

# The Removal of Color from Effluents Using Polyamide–Epichlorohydrin–Cellulose Polymer. I. Preparation and Use in Direct Dye Removal

M. C. HWANG and K. M. CHEN\*

Department of Textiles, National Taiwan Institute of Technology, 43, Keelung Road, Section 4, Taipei, Taiwan, Republic of China

## SYNOPSIS

A novel series of adsorbents have been prepared by reacting adipic acid, diethylenetriamine, epichlorohydrin, and cellulose. The structural features of these polyamide–epichlorohydrin–cellulose (PAE–Cell) polymers have been confirmed by IR analysis. The ability of PAE–Cell polymers to adsorb direct dyes from aqueous solution has been evaluated in a fixed bed column system. These PAE–Cell polymers have been found to exhibit a better capacities for direct dye removal than some commercial activated carbons. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Adsorption has attracted considerable interest as a feasible procedure for removing color from effluents.<sup>1,2</sup> Recently, a number of studies have been reported with regard to the adsorption equilibria and kinetics of dye removal processes using various adsorbents.<sup>3–11</sup> Commercially available adsorbents contain activated carbon,<sup>3–7,12–15</sup> chitin,<sup>8,16–18</sup> Fuller's earth,<sup>14</sup> silica gel,<sup>9,19,20</sup> wood,<sup>10,21</sup> peat,<sup>11,22</sup> bauxite,<sup>14</sup> and polymeric adsorbents.<sup>24–33</sup> Of these, activated carbon is one of the most widely used porous adsorbents because of its capability for efficiently adsorbing a broad range of different types of adsorbates.<sup>1</sup> Although the adsorption capacities of activated carbons are unmatched to any adsorbates, certain synthetic polymeric adsorbents may offer distinct advantages in specifically defined cases.<sup>1</sup> Direct dyes have been widely employed in textile dyeing; however, their low percentage of exhaustion to cotton fabrics<sup>34,35</sup> results in a considerable amount of dye molecules residual in the dye waste water. On the other hand, because the direct dyes have large molecules, their adsorption onto activated carbon

may be not optimal.<sup>17</sup> This paper describes the preparation and color removal ability of a novel series of polymeric adsorbents. These adsorbents were prepared from the reaction of polyamide–epichlorohydrin (PAE) resin and cellulose (Cell). The PAE resin has been reported to improve the wet- and dry-strength properties of paper<sup>36</sup> and to promote the shrink-proofing treatment of wool.<sup>37–40</sup> Recently, PAE resin has been used as a cationic agent for improving the dyeability of cellulose fibers.<sup>41,42</sup> However, only limited information is available regarding the use of PAE resin in removing color from effluents. The ability of PAE–Cell to adsorb direct dyes from aqueous solution under several experimental conditions has been studied. At the very least, the adsorption effect of PAE–Cell on direct dyes indicates the good potential of this procedure in achieving the desired objective.

## EXPERIMENTAL

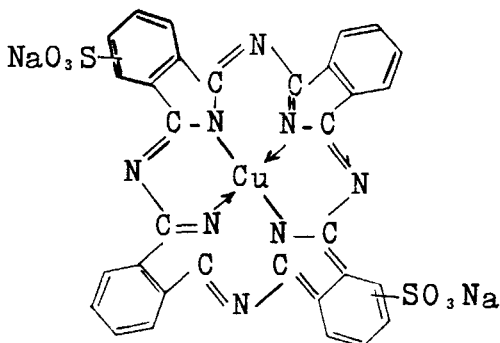
### Materials

The adipic acid, diethylenetriamine, and epichlorohydrin are extra pure reagents supplied by the Japan Hayashi Chemical Co. The  $\alpha$ -cellulose was supplied by Sigma Ltd. The activated carbons, supplied by Germany FERAK, Japan Daiyo, and Sigma Ltd.,

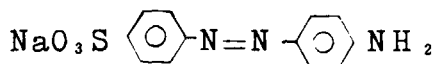
\* To whom correspondence should be addressed.

were sieved into discrete particle size range (150–106  $\mu\text{m}$ ). The dyes used in the adsorption experiments are shown and were used as in the form of commercial salts. Their names and molecular structures are:

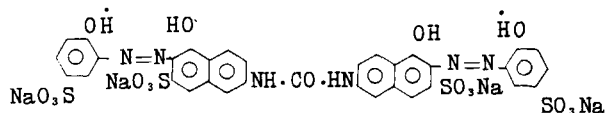
Solophenyl Turquoise Blue GLC (C. I. Direct Blue 86) as supplied by Ciba-Geigy:



Solophenyl Orange TGL (C. I. Direct Orange 34) as supplied by Ciba-Geigy:



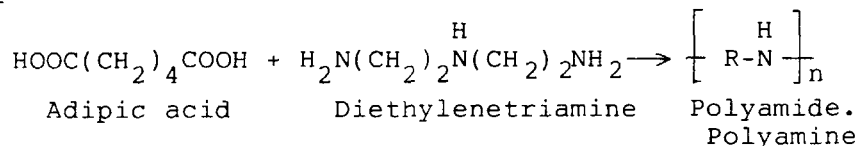
Everdirect Supra Rubine BL (C. I. Direct Red 83) as supplied by Taiwan Everlight Chemical Co.:



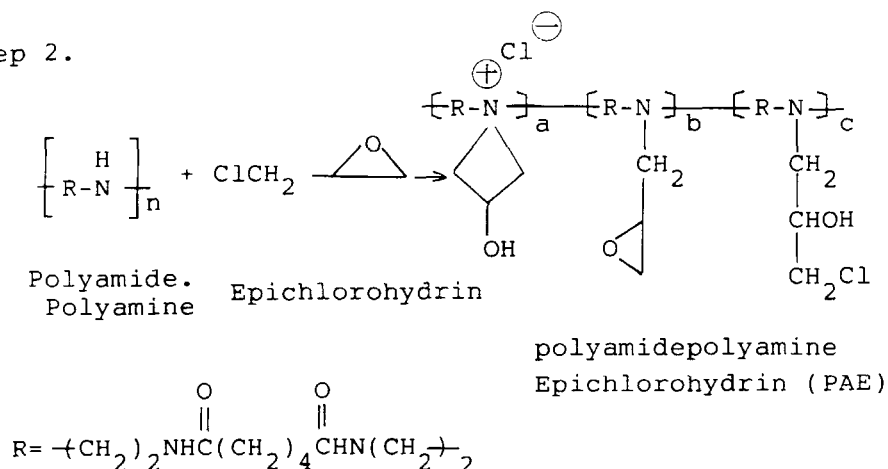
### Preparation of PAE-Cell Polymers

The polyamidepolyamine epichlorohydrin (PAE) was prepared in two steps. The first preparation step for PAE was the synthesis of adipic acid and diethylenetriamine (DETA). Adipic acid (220 g) was added to 100 g  $\text{H}_2\text{O}$  until the solution turned to slurry. Then 160 g of DETA was added to the solution. The solution was synthesized under a temperature of  $180^\circ\text{C}$  for about 1 hr, until it turned chrome yellow and became polyamidepolyamine. The second preparation step for the PAE was to let 100 g of polyamidepolyamine dissolve in 200 g of distilled water and then add 60 g of epichlorohydrin at  $13\text{--}15^\circ\text{C}$ . The solution was reacted under a temperature of  $60^\circ\text{C}$  for about 1 h, which resulted in PAE:

Step 1.



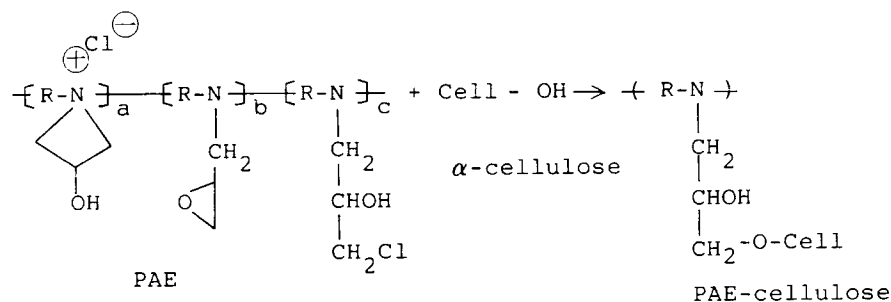
Step 2.



Scheme 1 Preparation of polyamidepolyamine epichlorohydrin.

The preparation of PAE-Cell was the reaction at  $85^\circ\text{C}$  for about 3 h between PAE and  $\alpha$ -cellulose to

form an interpolymer, PAE-Cell, crosslinked by both ionic and covalent bonds:



**Scheme 2** Preparation of PAE-cellulose.

The PAE-Cell compounds are classified as 10, 20, 25, and 30%, based on the  $\alpha$ -cellulose weight ratio. Next, we soaked the PAE-Cell compounds in distilled water at 25°C for about 24 h to remove the unreacted PAE, and then removed the compounds from the distilled water. We let the PAE-Cell dry at 70°C for about 72 h. Then, the dried PAE-Cell was broken up using an ultracentrifugal mill machine and was sieved into discrete particle size range (106, 150, 300, 600, and 710  $\mu\text{m}$ ).

### Analysis

The IR spectra of the PAE and PAE-Cell were measured with a Jasco FT/IR-3 spectrometer. Scanning electron micrographs were obtained with a Cambridge S-360 type instrument. The extent of amination was traced by determining the nitrogen content (% N) using the BUCHI Co. Kjeldahl system. The ultracentrifugal milling of PAE-Cell was done using a Retsch ZM 1 type machine. The adsorption plant for the fixed bed process was measured by the American Spectrum Medical Industries Inc. Lab. Chromatograph System. The residual dye concentration was determined with a Shimadzu UV-240 spectrometer operated at the wavelength corresponding to the maximum transmittance. The pore volume, surface area, and pore size data of the PAE-Cell were measured by the Quantachrome Autosorb Automated Gas adsorption system.

### Adsorption

Figure 1 is the adsorption plant for the fixed bed process. Polyester staple (0.2 g) was placed in the column bottom before the insertion of the PAE-Cell powder. A pyrex column of 1.5 cm internal diameter and 20 cm length was used. The dye bath in the beaker was pumped using a bath flow rate controller, and the initial dye bath was admitted into the column. When the dye bath passed through the column,

the direct dye was adsorbed or passed through the surface of the PAE-Cell. Then, the treated dye bath was collected into a glass tube on a fraction collector (each tube contained 10 mL of treated dye bath). Finally, the treated dye residual concentration was measured using a UV spectrometer. The adsorption experiment was stopped when the residual dye concentration ( $C_t$ ) approached the initial dye concentration ( $C_0$ ). The other adsorption experiment conditions are shown in Table I.

## RESULTS AND DISCUSSION

### Preparation

The reaction of adipic acid, diethylenetriamine, and cellulose can be represented as in Scheme 1. The nitrogen content analyses of the final products are shown in Table II. The cellulose ratios used in this study are from 0 to 30%. The nitrogen content of the PAE-Cell in a given series is thus generally found to decrease with increasing cellulose content; in addition, its appearance shades to white yellow.

Figure 2 shows the IR spectra of these products. The peaks at 1170–1040 and 3500–3300  $\text{cm}^{-1}$  in spectra (a) are due to the ether linkage and hydroxyl group of the cellulose. The peak at 1640–1400  $\text{cm}^{-1}$  in Figure 2 spectra (b) is due to the N—H bending of the PAE secondary amide band. The spectra (c), (d), (e), and (f) are PAE-Cell compounds which are classified as different cellulose ratios, for which the peaks are shown at 1170–1040 and 1640–1400  $\text{cm}^{-1}$ . The peak at 1170–1040  $\text{cm}^{-1}$  of the PAE-Cell compounds are generally found to increase with a cellulose ratio.

### Direct Dyes Removal Capacity

Direct dyes are inexpensive and easy to apply, and their use has spread with great rapidity because they

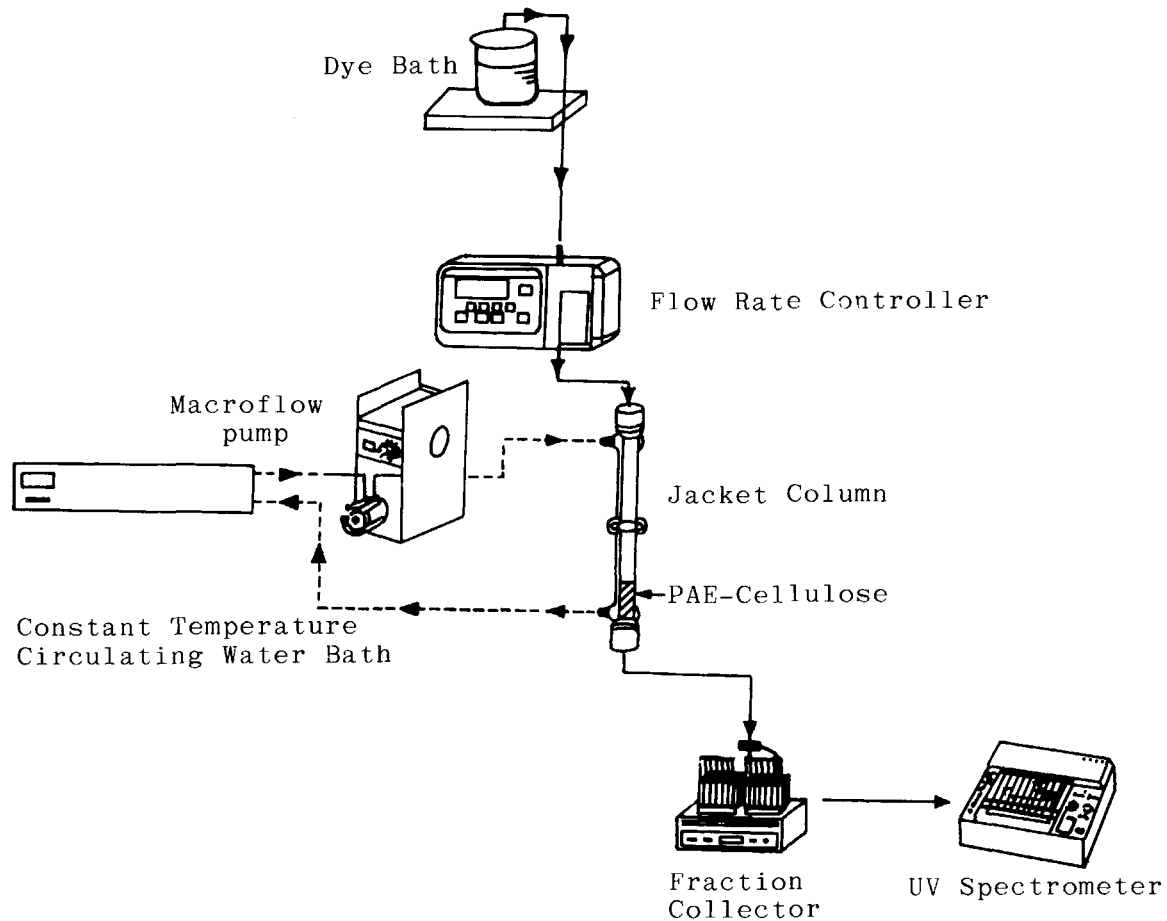


Figure 1 Adsorption plant for the fixed bed process.

fulfilled an obvious demand. Many of them can dye cotton, rayon, and protein fibers. However, direct dyes have an indifferent percentage of exhaustion to fibers because their molecules are so large (about 10–50 Å).<sup>34,35</sup> Therefore, the deep color system of direct dyes usually results in a large amount of dye molecules in the dye waste water.

The fixed bed, columnar configuration is the most widely used arrangement for conducting adsorption operations. The uppermost portions of the bed are constantly being contacted by fresh feed solution, whereas the lower portions of the bed are contacted by solution containing solute not adsorbed by the upper portion. Thus the bed becomes fully loaded

Table I The Experimental Conditions of the Fixed Bed Adsorption System

	General Condition	Variation Conditions
Direct dye type	C.I Direct Blue 86	C.I Direct Orange 34 C.I Direct Red 83
Initial dye concentration (mg dm <sup>-3</sup> )	2000	1000, 1500
Dye bath flow rate (ml min <sup>-1</sup> )	5	2, 8
PAE-Cell type (α-cellulose wt %)	25	10, 20, 30
PAE-Cell particle range (μm)	150–106	300–150, 600–300, 710–600
PAE-Cell filling density (g cm <sup>-3</sup> )	0.283	0.226, 0.189
Activated carbon	AC-1: Germany FERAK activated carbon AC-2: Japan Daiyo activated carbon AC-3: Sigma activated carbon	

**Table II The Appearance and Nitrogen Content of PAE-Cell Compounds**

	$\alpha$ -Cellulose (wt %)	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

at the top of the column first and then downward. Figure 3(a) shows the relationship between the adsorption fronts in a column as a function of treated volume and the loading curve. Figure 3(a) shows that four types of PAE-Cell have a higher adsorption capacity for CI Direct Blue 86 than three types of activated carbons. These results are possibly due to a number of reasons: (1) The planar structure of the dye molecule makes penetration of the dye between the PAE-Cell chains easier and promotes the tendency towards aggregation. (2) The linear molecular structure of the direct dye allows it to align itself on the surface of the PAE-Cell. (3) This low uptake of activated carbons are possibly due to the fact that C. I. Direct Blue 86 is a much larger dye molecule and the pore radii of the activated carbons are less than 20 Å in Table III, so that the dyes cannot penetrate the internal pore structure of the activated carbons. Initial estimates showed that the adsorption capacity of PAE-Cell-3 is three times greater than these commercial activated carbons at 50% extent of removal for C. I. Direct Blue 86 in Figure 3(a). In Figure 3(b) and Table II is shown the PAE-Cell compounds' adsorption effectiveness in the following order: PAE-Cell-3 > PAE-Cell-2 > PAE-Cell-4 > PAE-Cell-1. The adsorption effectiveness of the PAE-Cell compounds is generally found to increase with a cellulose content of less than 25%; on the other hand, the adsorption effect decreases with a cellulose content of more than 30%.

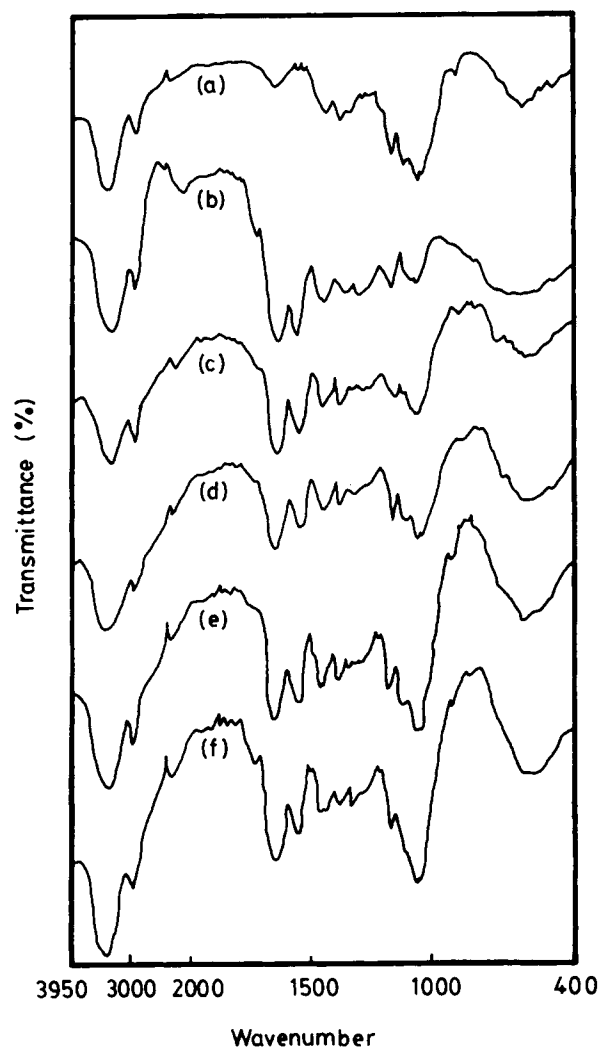
#### Effect of the Particle Size of Adsorbents

The surface area of an adsorbent is a fundamental property and is usually related to adsorption capacity. The surface area of all commercially significant adsorbents is contained within an internal pore structure of the adsorbent particles. Figure 4 shows that the smaller particles of PAE-Cell have better adsorption effectiveness than the larger particles. This is because the former have more surface area than the latter, so that they may adsorb more direct

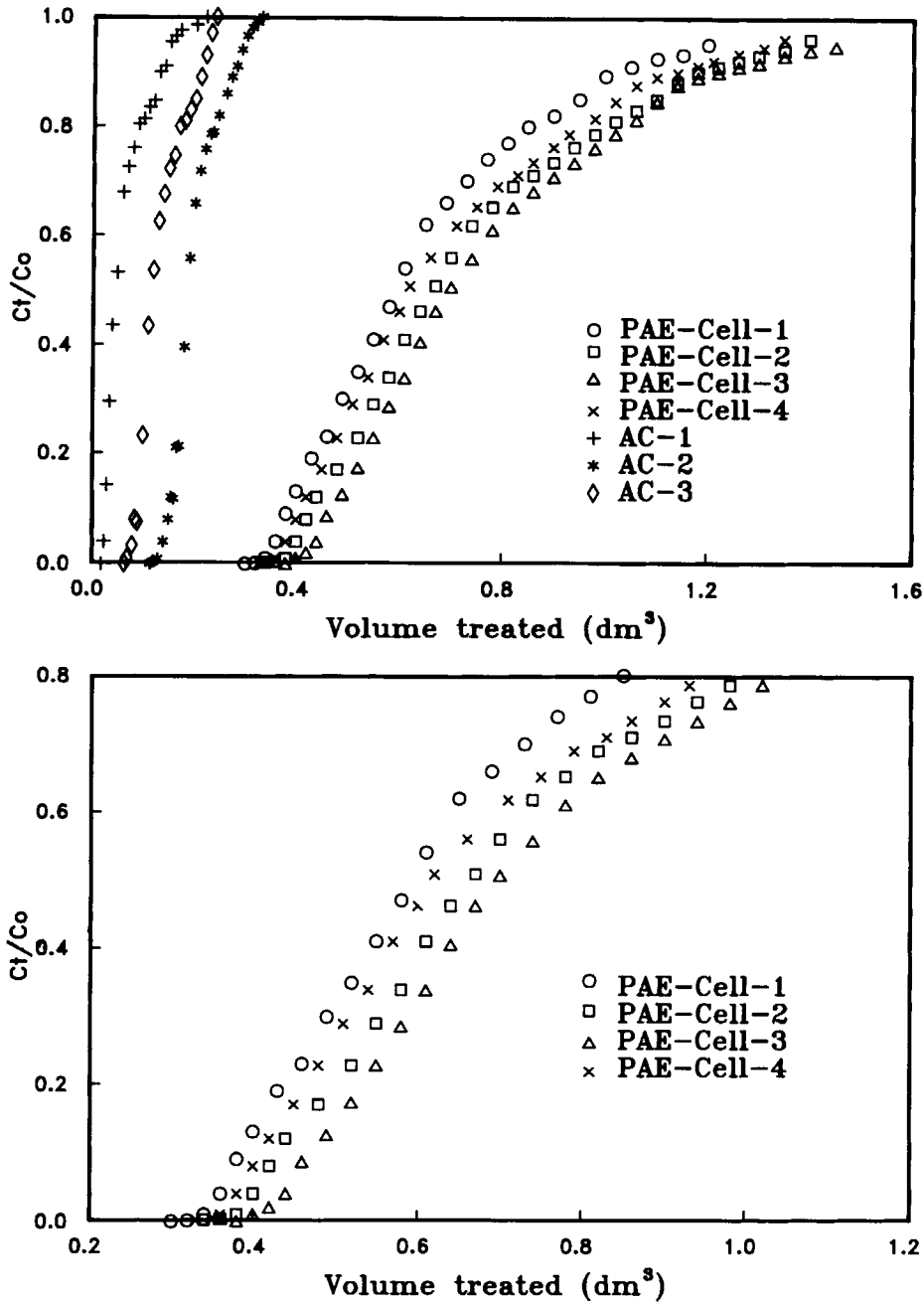
dye molecules. Table III shows the pore properties of these products. The PAE-Cell and the three activated carbons are about equal in pore radii in the same particle range; however, the surface area and pore volume of the PAE-Cell is much less than that of the three activated carbons. This is possibly because the internal pore structure of the PAE-Cell has fewer or no exits. The high adsorption capacities of PAE-Cell is possibly due to the fact that it has both hydroxyl groups and amide groups besides its pore structure.

#### Effect of PAE-Cell Filling Density and Dye Bath Velocity

The contact time of PAE-Cell and direct dyes is the most significant variable, and therefore the dye flow



**Figure 2** Infrared spectrum of  $\alpha$ -cellulose, PAE, and PAE-Cell: (a)  $\alpha$ -cellulose; (b) PAE; (c) 10%  $\alpha$ -cellulose; (d) 20%  $\alpha$ -cellulose; (e) 25%  $\alpha$ -cellulose; (f) 30%  $\alpha$ -cellulose.



**Figure 3** Breakthrough curves for C. I. Direct Blue 86. (a) Effect of PAE-Cell compounds and activated carbon. (b) Effect of PAE-Cell compounds.

**Table III** The Pore Properties of PAE-Cell and Activated Carbon

	Surface Area ( $\text{m}^2/\text{g}$ )	Pore Volume ( $\text{cc}/\text{g}$ )	Pore Radius ( $\text{Å}$ )
AC-1	> 900	0.69	15.1
AC-2	> 800	0.84	20.8
AC-3	> 600	0.63	18.5
PAE-Cell-3	< 10	0.0025	17.8

rate and PAE-Cell filling density in the column are the major design structures. A wide range of flow rates and filling densities were investigated in Table I. Figure 5 shows that the adsorptive effect of PAE-Cell at high filling density in the column was better than at low filling density. The reason is that direct dye molecules approach PAE-Cell at high filling density more easily, resulting in physical adsorption. The deviation of treated volume in the collector at

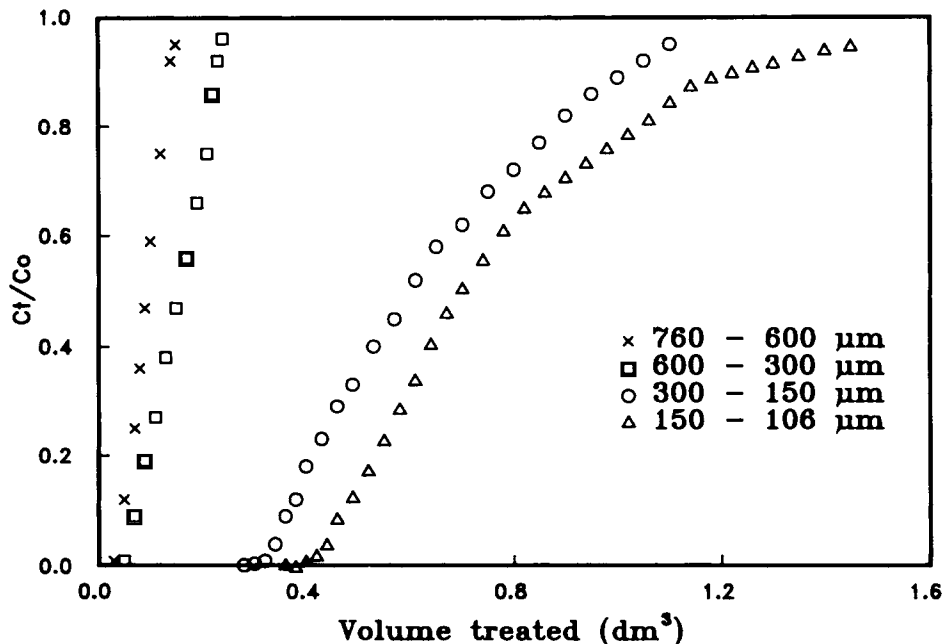


Figure 4 Breakthrough curves for C. I. Direct Blue 86. Effect of PAE-Cell particle size.

a filling density of more than  $0.3 \text{ g/cm}^3$  produces a pressure drop across the column; on the other hand, the adsorptive effect decreased at a filling density of less than  $0.1 \text{ g/cm}^3$ . Figure 6 shows that the low dye bath flow rate produced a better adsorptive effect

than a high flow rate. Because the former can increase dye bath contact time with PAE-Cell, it can allow the dye molecules to enter the internal pore structure and increase the amount of dye molecules adsorbed by the PAE-Cell.

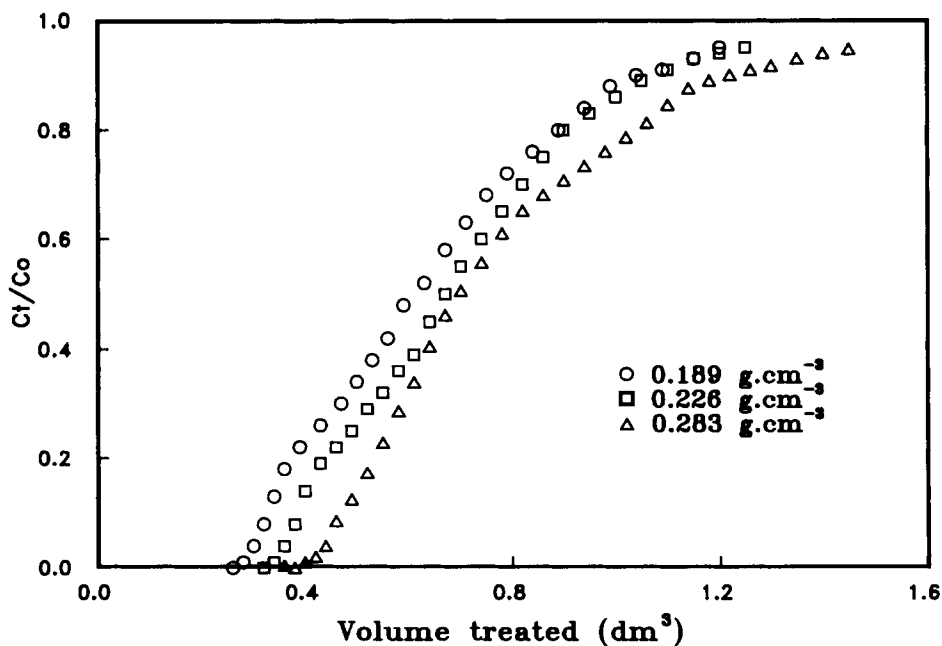
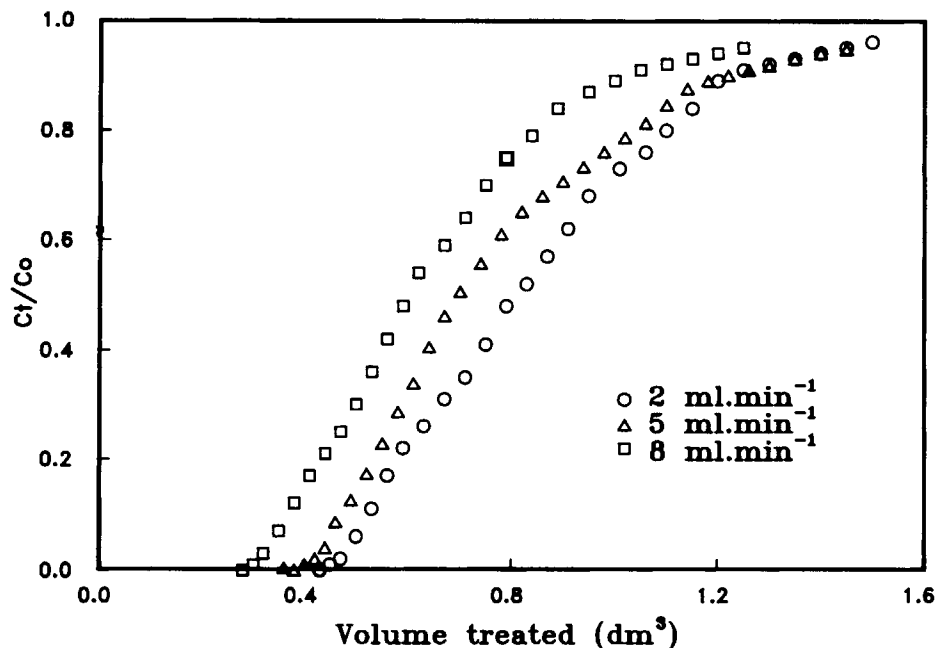


Figure 5 Breakthrough curves for C. I. Direct Blue 86. Effect of filling density of PAE-Cell on fixed bed column.

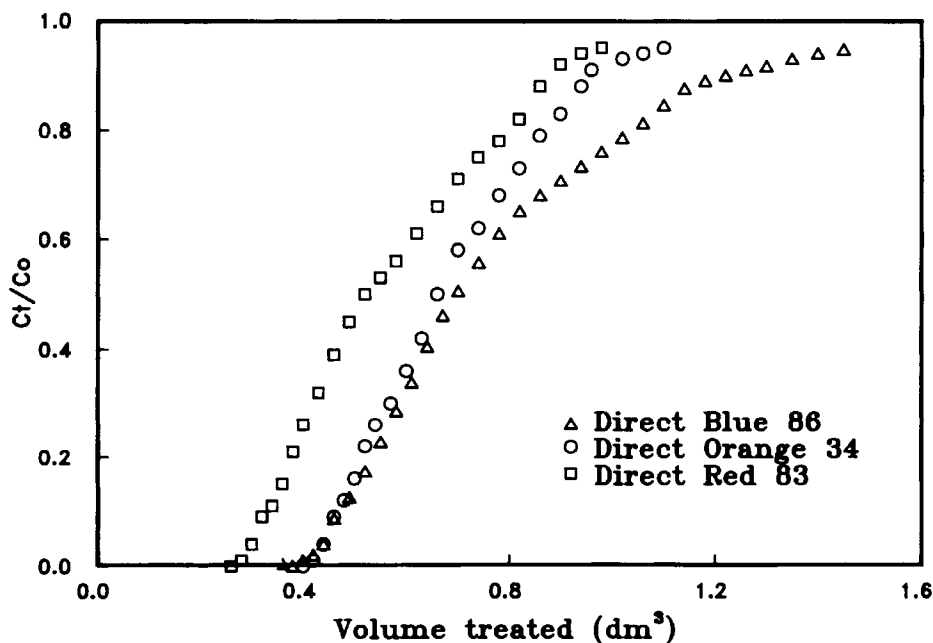


**Figure 6** Breakthrough curves for C. I. Direct Blue 86 of PAE-Cell. Effect of dye bath flow rate.

#### Effect of Dye Type and the Initial Dye Concentration

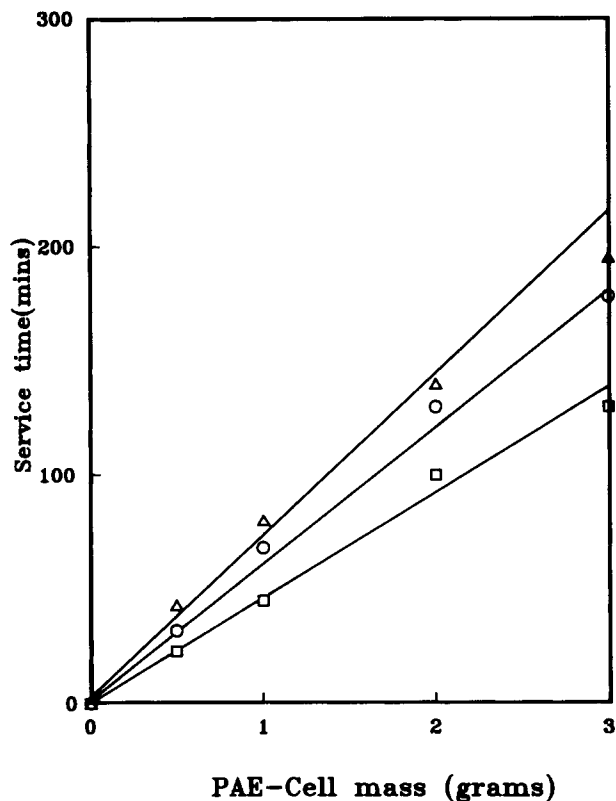
The PAE-Cell has no polar groups capable of forming salt linkages, so the assumption was that the binding forces were purely physical. The affinity of

PAE-Cell might be due to the interaction between electrons in an extended conjugated double bond of direct dyes and the hydrogen atoms of the hydroxyl of the PAE-Cell. The PAE-Cell contains hydroxyl groups capable of entering into hydrogen bond formation with groups such as  $-\text{OH}$ ,  $-\text{NH}_2$ , and



**Figure 7** Breakthrough curves for three direct dyes on PAE-Cell. Effect of dye type.





**Figure 8** Service time against mass of PAE-Cell at  $C_t/C_0 = 50\%$  breakthrough for three dyestuffs. Symbols as in Figure 7.

—N=N— in the dyestuff molecules. The bonding hydrogen atom may be contained in PAE-Cell as in formulas (1) and (2).

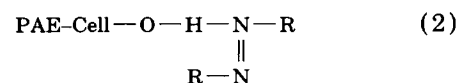
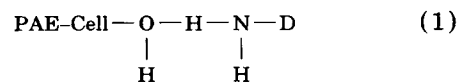
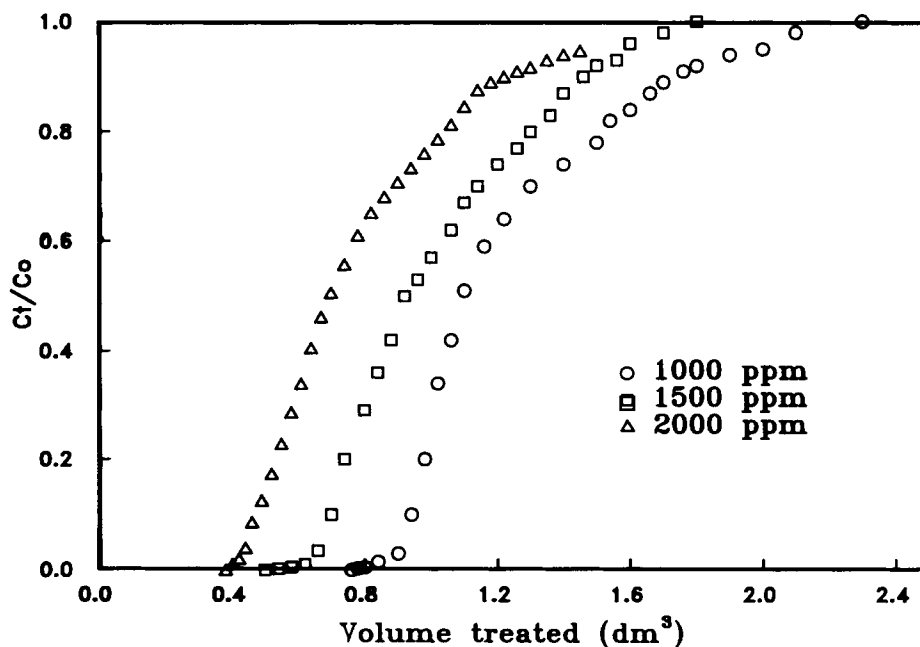
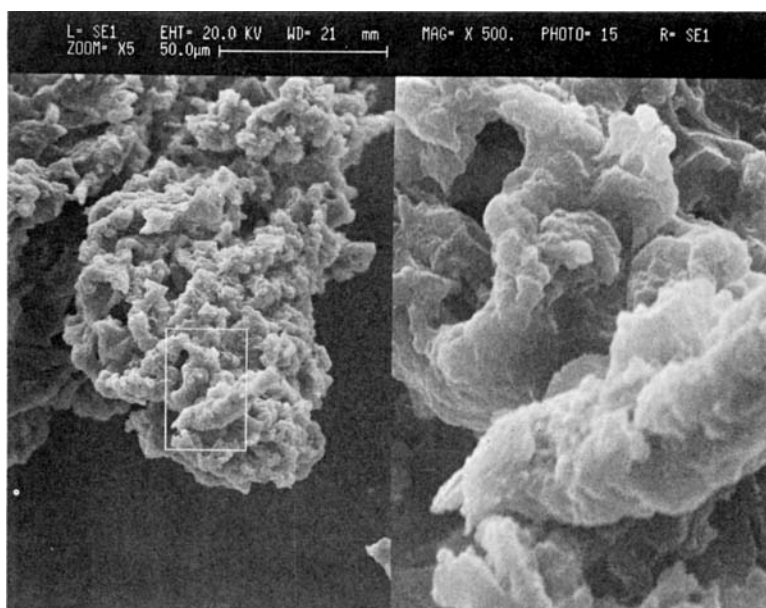
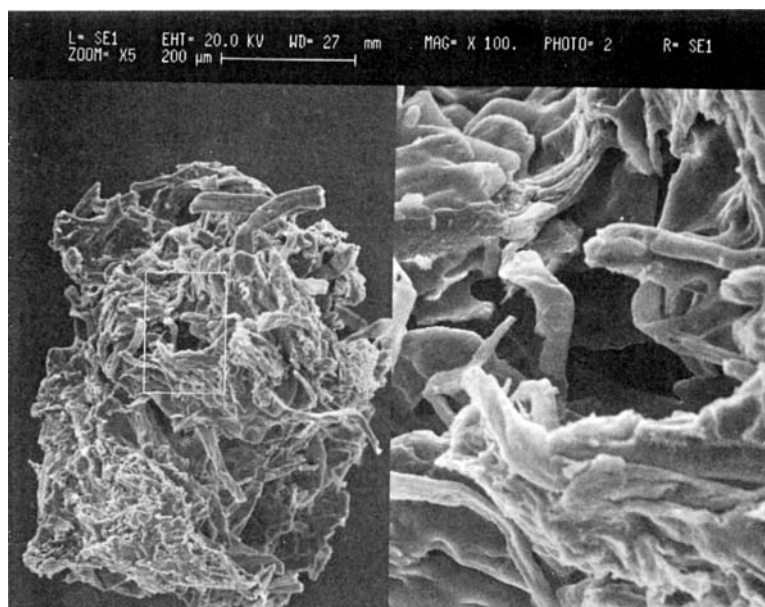


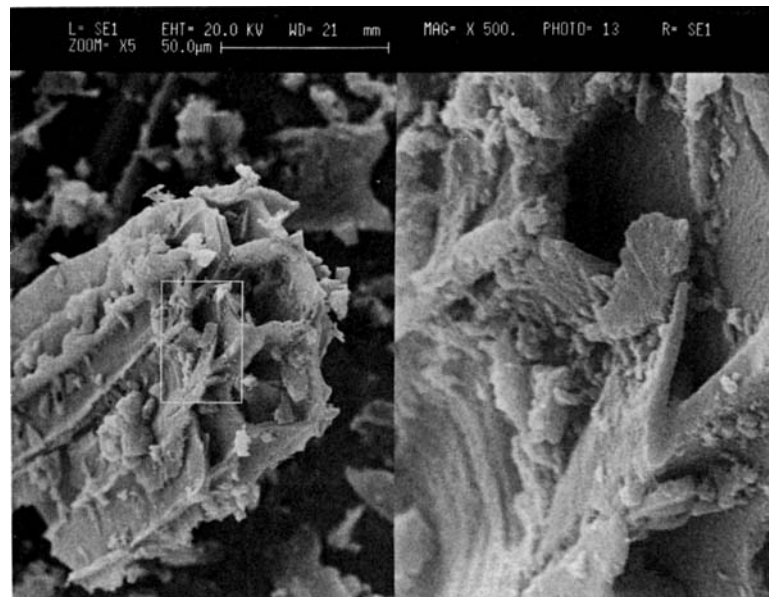
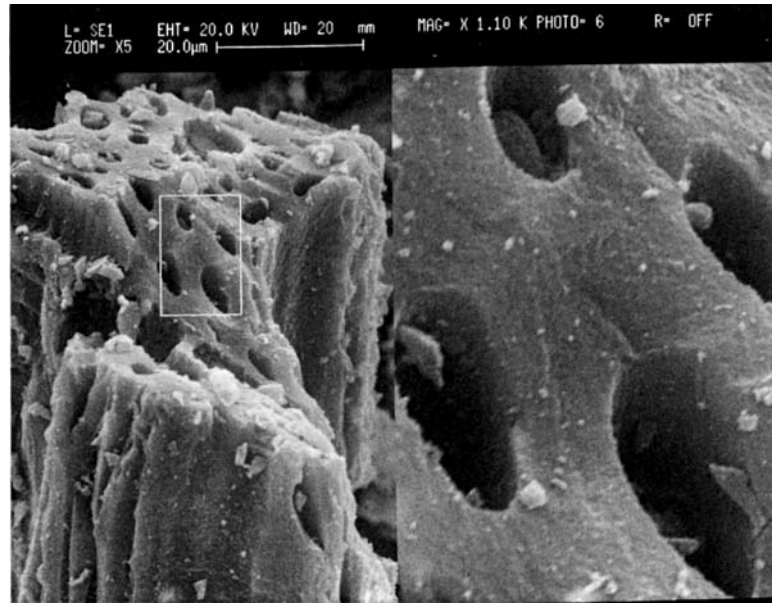
Figure 7 shows the breakthrough curves for three direct dyes onto PAE-Cell, and Figure 8 shows three direct dyes that were adsorbed by several PAE-Cell masses at 50% extent of removal. The adsorbed effect order of the results shown is Blue 86 > Orange 34 > Red 83. The low uptake is possibly due to the fact that CI Direct Red 83 has much larger dye molecules and a long chain than the others, so that it cannot penetrate the internal pore structure of the PAE-Cell particle. This result is same found in past studies.<sup>17</sup> CI Direct Orange 34 has few functional groups; therefore, its adsorption effect was not optimal. The influence of the initial dye concentration onto PAE-Cell was studied, and the results are shown in Figure 9 that the low initial dye concentration resulted in better adsorption into PAE-Cell than the high initial dye concentration. This is because the former could be adsorbed more slowly through the adsorbents. In other words, the dye



**Figure 9** Breakthrough curves for CI Direct Blue 86 on PAE-Cell. Effect of initial dye concentration.



**Figure 10** Scanning electron micrograph of PAE-Cell before adsorption of dye (upper) and after adsorption of Solophenyl Turquoise Blue GLC (CI Direct Blue 86), showing particles of aggregated dye (lower).



**Figure 11** Scanning electron micrograph of FREAK activated carbon before adsorption of dye (upper) and after adsorption of Solophenyl Turquoise Blue GLC (C.I. Direct Blue 86), showing some particles of aggregated dye (lower).

molecules cannot be adsorbed onto PAE-Cell in a short time period at the high initial dye concentration.

### SEM of Adsorbents Adsorbed Dyes

The scanning electron micrograph of PAE-Cell shows the pore structure and fiber as in Figure 10 (upper), and after adsorption of Solophenyl Turquoise Blue GLC (C.I. Direct Blue 86), it shows particles of aggregated dye as in Figure 10 (lower). The shadowing on the SEM photo clearly reveals that the visible particles were in the pore structure of the PAE-Cell; moreover, the largest particles were seen to be those nearest to the outer surface. The SEM photo of FERAK activated carbon also shows many regular pores as in Figure 11 (upper), and after adsorption of dyes it also shows some particles of aggregated dye as in Figure 11 (lower).

### CONCLUSIONS

It has been shown that direct dyes can be successfully adsorbed with PAE-Cell; in addition, the extent of removal of the direct dyes has been found to be better than with some commercial activated carbons. The PAE-Cell's capacity to adsorb direct dyes comes from both hydroxyl groups and amide groups as well as the pore structure; furthermore, it is suitable for the short chains of direct dyes. The adsorption effect on direct dye molecules is drastically reduced at an  $\alpha$ -cellulose content of more than 30% or less than 20% of the PAE-Cell. To avoid pressure drops in the dye bath across the column or having the dye molecules bypass the surface of the PAE-Cell, the PAE-Cell filling density in the column of the fixed bed adsorption plant should be set at  $0.1 \text{ g cm}^{-3}$  to  $0.3 \text{ g cm}^{-3}$ . The low initial dye concentration and low dye bath flow rate show better adsorption effectiveness than other experimental conditions.

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