following four groups, according to their dyeing and wet fastness properties: milling acid dyes, levelling acid dyes, neutral dyeing or super milling acid dyes, and metal-complex acid dyes. Milling acid dyes are used for hosiery, knitting yarns, and loose wool for the manufacture of tweeds, etc. Levelling acid dyes are widely used for the so-called "fashion colors" on ladies' dress goods, which require mixture of two or more dyes.²⁷ The metal-complex acid dyes usually contain sulphonic acid groups, and their metal derivatives (such as chromium, cobalt, or nickel complex) are to some extent soluble in water. Attachment to the fibre probably depends partly on the formation of metal-fiber bonds, and the strength of such bonds may be a factor contributing to the good wet-fastness properties often attained.²⁸

Figure 3 shows the breakthrough curves for three type of acid dyes ($C_0 = 2000 \text{ mg dm}^{-3}$) onto PAE-cell (2 g). The results in Figure 3(a) show that the order of adsorption effect for the milling type is Yellow 42 > Blue 113 > Red 85 > Red 114. The high uptake for C.I. Acid Yellow 42 is possibly due to the fact that Yellow 42 has more azo-groups than the others, so that it can form more hydrogen bonds with the hydroxyl groups of PAE-cell. On the other hand, the low uptake for C.I. Acid Red 114 is possibly

because Red 114 has much larger dye molecules and a long chain, so that it cannot easily penetrate into the internal pore structure of the PAE-cell. These results are similar to those of past studies.^{1,21} Figure 3(b) shows the breakthrough curves for levelling acid dyes. The excellent adsorption effect for C.I. Acid Orange 7 is possible due to the fact that Orange 7 has small dye molecules and a short chain. Figure 3(c) shows the breakthrough curves for metal-complex acid dyes. The high uptake for C.I. Acid Blue 158 is possibly due to the fact that Blue 158 has more hydrophilic groups than the others. The coupling of PAE-cell and metal-complex acid dyes may be described using formulas (1), (2), and (3):



The amide groups in PAE-cell can form hydrogen

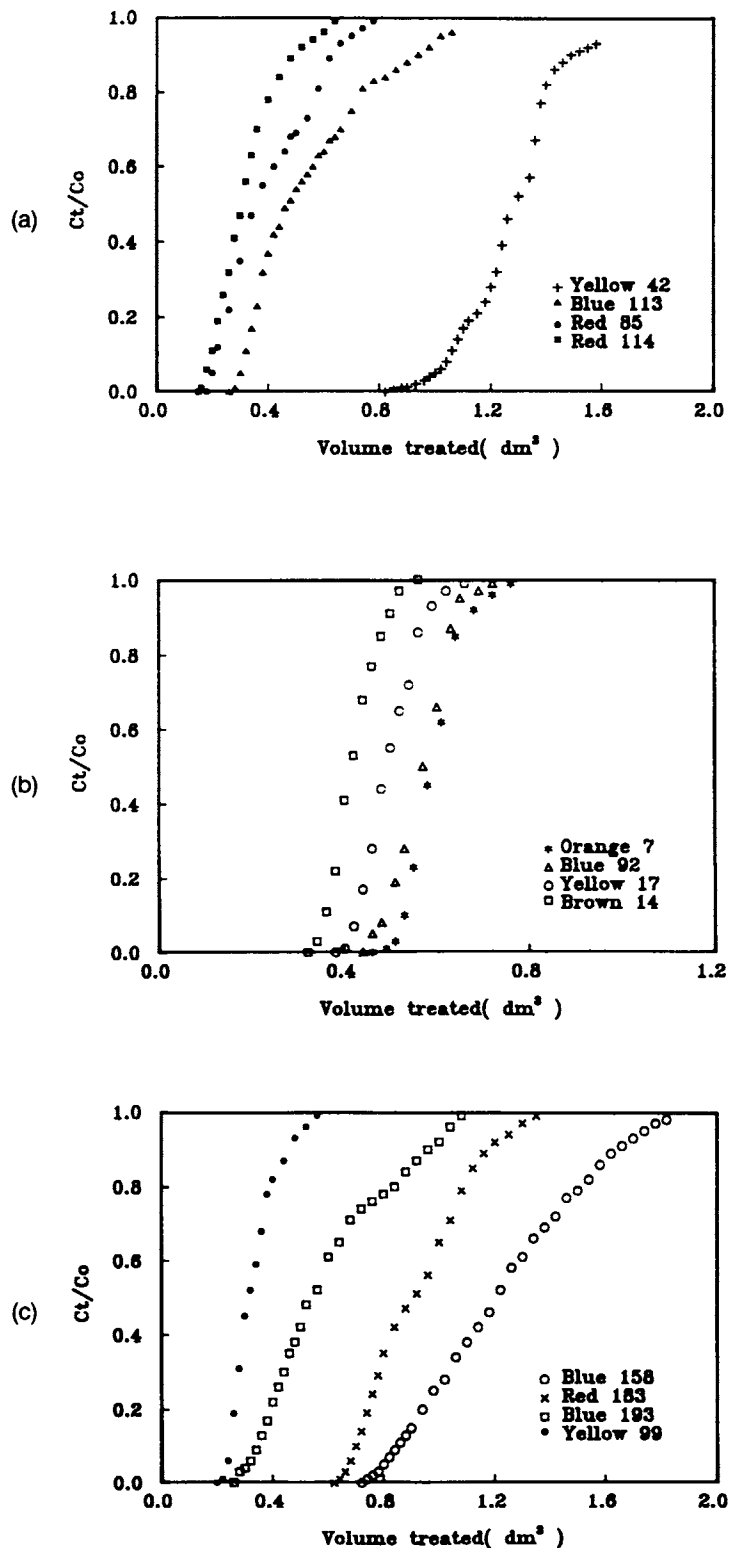


Figure 3 Breakthrough curves for three types of acid dyes on PAE-cell: (a) milling type; (b) levelling type; (c) metal-complex type.

bond (1) and coordinate bond (2) with hydroxyl groups and chromium in the metal-complex acid dye molecules. Furthermore, some of the affinity is due to van der Waals adsorption (3), but as the size of the complex is not very great, the contribution may not be as large as that of the other bondings. Actually many factors can affect the degree of adsorption: the fraction of colored ions in the commercial salt; the solubility and ionization of dyes in water; the molecular volume of dye and its planarity; the chelating ability of the adsorbent-dye system; and the dimerization ability of the dye.¹⁷

Effect of PAE-Cell Particle Size

Adsorption is a process in which an organic molecule is transferred from solution to the surface of a solid where the molecule is bound by physical/chemical force. Since adsorption is a surface phenomenon, economically-useful adsorbents are characterized by high surface area to provide sufficient active sites to allow a substantial amount of solute to be adsorbed. Thus, the size of the adsorbent particle is an important system parameter since it strongly affects the particle diffusion.²⁹ Therefore, a wide range of PAE-cell particle sizes was investigated (Table III). A dye bath of C.I. Acid Blue 113 with initial

dye concentration 2000 mg dm^{-3} was adsorbed using 2 g PAE-cell of four particle size ranges. Figure 4 shows that smaller PAE-cell particles have better adsorption effectiveness than larger particles. This is because the former have more surface area than the latter so that they may adsorb more acid dye molecules.

Effect of Contact Time of PAE-Cell and Acid Dyes

The contact time of adsorbates and adsorbents is the most significant factor in the fixed bed adsorption process. The contact time is very short in the fixed bed adsorption process. Therefore, a wide range in the dye bath velocity and PAE-cell filling density in the column was investigated, as shown in Table III. Figure 5 shows that the low dye bath flow rate produced a better adsorptive effect than a high dye bath flow rate. Because the former can increase the contact time of the dye bath and PAE-cell, it can allow the dye molecules to aggregate on the surface and/or to enter into the internal pore structure of the PAE-cell and thus increase the amount of dye molecules adsorbed by the PAE-cell. In other words, the dye molecules cannot be adsorbed onto PAE-cell in a short time period at a high dye bath flow rate. Figure 6 shows that the adsorption effect of

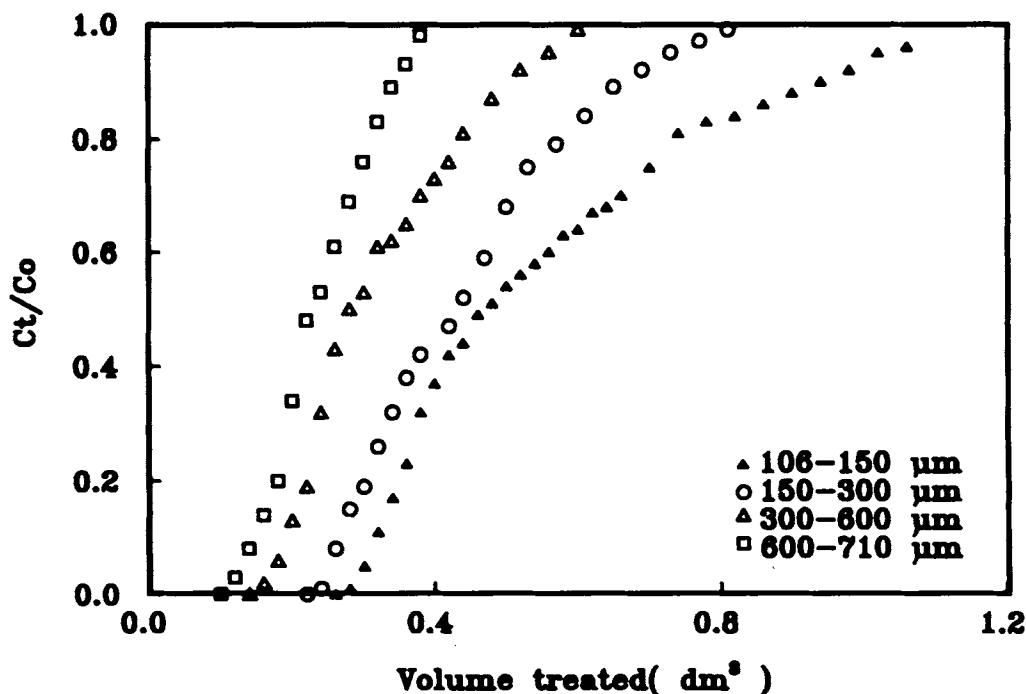


Figure 4 Breakthrough curves for C.I. Acid Blue 113 on PAE-cell. Effect of PAE-cell particle size.

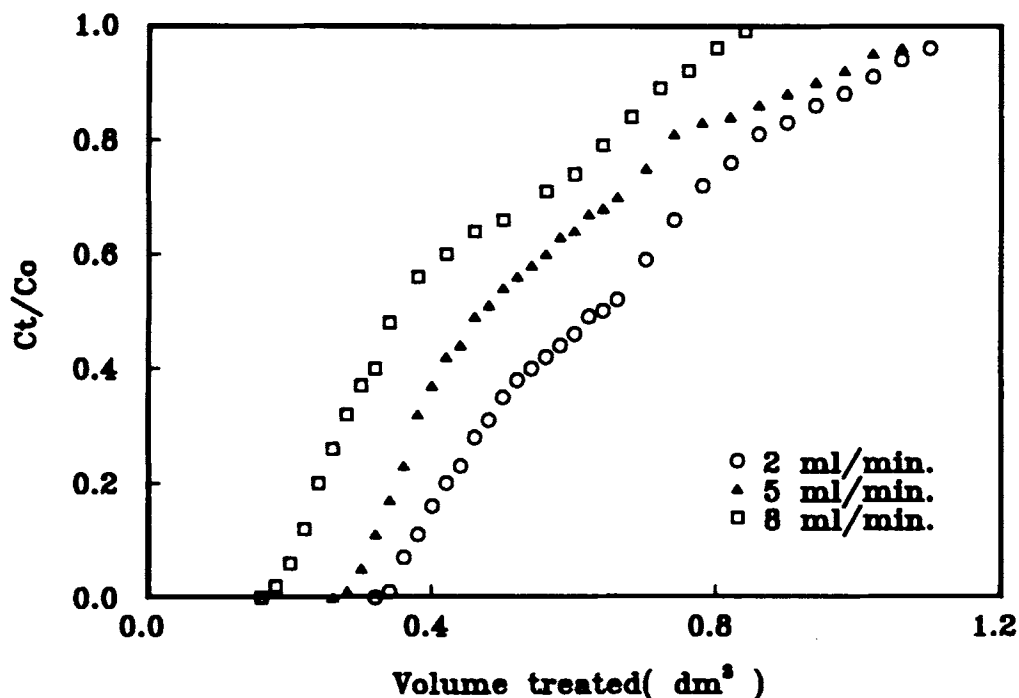


Figure 5 Breakthrough curves for C.I. Acid Blue 113 on PAE-cell. Effect of dye bath flow rate.

PAE-cell with high filling density in the column was better than with low filling density. This is because the dye molecules bypass or only pass through the

surface of PAE-cell at low filling density; thus, the dye molecules cannot be adsorbed by the PAE-cell, and there is a decrease in the adsorption efficiency

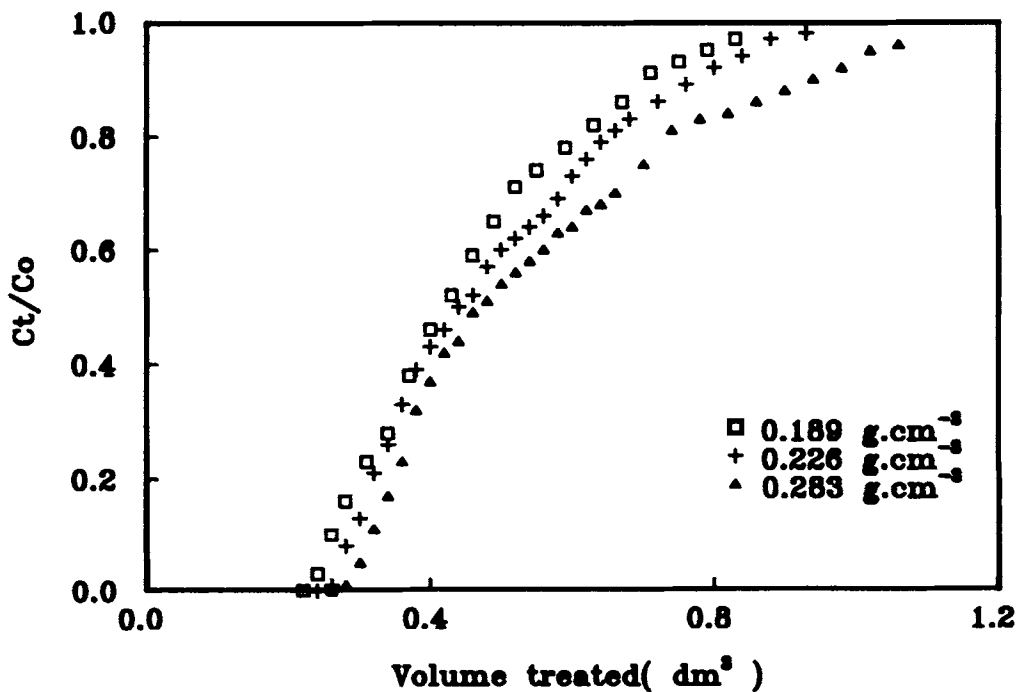


Figure 6 Breakthrough curves for C.I. Acid Blue 113 on PAE-cell. Effect of PAE-cell filling density on fixed bed column.

of the PAE-cell. The PAE-cell filling density must be less than 0.3 g cm^{-3} , otherwise, it may result in a high pressure drop and experimental error. These results are similar to those in Part I of this series under the same experimental conditions.

Effect of Initial Dye Concentration

Usually the service time of a fixed bed column system depends greatly on the concentration of the solution. Therefore, several experiments were undertaken to study the effect of varying the initial dye concentration on the rate of removal from solution (Table III). Figure 7 shows that the low initial dye concentration resulted in a longer service time than the high initial dye concentration. Higher initial concentration saturates the adsorbent much faster than lower initial concentration, hence reducing the service time of the column. The adsorbent may need a longer time to remove dyes from a less concentrated effluent.

Effect of Solution pH

Adsorption from solution can be highly pH dependent, as discussed earlier.²⁹ From an economic and practical standpoint, a fluid should always be evaluated at the ambient pH. In other words, the pH of

a solution is of significance for its effect on the adsorbent as well as on the adsorbate. Both adsorbate and adsorbent may have chemical characteristics that are affected by the concentration of hydrogen ions $[\text{H}^+]$ in the solution. Some adsorbents have affinity for $[\text{H}^+]$ or $[\text{OH}^-]$ ions and can directly affect the solution pH and therefore the solubility and the adsorption capacity.²⁹ The acid dyes are so called because they are applied in a bath containing mineral or organic acid, and therefore pH is a very important factor. A wide range of dye bath pH was investigated (Table III). Figure 8 illustrates the influence of pH on the adsorption of Acid Orange 7 (levelling type), Blue 158 (metal-complex type), and Blue 113 (milling type) onto PAE-cell. The results show two completely different effects. The adsorption of Orange 7 and Blue 158 increase with $[\text{H}^+]$ as Figure 8(a) and (b) show. This phenomenon is possibly caused by the electrostatic potential between the dye molecules and the PAE-cell surface's adsorbed hydrogen ion at low pH solutions. This electrostatic potential can improve the adsorption affinity between dye and PAE-cell. Figure 8(c) shows that adsorption effect was better between pH 5 to 7 for Blue 113. This is possibly because of the good adsorption affinity between PAE-cell and the anionic ion of Blue 113 at low $[\text{H}^+]$. According to these results, most of the acid dyes can be

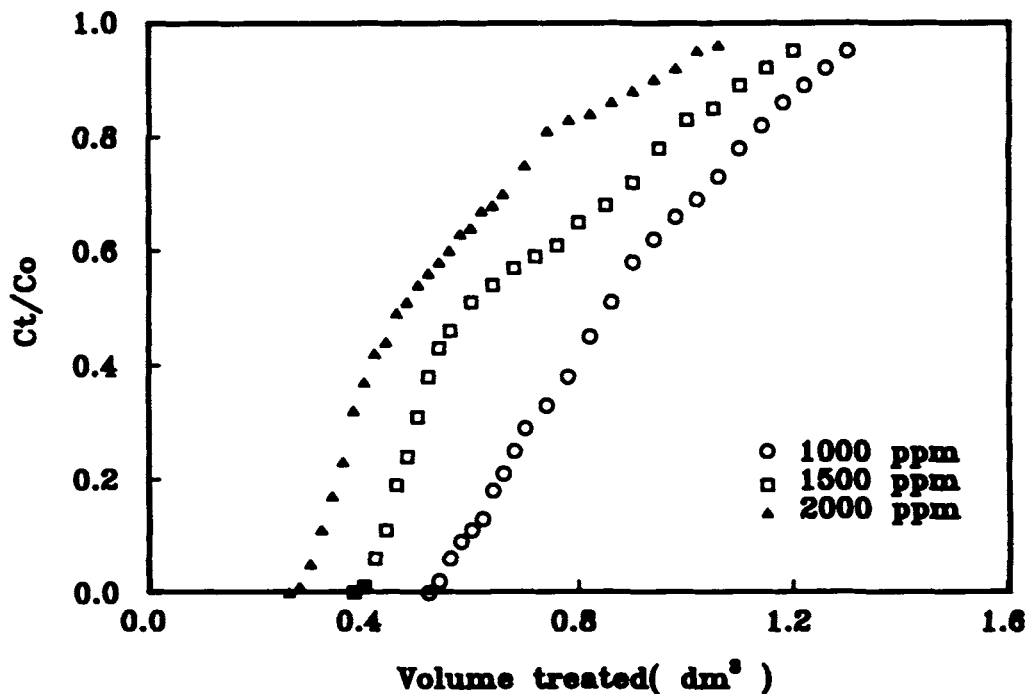


Figure 7 Breakthrough curves for C.I. Acid Blue 113 on PAE-cell. Effect of initial dye concentration.

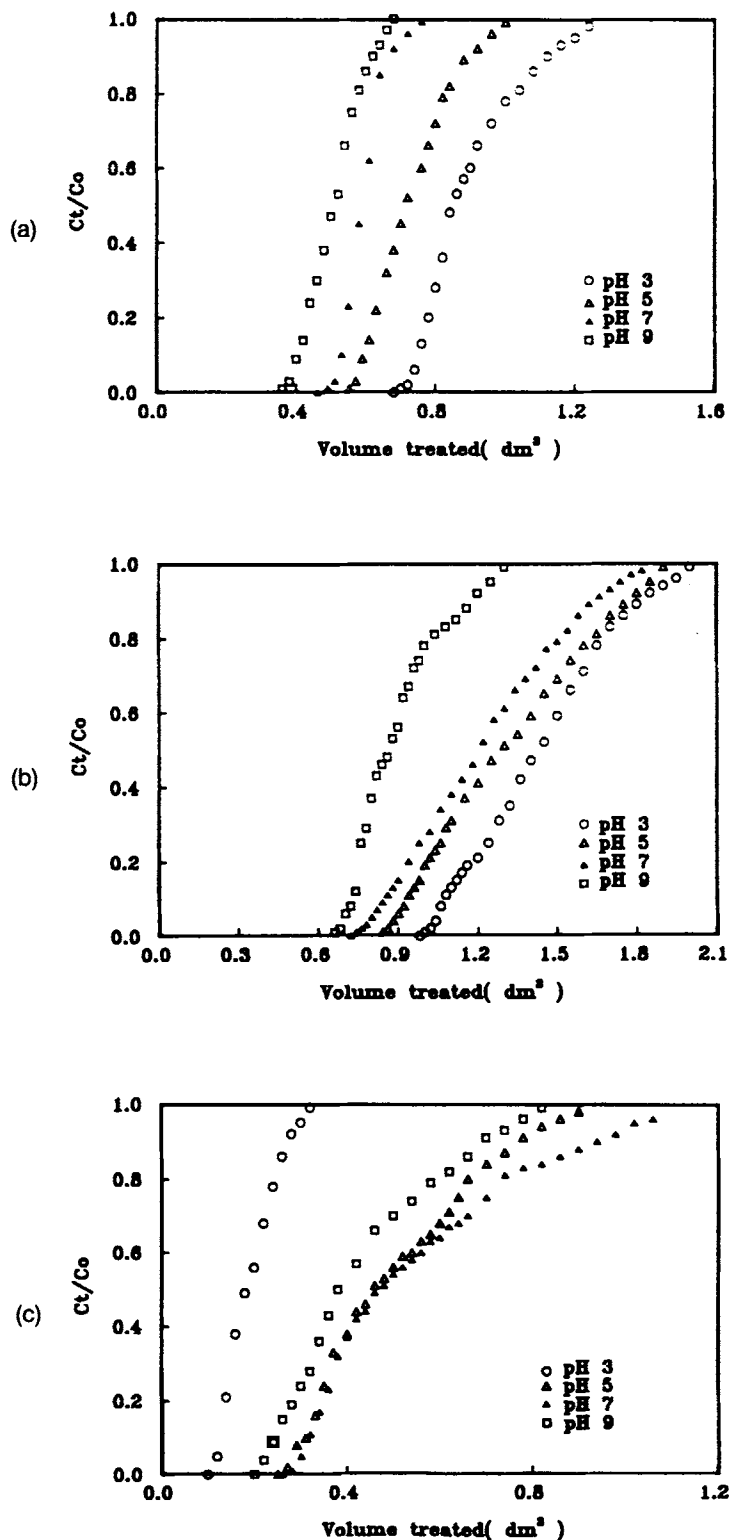


Figure 8 Breakthrough curves for C.I. Acid Orange 7, Blue 158, and Blue 113 on PAE-cell. Effect of solutions' pH: (a) Acid Orange 7 (levelling type); (b) Acid Blue 158 (metal-complex type); (c) Acid Blue 113 (milling type).

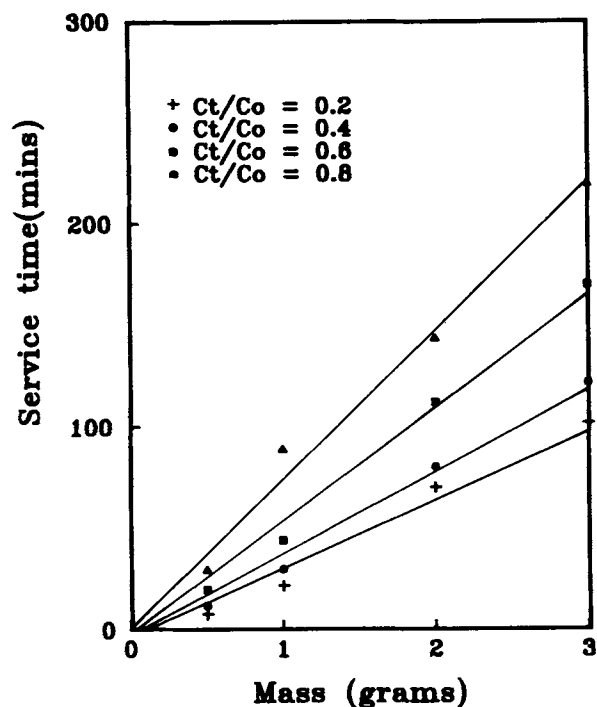


Figure 9 Service time against mass of PAE-cell at several C_t/C_0 breakthrough for C.I. Acid Blue 113.

adsorbed onto PAE-cell at a weak acid level (pH 5-7).

Effect of Adsorbent Mass

Adsorbent mass is usually the major concern in the conceptual design of an adsorption system, and

Table IV Effect of PAE-Cell and Three Activated Carbons

Dyes	Adsorbent			
	PAE-cell	AC-1	AC-2	AC-3
Yellow 42	250	44	54	38
Blue 113	96	38	51	42
Red 85	72	34	44	30
Red 114	62	40	48	32
Orange 7	118	40	50	34
Blue 92	114	26	34	26
Yellow 17	106	34	34	28
Brown 14	82	26	30	20
Blue 158	243	64	66	36
Red 183	166	52	50	32
Blue 193	108	32	46	30
Yellow 99	62	26	34	22

Service time (min) of adsorbent (2 g) at $C_t/C_0 = 50\%$ breakthrough for several acid dyes ($C_0 = 2000 \text{ mg dm}^{-3}$).

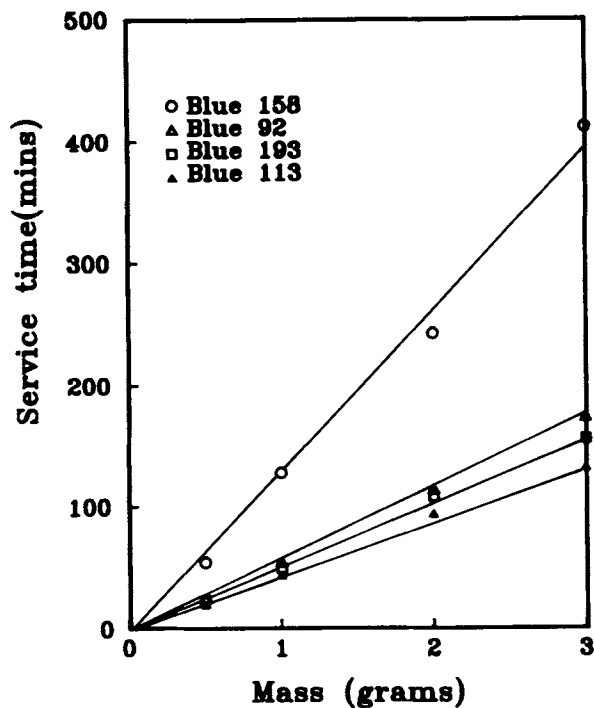


Figure 10 Service time against mass of PAE-cell at $C_t/C_0 = 50\%$ breakthrough for four blue acid dyes.

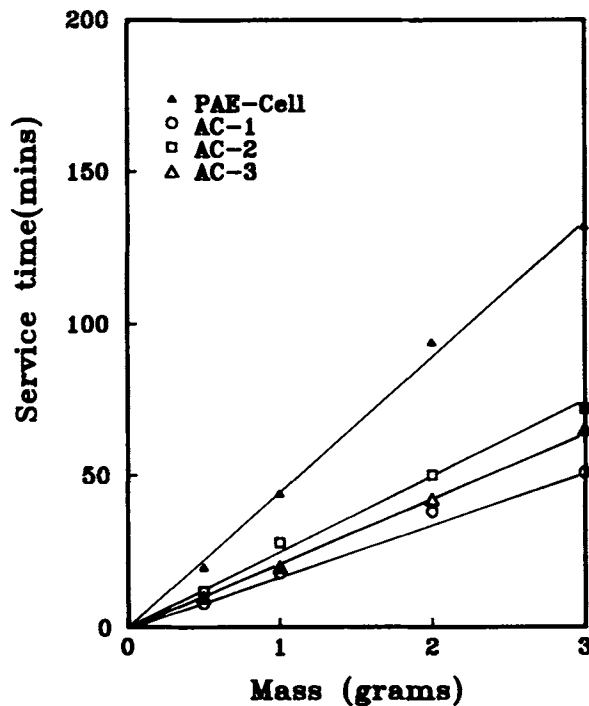


Figure 11 Service time against mass at $C_t/C_0 = 50\%$ breakthrough for C.I. Acid Blue 113. Effect of PAE-cell and activated carbon masses.

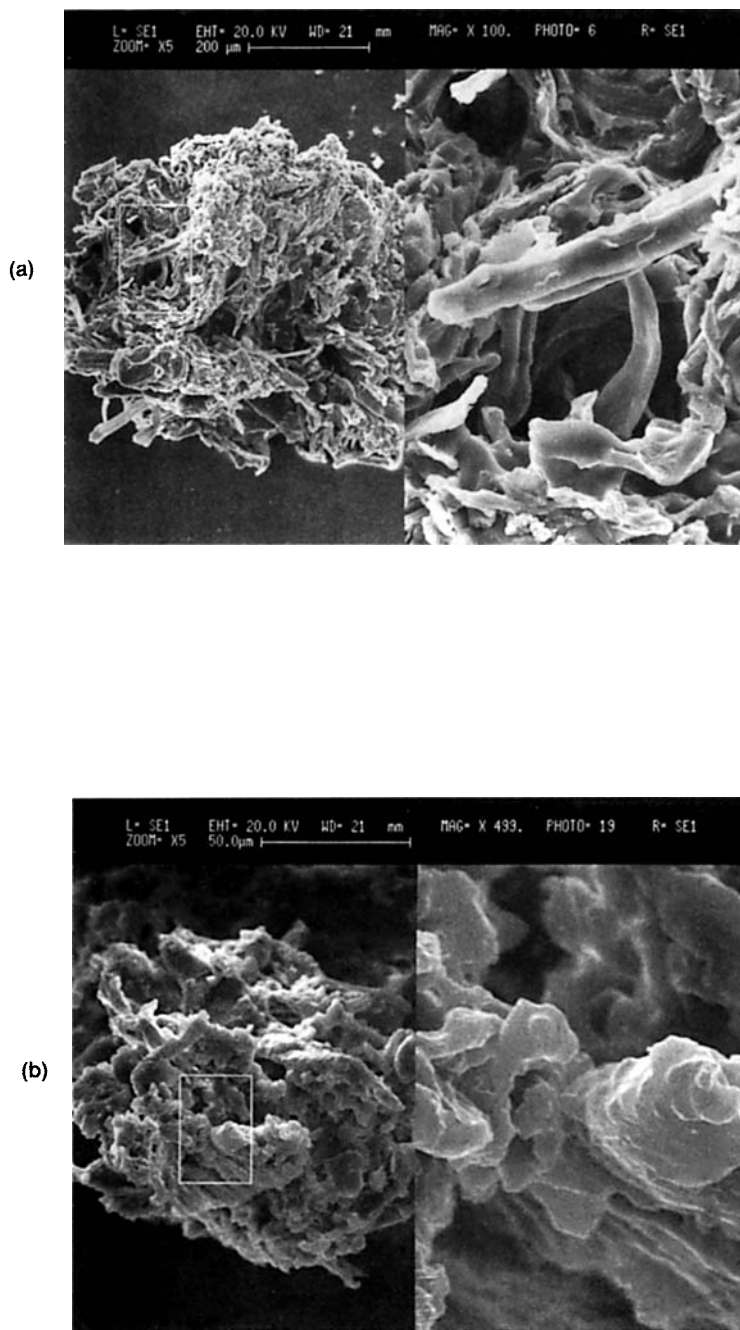


Figure 12 Scanning electron micrograph of PAE-cell (a) before adsorption of dye, (b) and (c) after adsorption of C.I. Acid Blue 113, showing particles of aggregated dye, and (d) FERAK, (e) Daiyo, and (f) Sigma activated carbon after adsorption of Acid Blue 113, showing some particles of aggregated dye.

therefore a wide range of adsorbent masses was investigated (Table III). The influence of PAE-cell mass at various C_t/C_0 on the adsorption of Acid Blue 113 ($C_0 = 2000 \text{ mg dm}^{-3}$) was studied, and the results are shown in Figure 9. The results of various C_t/C_0 may be used to predict the design of the batch ad-

sorption process in future studies of this series. A similar set of data is shown in Figure 10 for four blue dyes. An initial dye concentration of 2000 mg dm^{-3} is assumed, and 50% removal, that is, $C_t/C_0 = 0.5$, is chosen. The results illustrate how much each dye can be removed using a specific amount of

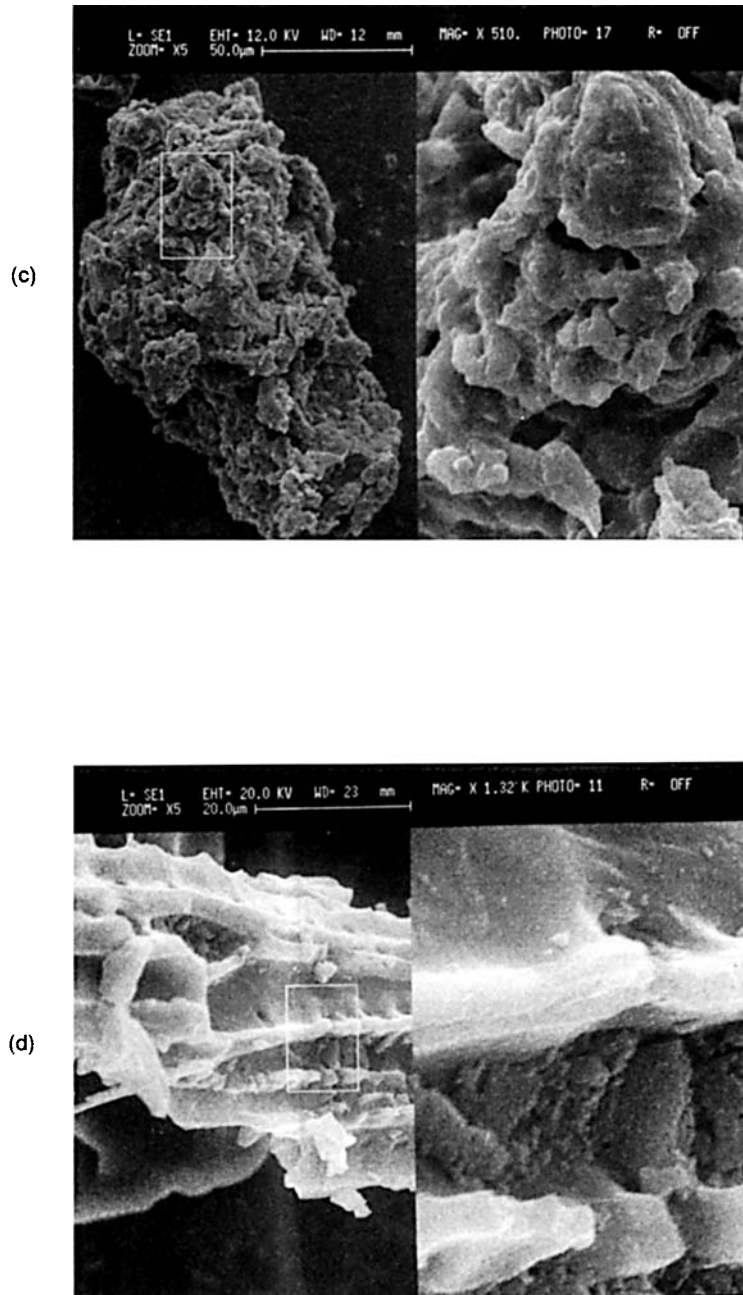


Figure 12 (Continued from the previous page)

PAE-cell for 50% breakthrough. The effect of the adsorbent mass at $C_t/C_0 = 0.5$ on the adsorption of Blue 113 is shown in Figure 11; in addition, the service time of 2 g PAE-cell or activated carbon for the adsorption of acid dyes ($C_0 = 2000 \text{ mg dm}^{-3}$) at 50% removal was determined. The data are given in Table IV. Initial estimates of PAE-cell are three times greater than those of commercial activated carbon at 50% extent of removal for Yellow 42, Blue 92, Yellow 17, Blue 158, and Red 183 (Table IV).

SEM of Adsorbent Adsorbed Dyes

The surface of a macroreticular adsorbent was observed by scanning electron microscope (SEM). The SEM photo of PAE-cell shows the pore structure and fiber structure [Fig. 12(a)]. After adsorbing a low initial concentration of C.I. Acid Blue 113, the SEM photo showed particles of aggregated dye, but some pore and fiber structures also were observed in Figure 12(b). In addition, the shadowing on the

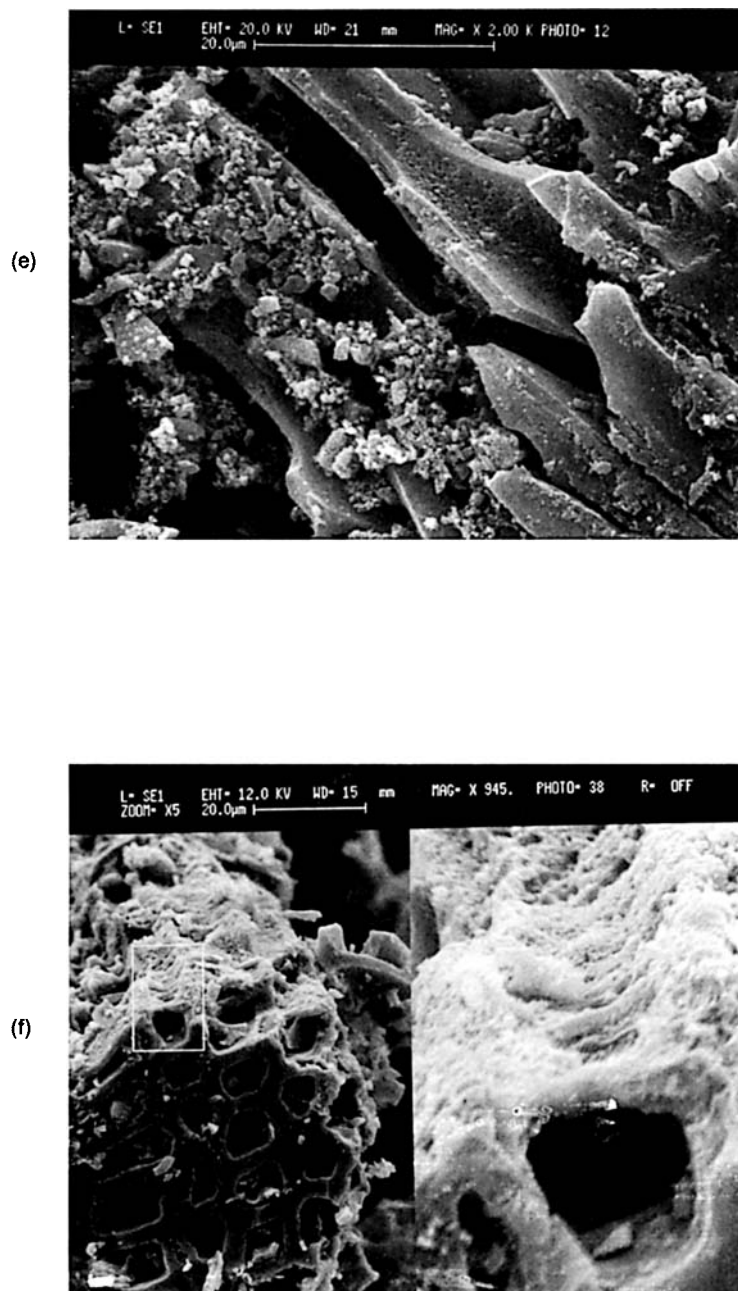


Figure 12 (Continued from the previous page)

SEM photo clearly reveals that the visible particles are in the pore structure of the PAE-cell, and the largest particles were seen to be those nearest to the outer surface, as shown in Fig. 12(c). The SEM photos of FERAK, Daiyo, and Sigma activated carbon after adsorbing the C.I. Acid Blue 113 show some particles of aggregated dye, as shown in Figure 12(d)–(f).

CONCLUSIONS

The adsorbent of PAE-cell has been found to exhibit excellent ability to adsorb many types of acid dyes, and the extent of removal of the acid dyes from solutions was found to be better than that achieved with some commercial activated carbons. The adsorption capacity of PAE-cell is better for acid dyes

with a short chain, low molecular weight, and more hydrophilic groups. Better adsorption efficiency can be achieved at low initial dye concentration, low dye bath flow rate, small PAE-cell particle size, and proper pH in a fixed bed column system for acid dye removal.

The authors are pleased to thank Mr. H. C. Chin, Mr. K. C. Jan, Ms. S. L. Liao, and Ms. M. W. Hao for their assistance in the experimental work. This work was supported in part by research grants from the National Science Council of the R.O.C. under contract number NSC77-0405-E011-06.

REFERENCES

1. M. C. Hwang and K. M. Chen, *J. Appl. Polym. Sci.*, to appear.
2. L. Diserens, *The Chemical Technology of Dyeing and Printing*, Vol. II, Reinhold Publishing Corporation, New York, 1951, p. 311.
3. P. B. Dejogn and R. A. Huntchins, *Text. Chem. Color.*, **8**, 69 (1976).
4. G. McKay, M. S. Otterburn, and A. G. Sweeney, *J. Soc. Dyers Colour*, **94**, 357 (1978).
5. G. McKay, *J. Chem. Tech. Biotechnol.*, **32**, 759 (1982).
6. G. McKay, *J. Chem. Tech. Biotechnol.*, **32**, 773 (1982).
7. G. McKay, *Chem. Eng. Res. Des.*, **61**, 29 (1983).
8. G. McKay, *Chem. Eng. J.*, **27**, 187 (1983).
9. G. McKay, *AIChE Journal*, **31**, 335 (1985).
10. V. J. P. Poots, G. McKay, and J. J. Healy, *Water Res.*, **10**, 1067 (1976).
11. G. McKay and V. J. P. Poots, *J. Chem. Tech. Biotechnol.*, **30**, 279 (1980).
12. G. McKay and I. F. McConvey, *J. Chem. Tech. Biotechnol.*, **31**, 401 (1981).
13. G. McKay, *Chem. Eng. Process.*, **19**, 287 (1985).
14. V. J. P. Poots, G. McKay and J. J. Healy, *Water Res.*, **10**, 1061 (1976).
15. G. McKay and S. J. Allen, *Canadian J. Chem. Eng.*, **58**, 521 (1980).
16. S. J. Allen, G. McKay, and K. Y. H. Khader, *J. Coll. Interface Sci.*, **126**, 517 (1988).
17. G. McKay, H. S. Blair, and J. R. Gardner, *J. Appl. Polym. Sci.*, **27**, 3043 (1982).
18. G. McKay, H. S. Blair, and J. R. Gardner, *J. Appl. Polym. Sci.*, **27**, 4251 (1982).
19. G. McKay, H. S. Blair, and J. R. Gardner, *J. Appl. Polym. Sci.*, **28**, 1767 (1983).
20. G. McKay, H. S. Blair, and J. R. Gardner, *J. Coll. Interface Sci.*, **95**, 108 (1983).
21. G. McKay, H. S. Blair, and J. R. Gardner, *J. Appl. Polym. Sci.*, **29**, 1499 (1984).
22. G. McKay, H. S. Blair, and J. R. Gardner, *J. Appl. Polym. Sci.*, **30**, 4325 (1985).
23. J. Guthrie, H. S. Blair, and R. P. O'Donnell, *Polym. Commun.*, **27**, 53 (1986).
24. H. Yoshida, S. Fukuda, A. Okamoto, and T. Kataoka, *Water Sci. Tech., Kyoto*, **23**, 1667 (1991).
25. G. McKay, M. S. Elgeundi, and I. S. Mansour, *J. Appl. Polym. Sci.*, **36**, 43 (1988).
26. G. McKay, G. Ramprasad, and P. Pratapamoli, *Water, Air, and Soil Pollution*, **29**, 273 (1986).
27. C. H. Giles, *A Laboratory Course in Dyeing*, The Society of Dyers and Colourists, England, 1974.
28. R. L. M. Allen, *Colour Chemistry*, Thomas Nelson and Sons Ltd., London, 1971.
29. F. L. Slejko, *Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application*, Dekker, New York, 1985.

Received October 15, 1992

Accepted November 13, 1992