

The Removal of Color from Effluents Using Polyamide-Epichlorohydrin-Cellulose Polymer. III. Use in Anionic Dye Removal in a Batch Process

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

Polyamide-epichlorohydrin-cellulose (PAE-Cell) can adsorb substantial quantities of several direct dyes and acid dyes from aqueous solutions using a batch process. The adsorption kinetics of these dyes on PAE-Cell was studied using Langmuir and Freundlich isotherm equations at different temperatures. Other adsorption parameters studied were initial dye concentration, the pH of the solution, particle size, treated time, and salt added. The PAE-Cell was found to have monolayer equilibrium saturation capacities of more than 500 mg dye per PAE-Cell for these anionic dyes. These results show that PAE-Cell polymers exhibit better capacity than do some types of commercial activated carbon.

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INTRODUCTION

The ability of polyamide-epichlorohydrin-cellulose (PAE-Cell) to adsorb direct dyes and acid dyes from aqueous solution using a fixed-bed column has been reported in Parts I and II of this series.^{1,2} A fixed-bed column has the advantage of having a constant concentration at a given axial position, because the adsorbent is continuously in contact with fresh solution. However, the pressure drop is high in a fixed bed due to the fine-packing particles and/or high-packing density in the column.³ In addition, a fixed bed cannot be used to determine the adsorbing capacity of the adsorbent, since it is not an equilibrium process. On the other hand, the batch adsorption process can provide data relating the adsorbate adsorbed per unit weight of adsorbent to the amount of adsorbate remaining in solution under adsorption equilibrium isotherms.⁴ The aim of the present work was to study the adsorption of anionic dyes on PAE-Cell when using a batch process to determine the equilibrium processes involved. The dyes studied include three direct dyes, four milling-type acid dyes,

four leveling-type acid dyes, and four metal-complex-type acid dyes. Finally, the equilibrium isotherms were determined while adsorbing these dyes with PAE-Cell at 30–90°C in a batch process using Langmuir and Freundlich isotherm equations.

EXPERIMENTAL

Materials

The 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 has been described in Part I of this series.¹ The activated carbon obtained from Germany's FERAK, Japan's Daiyo, and Sigma Ltd. was sieved into discrete ranges of particle size. The acid dyes used in the adsorption experiments were Yellow 42, Blue 113, Red 85, Red 114, Orange 7, and Yellow 17 supplied by the Taiwan Everlight Chem. Co.; Blue 92 and Brown 14, by the Taiwan Oriental Giant Dyes & Chem. Ind. Co.; Blue 158, Red 183, Blue 193, and Yellow 99, by the BASF Co.; Direct Blue 86 and Direct Orange 34, by Ciba-Geigy; and Direct Red 83, by the Taiwan Everlight Chem. Co. Their mo-

* To whom correspondence should be addressed.

Table I The Experimental Conditions of the Batch Process

	General Condition	Variation Conditions
Dyes	Blue 86	The others
Initial dye concentration (g/L)	2	1, 1.25, 1.5, 3
pH	7	3, 5, 9
Particle size range (μm)	150–106	300–150 500–300 710–600
Time (h)	72	0.5, 1, 2, 3, 6
Salt (0.1N)		LiCl, NaCl, KCl, RbCl
Activated carbon		AC-1:FERAK AC-2:Dai Yo AC-3:Sigma
T ($^{\circ}\text{C}$)	30	50, 70, 90
Mass (g)	0.2	
Dye solution volume (dm^3)	0.1	

lecular structures and trade names are shown in Parts I and II of this series.^{1,2} They were used in the form of commercial salts.

Method

To clean the activated carbon and PAE-Cell before use, they were soaked in distilled water for 30 min and then removed from the water. This procedure was repeated three times, followed by drying at 70°C for 1 day. Then, the carbon and PAE-Cell were sieved into discrete particle-size ranges. We adjusted the pH of the dye solution using hydrogen chloride,

acetic acid, and sodium hydroxide. Then, we put 0.2 g PAE-Cell (or activated carbon) and 0.1 dm^3 dye solution into a 0.15 dm^3 flask, which was then agitated (50 rpm) in a Frister constant temperature shaker-bath for 3 days. Afterward, the PAE-Cell was filtered from the solution. The initial dye concentration (C_0) and residual dye concentration (C_t) were measured using a Shimadzu Model UV-240 spectrophotometer at the maximum wavelength (λ_{max}) of the adsorbance. These wavelengths were determined for each dyestuff and are shown in Parts I and II of this series. The other adsorption experiment conditions are shown in Table I.

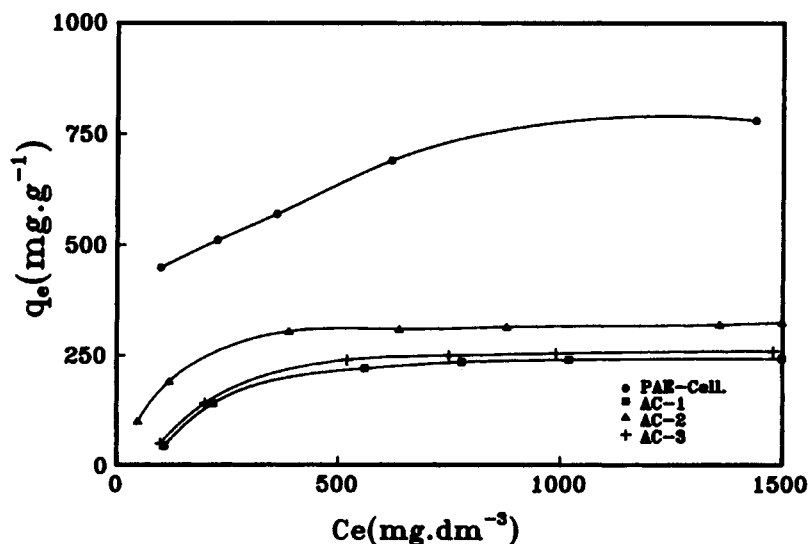


Figure 1 Equilibrium adsorption isotherms at 30°C for C. I. Direct Blue 86 on PAE-Cell and three activated carbons.

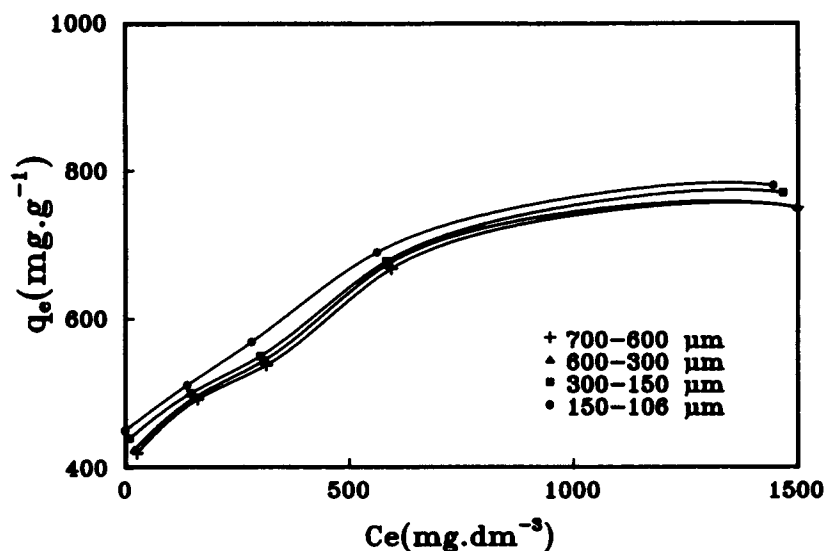


Figure 2 Effect of PAE-Cell particle size on the equilibrium adsorption isotherms of Direct Blue 86 at 30°C.

RESULTS AND DISCUSSION

Effect of Adsorbents

The adsorption of a substance from one phase to the surface of another phase in a specific system leads to a thermodynamically defined distribution

of that substance between the phases when the system reaches equilibrium, i.e., when no further net adsorption occurs. The common manner in which to depict this distribution is to express the amount of substance adsorbed per unit weight of adsorbent,

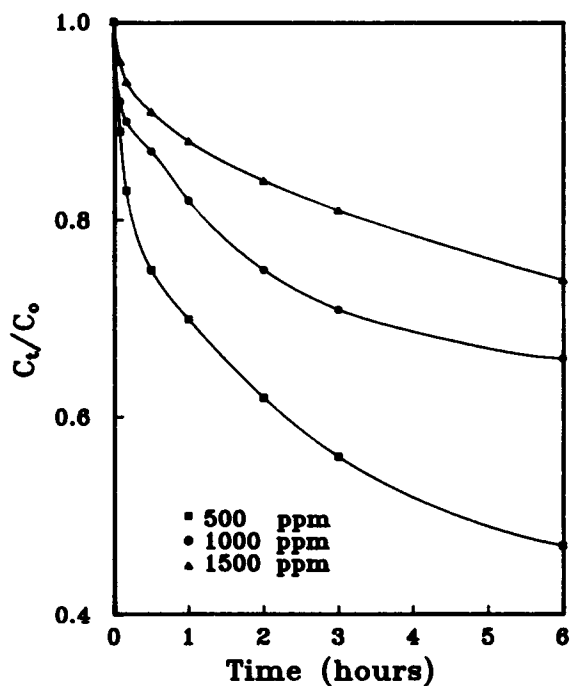


Figure 3 Effect of varying the initial dye concentration for the adsorption of Direct Blue 86 on PAE-Cell at 30°C.

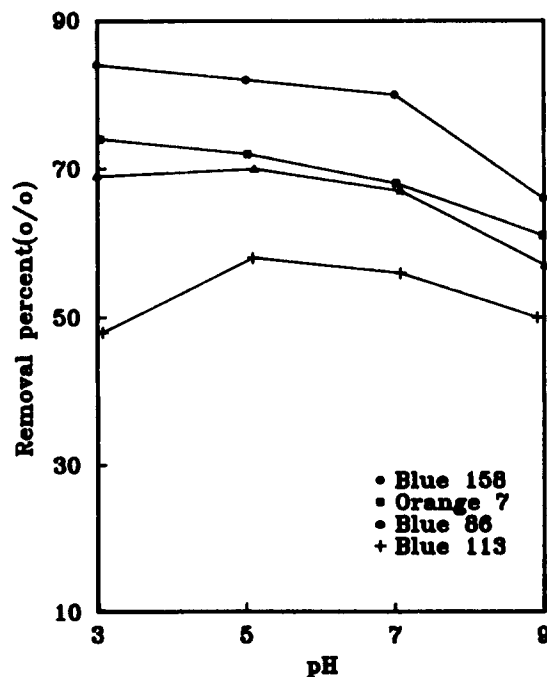


Figure 4 Effect of pH value on the removal percentage of the Blue 158 (metal-complex acid dyes), Blue 86 (Direct dyes), Orange 7 (leveling-type acid dyes), and Blue 113 (milling-type acid dyes) on PAE-Cell. $T = 30^\circ\text{C}$; $C = 2 \text{ g/L}$; time = 72 h.

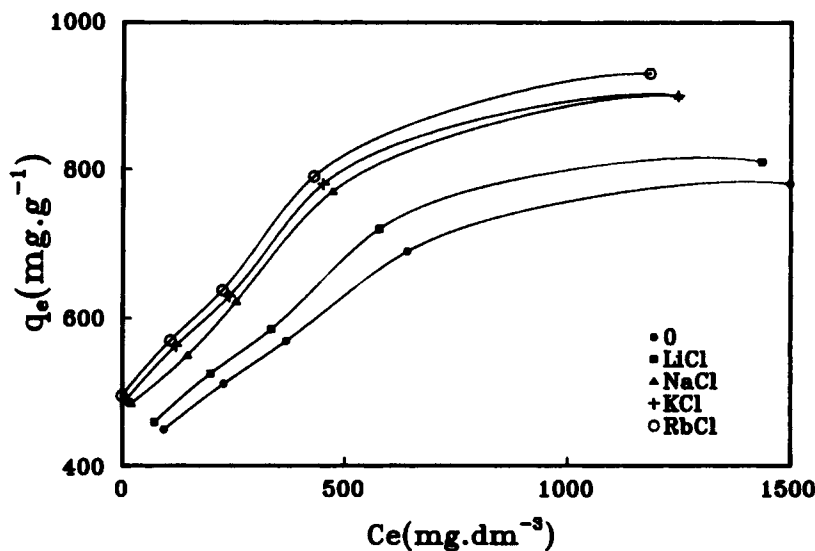


Figure 5 Equilibrium adsorption isotherms at 30°C for Direct Blue 86 on PAE-Cell in the presence of 0.1N alkali metal chlorides.

q_e , as a function of the residual equilibrium concentration, C_e , of the substance remaining in the solution phase. An expression of this type, termed an adsorption isotherm, defines the functional equilibrium distribution of adsorption with a concentration of adsorbate in solution at constant temperature.⁴ Figure 1 shows curves of q_e vs. C_e for the adsorption of Direct Blue 86 onto PAE-Cell and three types of activated carbon, using a particle-size range of 106–150 μm at 30°C for 3 days. The results show that the PAE-Cell has a higher adsorption capacity for

Direct Blue 86 than that of the three activated carbons. The results obtained with the other two direct dyes are similar to Figure 1. This is possibly due to a number of reasons: (1) The direct dyes have a much larger dye molecule, so that the dyes cannot penetrate into the internal pore structure of the activated carbons. (2) The PAE-Cell has both hydroxyl groups and amide groups. On the other hand, the activated carbon is nonpolar. There is probably anionic repulsion at the surface of the carbon, since direct dyes are anionic in water. (3) The planar

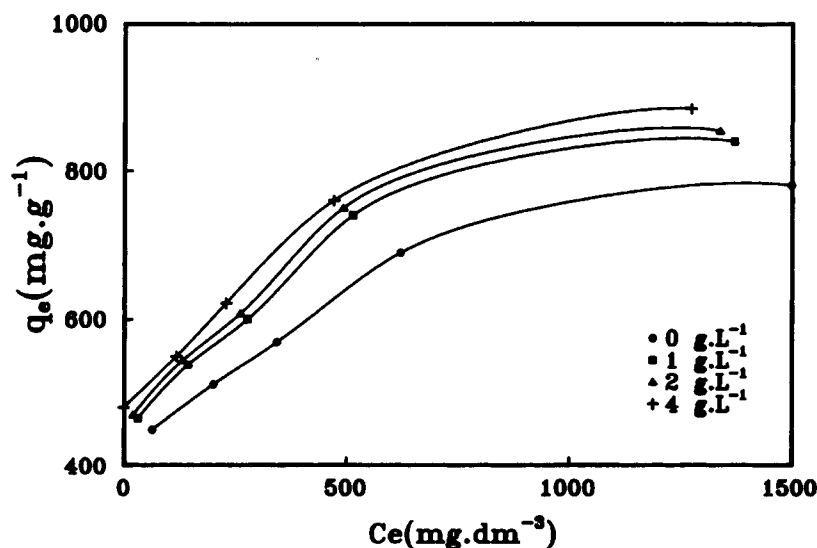


Figure 6 Effect of NaCl concentration on the equilibrium adsorption isotherms at 30°C of Direct Blue 86 on PAE-Cell.

structure of the direct dye molecule makes penetration of the dye between the PAE-Cell chains easier and promotes the tendency toward aggregation. (4) The linear molecular structure of the direct dye always aligns itself to the surface of the PAE-Cell. This result is similar to that of past studies.^{1,2,5} Probably, we can estimate that the Direct Blue 86 adsorbed per unit weight of PAE-Cell using a batch process is 40% greater than that using a fixed-bed system at 50% dye removal.¹

Effect of Particle Size

The surface area with respect to pore size generally is the primary determinant of adsorption capacity. The nature of the intraparticle surface markedly affects the type of adsorption mechanism and is a major distinguishing factor between activated carbon and synthetic adsorbents. Therefore, a wide range of PAE-Cell particle sizes was investigated, as shown in Table I. A dye bath with an initial dye

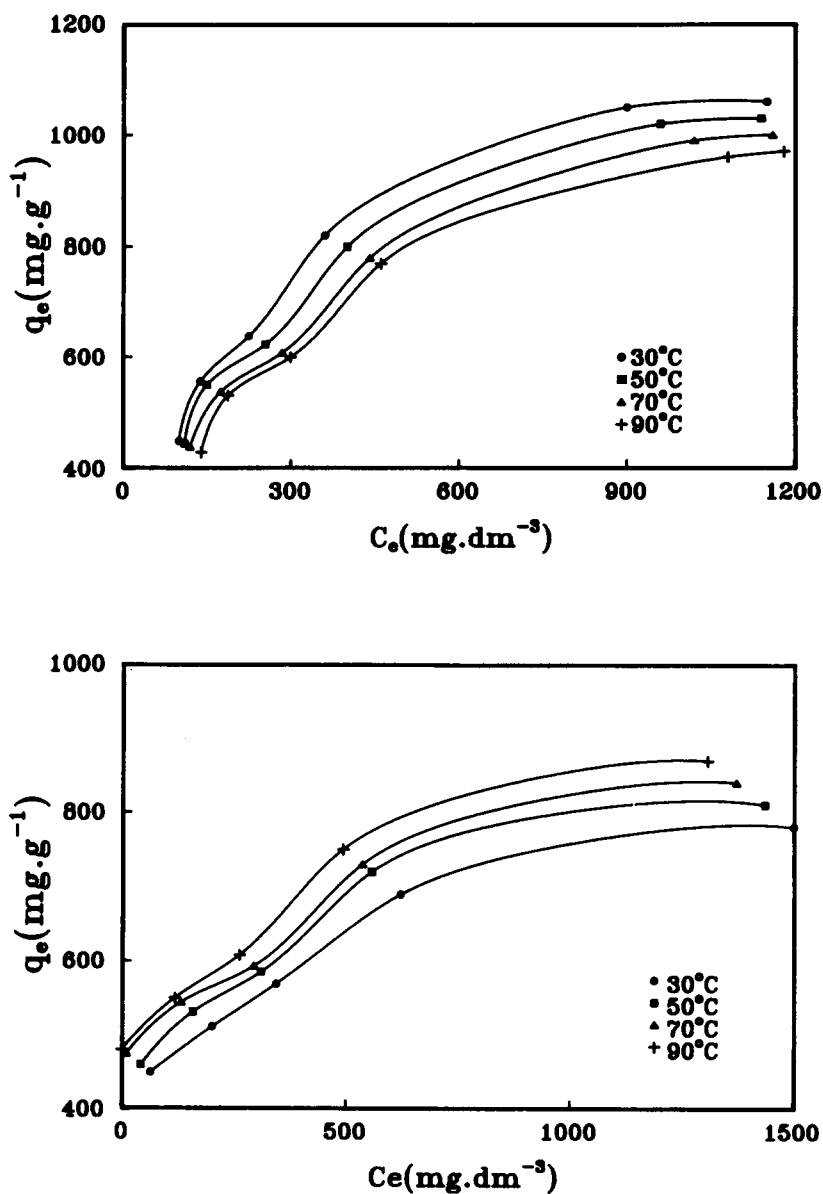


Figure 7 (a) Effect of temperature on the equilibrium adsorption isotherms on PAE-Cell for C. I. Acid Blue 158. (b) Effect of temperature on the equilibrium adsorption isotherms on PAE-Cell for C. I. Direct Blue 86.

Table II Langmuir Constants, Enthalpies, and Freundlich Constants of Adsorption from Eqs. (1)–(8)

Dye	T (°C)	Langmuir Constants			ΔH (kJ/mol)	Freundlich Constants	
		K_L (L/g)	Q (mg/g)	b (L/g)		K_F	n
Blue 86	30	6.17	846	7.29	12.35	160	4.57
	50	7.73	871	8.87		181	4.75
	70	8.58	895	9.59		231	5.67
	90	9.77	920	10.62		234	5.52
Orange 34	30	3.72	768	4.84	9.24	130	4.45
	50	4.27	802	5.32		135	4.37
	70	4.90	847	5.79		159	4.76
	90	5.13	884	5.80		173	4.91
Red 83	30	3.63	644	5.64	6.19	161	5.83
	50	4.17	693	6.02		163	5.42
	70	4.37	761	5.74		167	5.24
	90	4.57	803	5.69		178	5.27
Yellow 42	30	6.09	1127	4.96	25.59	83	2.70
	50	8.23	1125	6.72		114	3.01
	70	10.29	1139	8.31		134	3.17
	90	15.45	1155	12.31		188	3.68
Blue 113	30	2.26	814	2.78	12.52	71	3.29
	50	2.66	814	3.27		79	3.40
	70	3.02	834	3.62		91	3.55
	90	3.56	837	4.25		104	3.77
Red 85	30	2.91	719	4.05	6.93	103	4.06
	50	3.14	752	4.17		102	3.96
	70	3.45	785	4.39		99	3.76
	90	3.74	818	4.57		109	3.85
Red 114	30	3.38	654	5.17	-4.98	133	4.99
	50	3.34	622	5.37		118	4.72
	70	2.92	610	4.79		127	5.17
	90	2.87	587	4.89		126	5.26
Orange 7	30	6.80	839	8.10	23.61	163	4.62
	50	8.08	866	9.33		201	5.26
	70	11.47	860	13.33		226	5.53
	90	15.62	878	17.79		275	6.31
Blue 92	30	3.17	791	4.00	11.35	106	3.94
	50	3.61	800	4.51		118	4.12
	70	4.04	828	4.88		144	4.47
	90	4.76	838	5.68		173	4.95
Yellow 17	30	4.20	624	6.73	-5.42	221	8.55
	50	3.82	595	6.42		198	7.84
	70	3.76	561	6.70		219	9.70
	90	3.39	534	6.35		208	9.57
Brown 14	30	4.35	524	8.30	8.23	115	9.09
	50	4.56	567	8.04		134	9.32
	70	4.90	610	8.03		151	9.12
	90	5.69	635	8.96		203	9.62

Table II (Continued)

Dye	T (°C)	Langmuir Constants			ΔH (kJ/mol)	Freundlich Constants	
		K_L (L/g)	Q (mg/g)	b (L/g)		K_F	n
Blue 158	30	6.62	1162	5.25	-9.81	82	2.64
	50	5.84	1138	4.72		84	2.73
	70	5.12	1111	4.23		70	2.58
	90	4.70	1074	4.00		67	2.59
Red 183	30	3.74	1035	3.61	-11.77	73	2.89
	50	3.23	1010	3.20		69	2.89
	70	2.92	961	3.04		62	2.84
	90	2.57	911	2.82		61	2.95
Blue 193	30	3.89	792	4.91	-11.97	109	3.91
	50	2.96	801	3.70		85	3.51
	70	2.70	777	3.47		82	3.52
	90	2.52	742	3.40		79	3.56
Yellow 99	30	3.63	622	5.84	-16.57	165	5.99
	50	2.88	614	4.69		140	5.40
	70	2.57	604	4.25		124	5.39
	90	1.95	606	3.22		101	4.57

concentration of 1 g/L of Direct Blue 86 was adsorbed using PAE-Cell of four particle-size ranges. The influence of particle size is shown in the curves of q_e vs. C_e in Figure 2, indicating that PAE-Cell particle size has little influence on the equilibrium distribution for Direct Blue 86.

Effect of Initial Dye Concentration

The initial dye concentration of an effluent is important since a given mass of adsorbent can only adsorb a fixed amount of dye. Therefore, the more concentrated an effluent is, the smaller the volume of effluent that a fixed mass of adsorbent can purify.⁶ The influence of initial dye concentration on the difference in batch contact time was studied. Figure 3 shows the experimental results for the adsorption of Direct Blue 86 onto 150–106 μm PAE-Cell using three initial dye concentrations: 0.5, 1, and 1.5 g/L. The uptake of dye at low concentration is rapid, indicating the rapid onset of surface diffusion in the beginning. In other words, the dye molecules cannot be adsorbed on PAE-Cell in a short time period at high initial dye concentration.

Effect of pH

Because hydrogen and hydroxide ions often interact with adsorbents commonly used in aqueous phase

applications, the adsorption of other ions may thus be influenced by solution pH. Hence, the pH of the solution being treated may also profoundly affect the response of solutes to adsorption. A wide range of dye bath pH was investigated, as shown in Table I. Figure 4 illustrates the influence of the pH on the adsorption of Direct Blue 86, Acid Blue 158 (metal-complex type), Acid Orange 7 (leveling type), and Acid Blue 113 (milling type) onto PAE-Cell, using 0.2 g PAE-Cell, $C_0 = 2$ g/L, and 0.1 dm^3 dye bath volume at 30°C. The results show four phenomena in Figure 4: (1) Most of these dyes can be adsorbed more onto PAE-Cell at weak acidity (pH 5–7). (2) The removal of these dyes almost always will decrease with pH greater than 5. (3) The adsorption of PAE-Cell for Acid Blue 158, Acid Orange 7, and Direct Blue 86 increases with high $[\text{H}^+]$ (pH 3–5). (4) The adsorption of PAE-Cell for Acid Blue 113 decreases with high $[\text{H}^+]$ (pH 3–5). The former three phenomena are thought to be improbable since the $[\text{H}^+]$ was adsorbed onto the surface of the PAE-Cell, increasing the number of protons on the surface of the PAE-Cell. The protonation of the PAE-Cell surface increases the electrostatic potential with positive charge for interaction with the dye anions. This electrostatic potential can improve the adsorption affinity between dye molecules and PAE-Cell. In the fourth case, higher $[\text{H}^+]$ (pH 3–5) may

keep Acid Blue 113 molecules separated; hence, the dye cannot easily be adsorbed.

Effect of Salts

In practice, adding salts to the dye bath is known to have a very important effect.⁷ Thus, the equilibrium adsorption isotherms for Direct Blue 86 on PAE-Cell in the presence of several alkali metal chlorides were investigated, as shown in Table I. Figure 5 shows a series of alkali metal ions at a concentration of 0.1*N*. The sorption is considerably increased in going from lithium to rubidium. It is possible that the polarity of Direct Blue 86 was decreased by the salt, hence, lowering the effective size of the dye molecule and the solubility of the dye in water. It is also possible that the cations modified the structure of the water. The hydrated ion, by virtue of its strong electrostatic field, acquires an envelope of a molten zone in which there is more disorder than in the hydration zone or the bulk water.⁸ This structure-breaking effect increases with the size of the ion, i.e., from Li to Cs. On the other hand, it can increase the dye aggregation.⁸ The adsorption capacity of PAE-Cell increases with the radius of the cation. Figure 6 shows that the affinity formed between Direct Blue 86 and PAE-Cell will increase with the NaCl content. Hence, the adsorption capacity of PAE-Cell improves with the NaCl content in the dye bath. This result can be attributed to the same reasons discussed above.

Effect of Temperature

The temperature of a solution affects two major aspects of adsorption: the rate of diffusion of the adsorbate molecules through the solution to the adsorbent, and the solubility of the adsorbate and the swelling property of the adsorbent. It will therefore affect the extent of adsorption or capacity of the adsorbents. Thus, the adjustment of temperature may be required in adsorption processes. The effect of temperature on the adsorption of dyes such as Direct Blue 86 and Acid Blue 158 on PAE-Cell is shown in Figure 7(a) and (b), respectively. The results show two completely different effects: For dyes such as Acid Blue 158, the adsorption capacity of PAE-Cell decreases with increasing temperature. This is possibly due to the exothermic effect from the surroundings during the adsorption process. On the other hand, the capacity of PAE-Cell for dyes such as Direct Blue 86 increases with the temperature. This phenomenon is possibly due to the endothermic effect from the surroundings during the

adsorption process. It may increase the mobility of the large dye ion, hence, increasing the rate of diffusion of the dye molecules through the solution to PAE-Cell. Furthermore, increasing the temperature may produce a swelling effect within the internal structure of the PAE-Cell, facilitating the large dyes in penetrating further. These results are similar to those of past studies.⁵ The thermodynamic behavior can be explained using the Langmuir isotherm, as discussed in the next section. The capacity data of PAE-Cell for the 15 dyes are listed in Table II.

Adsorption Isotherms

The experimental equilibrium data for the uptake of 15 dyes by PAE-Cell at 30, 50, 70, and 90°C have been correlated with the rearranged Langmuir's model of adsorption:^{4,5,9}

$$q_e = \frac{Q \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (1)$$

where Q is the solid-phase concentration corresponding to complete coverage of the available site, or the limiting adsorption capacity, and b is the adsorption coefficient. Equation (1) can be written in

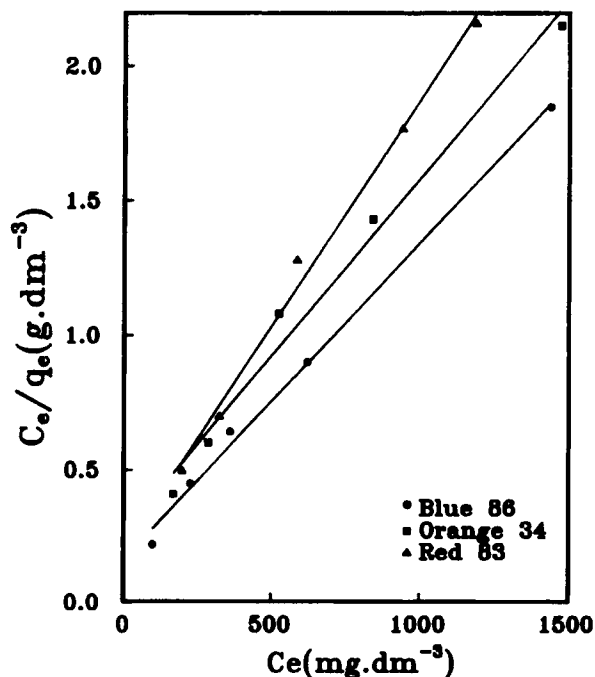


Figure 8 Langmuir plots for the removal of the three direct dyes on PAE-Cell. $T = 30^\circ\text{C}$.

a linear form to facilitate the fitting of the experimental data for parameter evaluation:

$$\frac{C_e}{q_e} = \frac{1}{Q \cdot b} + \frac{C_e}{Q} \quad (2)$$

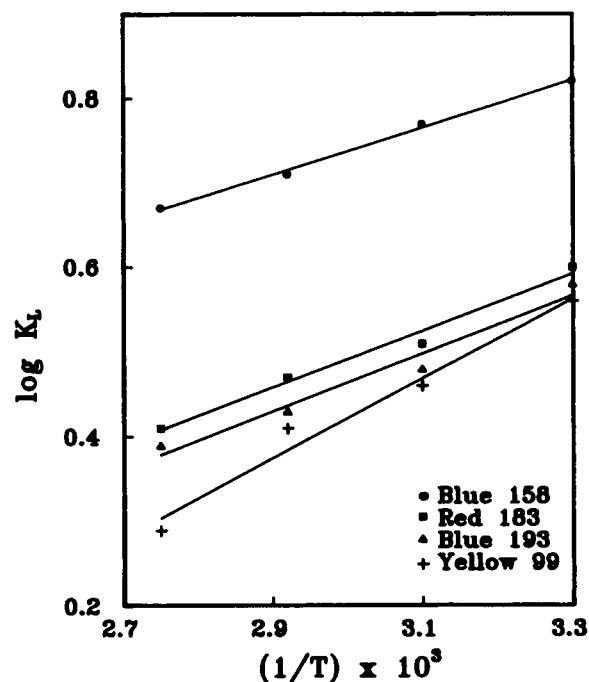
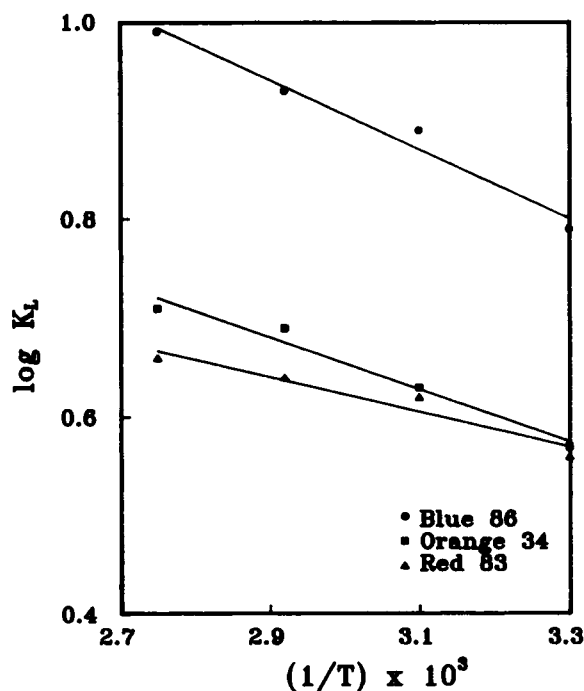


Figure 9 (a) Log K_L vs. reciprocal temperature for the adsorption of the three direct dyes on PAE-Cell. (b) Log K_L vs. reciprocal temperature for the adsorption of the four acid dyes on PAE-Cell.

A plot of C_e/q_e vs. C_e yields Q and b . Figure 8 shows the plot of eq. (2) for three direct dyes at 30°C. Table II lists the isotherm constants for the 15 dyes at various temperatures. In eq. (1), Q represents the monolayer coverage of the adsorbent particle in terms of mg dye/g PAE-Cell and is related to the Langmuir equilibrium constant, K_L , by eq. (3):

$$K_L = Q \cdot b \quad (3)$$

and the form of eq. (1) thus becomes

$$q_e = \frac{K_L \cdot C_e}{1 + (K_L/Q) \cdot C_e} \quad (4)$$

The equilibrium constant, K_L , may be used to determine the enthalpy of adsorption, ΔH , using the Clausius-Clapeyron equation:

$$K_L = A \exp(-\Delta H/RT) \quad (5)$$

$$\therefore \log K_L = \frac{-\Delta H}{2.303R} \frac{1}{T} + \log A \quad (6)$$

Figure 9(a) and (b) shows the plots of $\log K_L$ vs. $1/T$ for the enthalpies of adsorption for three direct dyes and four metal-complex acid dyes, respectively. The results of slope in Figure 9(a) and (b) show two completely different phenomena and Table II lists the enthalpies for the 15 dyes at various temperatures. The highest adsorption enthalpies of PAE-Cell are for Yellow 42 and Orange 7 at 25.59 and 23.61 kJ/mol, respectively. The higher positive values of the enthalpies for these dyes indicate that heat is absorbed from the surroundings during the adsorption of the dyes. Higher temperature helps PAE-Cell to adsorb more of these dyes. On the other hand, the negative value of the enthalpies for Red 114, Yellow 17, Blue 158, Red 183, Blue 193, and Yellow 99 indicate that heat is released during the adsorption process, which hinders PAE-Cell in adsorbing these dyes at high temperatures. These results are the same as those found in the past studies.⁵

The Freundlich equation has the general form^{4,5,10}

$$q_e = K_F \cdot C_e^{1/n} \quad (7)$$

where K_F and $1/n$ are characteristic constants. Equation (7) linearizes in logarithmic form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

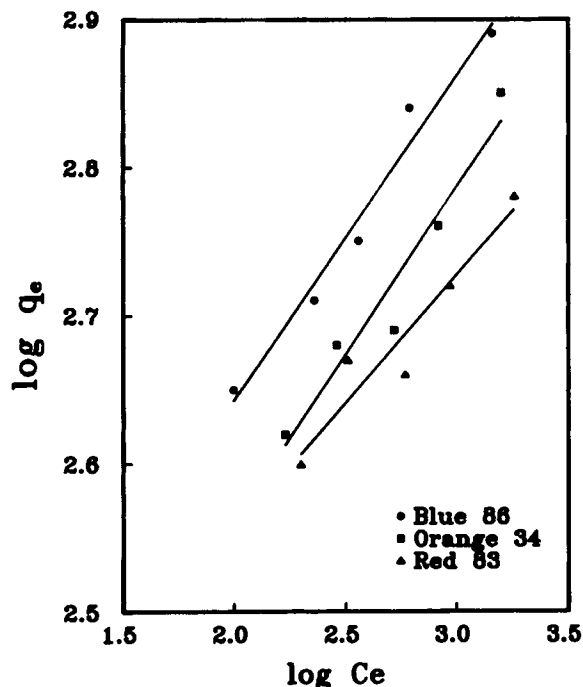


Figure 10 Freundlich analysis for the adsorption of three direct dyes on PAE-Cell. $T = 30^{\circ}\text{C}$.

for convenience of data fitting and parameter evaluation. K_F was taken as a relative indicator of adsorption capacity, while $1/n$ is indicative of the energy or intensity of the reaction. Figure 10 shows typical Freundlich plots for three direct dyes and Table II lists the Freundlich constants K_F and n for 15 anionic dyes using various temperatures. The magnitude of the exponent n gives an indication of the favorability and capacity of the adsorbent/adsorbate system. Values of $n > 1$ represent favorable adsorption conditions according to the theories.⁴ In all cases, the exponents are $1 < n$, showing that the adsorption is favorable.

CONCLUSIONS

The factors affecting anionic dye removal from aqueous solutions have been studied on PAE-Cell

using a batch process. For the direct dyes and acid dyes, PAE-Cell is an excellent adsorbent and the trends observed for the different variables are similar. The Langmuir and Freundlich isotherms were shown to be favorable and the effect of PAE-Cell was significant for these anionic dyes. The influence of temperature on the enthalpies of PAE-Cell to adsorb these anionic dyes was determined. The amount of adsorption of C. I. Direct Blue 86 on PAE-Cell was much larger than that on some commercial activated carbons. In this study, we can determine whether the added cost of pH adjustment and added salts will be offset by savings in the quantity of PAE-Cell used.

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