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Recovery of Amine and Paints from Electrodeposition Wastewater by an H-Form Ion Exchanger: Desorption Process

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Wastewater of anodic electrodeposition painting process contained diisopropanolamine, three unknown paints, and solvents (butyl Cellosolve and/or ethyl Cellosolve). The amine ($R'-NH_2$) was immobilized on H-form resin by the neutralization reaction $R-H + R'-NH_2 \rightarrow R-NH_3-R'$. The paints were adsorbed on the resin, too. Here we propose a desorption method of the immobilized amine from the wastewater-H-form resin complex by using the irreversible reaction $R-NH_3-R' + NaOH \rightarrow R-Na + R'-NH_2 + H_2O$. The experimental equilibrium isotherms and elution curves showed the amine and paints were desorbed well by NaOH aqueous solution. Experiments of adsorption, elution, and regeneration also have been reported. The adsorption capacity of the amine did not change with repeat times. The intraparticle effective diffusivities of the amine and Na^+ in the elution process were constant after the third cycle, and the intraparticle effective diffusivity of the amine in adsorption process was constant after the second cycle.

1. Introduction

Organic amines are used commonly as the dispersing agents for water-soluble paints in the anodic electrodeposition painting process which is widely used to paint metal panels with complicated shapes, such as office instruments and office furniture. Washing of the finished products gives a dilute aqueous solution of the amine and paints as an undesirable wastewater byproduct. Recovery of the amines and paints from these effluents is highly desirable both for the overall economics and for meeting environmental standards.

An H-form strong acid ion exchanger adsorbs amine and ammonia almost irreversibly (Yoshida and Kataoka, 1986, 1987), and the amine is eluted almost irreversibly from the amine-H-form resin complex by using the aqueous solution of caustic soda (Yoshida and Kataoka, 1989). This makes it possible to have a process that has the advantages of amine recovery and higher removal efficiency.

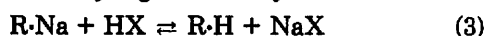
In contact with an H-form strong acid ion exchanger, the amine species are immobilized on the resin by the acid/base neutralization reaction:



where $R'-NH_2$ denotes the amine and $R-NH_3-R'$ is the amine-H-form resin complex. The amine is desorbed by the following irreversible neutralization reaction:



and the resin is finally regenerated by acid:



Yoshida et al. (1990) have applied eq 1 to adsorption of amine from the wastewater of electrodeposition painting, which contained diisopropanolamine, two solvents, three paints which are not pigments but polymers, and Fe^{2+} . The equilibrium isotherm for adsorption of the amine on the H-form resin was very favorable. The experimental breakthrough curves for adsorption of the components showed that the amine and paints were removed well by

the H-form resin and this method may be feasible technically.

In this paper, we present experimental data for desorption of the amine and paints from the wastewater-H-form resin complex to show that they are desorbed well by aqueous caustic soda solution (irreversible reaction, eq 2). We measured the equilibria for desorption of the amine by caustic soda. The experimental elution curves for the desorption of each component from the virgin wastewater-H-form resin complex and for repeat experiments are presented to demonstrate that it is feasible for the proposed process to recover the amine and paints from the wastewater of the electrodeposition painting process.

2. Electrodeposition Painting Process

The electrolytic cell contains various polymers (hereafter called paints), amines, and solvents that are dissolved in distilled water or deionized water. Amines are used as dispersing agents for the water-soluble paints. A metal panel is set at the anode, and painting is carried out by applying the electric current for several minutes. The finished products are then removed from the electrolytic cell and are washed. After washing, the solution flows through an ultrafilter (UF) to reuse the paints. Although high molecular weight paints can be recovered from the UF, the amine, low molecular weight paints, solvents, and Fe^{2+} pass through the filter; 90% of the solution which passes through the filter is recycled to wash finished products. To avoid accumulation of the contents in the solution of the washing process, 10% of the solution is exchanged for distilled water or deionized water. This is the wastewater of the electrodeposition painting process.

Table I shows the contents and their concentrations in the three wastewaters. The paints are not pigments but the low molecular weight polymers as mentioned above. The wastewater contained diisopropanolamine, one or two solvents, three paints, and Fe^{2+} . Concentration of diisopropanolamine was relatively high, and it had to be removed. The concentration of Fe^{2+} was very low. The three

Table I. Components and Concentrations of the Real Wastewater of the Electrodeposition Painting Process

component	concentration
No. 1 (June 1984)	
amine: diisopropanolamine	0.026 mol/dm ³
solvent: butyl Cellosolve (S1)	~2 vol %
paints: unknown (P1, P2, P3)	
others: Fe ²⁺	~9 × 10 ⁻⁶ mol/dm ³
No. 2 (June 1985)	
amine: diisopropanolamine	0.0293 mol/dm ³
solvents: butyl Cellosolve (S1) and ethyl Cellosolve (S2)	~2 vol %
paints: unknown (P1, P2, P3)	unknown
others: Fe ²⁺	~9 × 10 ⁻⁶ mol/dm ³
No. 3 (November 1986)	
amine: diisopropanolamine	0.033 mol/dm ³
solvents: butyl Cellosolve (S1) and ethyl Cellosolve (S2)	~2 vol %
paints: unknown (P1, P2, P3)	unknown
others: Fe ²⁺	~9 × 10 ⁻⁸ mol/dm ³

Table II. Basic Physical Properties of DIAION SK1B Resin (298 K)

gel type	
sulfonated	
styrene-divinylbenzene	
degree of cross-linking	8 wt %
exchange capacity (Q)	2.85 mol/dm ³ wet resin
ratio of particle diam	
d_{PW}/d_{PNa}	1.090 ($C_{NaOH,0} = 0.5$ mol/dm ³)
	1.076 ($C_{NaOH,0} = 1$ mol/dm ³)
	1.050 ($C_{NaOH,0} = 2$ mol/dm ³)
d_{PA}/d_{PNa}	1.064 ($C_{NaOH,0} = 0.5$ mol/dm ³)
	1.051 ($C_{NaOH,0} = 1$ mol/dm ³)
	1.026 ($C_{NaOH,0} = 2$ mol/dm ³)
equilibrium constant	
diisopropanolamine-H-form resin complex + 0.1 mol/dm ³ NaOH	
$K = 74$ (sorption of Na ⁺ , very favorable)	
$K = 0.014$ (sorption of diisopropanolamine, very unfavorable)	
wastewater (no. 1)-H-form resin complex + 0.1 mol/dm ³ NaOH	
$K = 34$ (sorption of Na ⁺ , very favorable)	
$K = 0.029$ (sorption of diisopropanolamine and three paints, very unfavorable)	

paints are not identified here because they are proprietary information.

3. Physical Properties

Table II shows the experimental physical properties of the resin. The ion exchanger used is strong acid gel type with sulfonic acid groups (H-form), because intraparticle effective diffusivities of the amine in gel-type resin were about 5 times greater than those in MR-type resin (Yoshida and Kataoka, 1987). d_{PNa} , d_{PA} , and d_{PW} are the particle diameters of Na-form resin in aqueous NaOH solution, diisopropanolamine-H-form resin complex in 0.026 mol/dm³ aqueous diisopropanolamine solution, and wastewater-H-form resin complex in the wastewater, respectively. They were determined by averaging the diameters of 50 particles. Particle diameters of the three different forms differ slightly.

4. Experimental Section

Equilibria for desorption of diisopropanolamine from diisopropanolamine-H-form resin complex and from wastewater-H-form resin complex by aqueous NaOH solution were measured by the batch method. The particles of diisopropanolamine-H-form resin complex and wastewater-H-form resin complex were prepared by the column method: 0.026 mol/dm³ aqueous diisopropanolamine so-

Table III. Experimental Conditions for the Elution Curve and Intraparticle Effective Diffusivity Determined from the Theoretical Curve for a Rectangular Isotherm in a Single-Component System (Tables IV and V)

run	resin ^a	$C_{NaOH,0}$ mol/dm ³	H , m	Re'	$10^{11}D_{eff}$, m ² /s	
					amine	Na ⁺
1	W (no. 1)	0.493	0.368	0.596		2.12
2	W (no. 2)	0.514	0.385	0.941	1.56	1.89
3	W (no. 2)	0.546	0.376	1.23	1.29	3.13
4	W (no. 2)	2.07	0.740	0.533		2.82
5	W (no. 3)	2.01	0.734	0.250	2.10	1.43
					1.65 ^b	2.28 ^b
6	S	0.487	0.366	1.01		2.83
7	S	1.03	0.717	1.11	2.79	2.79
8	S	1.15	0.705	2.06	3.53	3.44
					3.16 ^c	3.02 ^c

^a W = virgin wastewater-H-form resin complex; S = virgin diisopropanolamine-H-form resin complex. ^b Mean value of D_{eff} (runs 1-5). ^c Mean value of D_{eff} (runs 6-8).

lution and wastewater were flowed through the different H-form resin beds, respectively. After reaching an equilibrium, the resin particles were washed with deionized, distilled water and dried at room temperature. The particles of diisopropanolamine-H-form resin complex or wastewater-H-form resin complex were brought into contact with 0.1 mol/dm³ aqueous NaOH solution. The solution and the resin particles were well mixed. The equilibrium was fully reached in 4 days. The resin-phase concentration of Na⁺ was calculated according to the equation

$$q_{Na} = \frac{V(C_{Na,0} - C_{Na})}{W} \quad (4)$$

The resin-phase concentration of the amine in diisopropanolamine-H-form resin complex + NaOH system and the resin-phase concentration of amine + paints in wastewater-H-form resin complex + NaOH system were calculated from eqs 5 and 6, respectively.

$$q_{amine} = Q - q_{Na} \quad (5)$$

$$q_{amine+paints} = Q - q_{Na} \quad (6)$$

The systems and conditions used in an experimental study for the elution curve are shown in Table III. The elution curves (runs 1-5) were measured as follows. The virgin particles of H-form resin were placed in a column which was 0.01 m in diameter with a jacket and was set at heights of about 0.4 and 0.8 m. The wastewater was flowed through the bed until the equilibrium was fully reached. Thereafter the bed was not washed with water but aqueous NaOH solution was flowed through the bed. The flow rates and the concentration of caustic soda are shown in Table III. The repeat experiments of adsorption, elution, and regeneration were carried out by using wastewater no. 2. The flow rate of the wastewater in adsorption cycle was about $Re' = 3.6$ -3.9. The first elution cycle was run 2 in Table III. The molecules adsorbed were eluted by 0.5 mol/dm³ aqueous NaOH solution (about $Re' = 0.94$ -1.0). Na-form resin particles were finally regenerated by 0.5 mol/dm³ aqueous HCl solution (about $Re' = 1.1$ -1.3). The periods of time of the adsorption, elution, and regeneration processes were 185, 60, and 50 min, respectively.

Concentrations of the amine, paints, and solvents in the solution were determined by gas chromatography with an flame ionization detector (Schimadzu GC-7A). Since the three paints were not identified here, we could not measure the absolute concentrations of the paints but determined

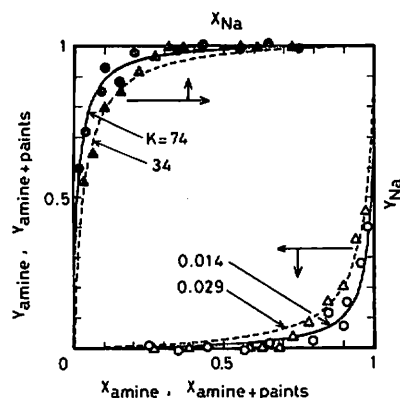


Figure 1. X - Y plots of equilibrium data. (●, ○) diisopropanolamine-H-form complex + 0.1 mol/dm³ NaOH system; (▲, △) wastewater-H-form resin complex + 0.1 mol/dm³ NaOH system. (—, ---) eq 8 or 9.

the ratio of the effluent concentration of the column and the concentration of the wastewater according to the equation

$$X_{Pi} = \frac{C_{Pi}}{C_{Pi,0}} = \frac{S_{Pi}}{S_{Pi,0}} \quad (7)$$

where $S_{Pi,0}$ and S_{Pi} denote the areas of the chromatogram of paint P_i ($i = 1, 2, 3$) determined by gas chromatography for the wastewater and for the effluent solution, respectively. The concentration of Na⁺ was analyzed by plasma spectroscopy (SMI Spectraspan III) and frame analysis.

All experiments were carried out at 298 K.

5. Results and Discussion

5.1. Equilibrium Isotherm. Figure 1 shows the X - Y plots of the equilibria for desorption of diisopropanolamine from diisopropanolamine-H-form resin complex and for elution of diisopropanolamine + paints from wastewater-H-form resin complex by 0.1 mol/dm³ NaOH aqueous solution. The wastewater-H-form resin complex was prepared by using wastewater no. 1 in Table I. In the case of diisopropanolamine-H-form resin complex, the selectivity for sorption of Na⁺ is fairly high and the equilibrium isotherm for the amine is very unfavorable, because diisopropanolamine is exchanged for Na⁺ by the irreversible neutralization reaction (eq 2). The solid lines represent the theoretical lines calculated from eqs 8 and 9, which are

$$K = \frac{q_{Na}(C_{NaOH,0} - C_{NaOH})}{(Q - q_{Na})C_{NaOH}} \quad (8)$$

$$K = \frac{(Q - q_{Na})C_{NaOH}}{q_{Na}(C_{NaOH,0} - C_{NaOH})} \quad (9)$$

derived by applying the mass action law to eq 2, using the value of K in Table II, respectively. The solid lines are correlated reasonably well with the data.

We have shown that the concentration of the amine and the total concentration of the three paints in the resin phase of the wastewater-H-form resin complex are about 79% and 21% of the exchange capacity of the resin, respectively (Yoshida et al., 1990). Since the paints were not identified, we could not determine their absolute concentrations. We have also shown that the solvents were not adsorbed on the resin and the adsorption of Fe²⁺ was negligible because of the very low concentration as shown in Table I. In order to make clear whether the amine and the paints can be desorbed from the wastewater-H-form resin complex by aqueous NaOH solution or not, we measured the equilibrium concentration of Na⁺ in the

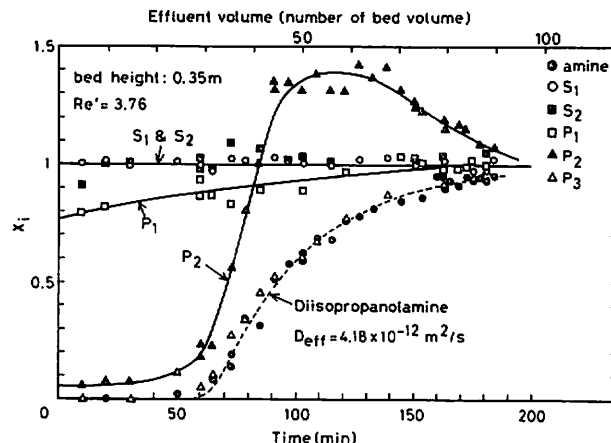


Figure 2. Breakthrough curves for adsorption of the components in wastewater no. 2 on virgin H-form resin. (---) Theoretical line calculated from the analytical solution for a rectangular isotherm in a single-component system.

liquid phase. The resin-phase concentration of Na⁺ was determined according to eq 4. Figure 1 shows that the maximum concentration of Na⁺ in the resin phase coincides with the exchange capacity ($Y_{Na} = 1$). The selectivity for adsorption of Na⁺ is fairly high. The equilibrium isotherm for adsorption of the amine and the paints is very unfavorable. The selectivity of Na⁺ in the wastewater-H-form resin complex + NaOH system is slightly lower than that in the diisopropanolamine-H-form resin complex + NaOH system. This may be caused by the effect of the coexisting three paints. The dotted lines show the theoretical lines calculated according to eqs 8 and 9 using the value of K in Table II. They correlate the data a little worse than the diisopropanolamine-H-form resin complex + NaOH system.

5.2. Breakthrough Curve (Adsorption of the Components on Virgin H-Form Resin). In this section, we use the term "breakthrough curve" as the concentration history at the end of the bed for adsorption of the components of the wastewater on virgin H-form resin during the adsorption cycle.

Figure 2 shows typical experimental breakthrough curves for the wastewater no. 2. The number of bed volume in the figure is defined:

$$\text{number of bed volume} = \frac{\text{effluent volume}}{\text{bed volume}}$$

The amine is removed well by the H-form resin from the wastewater of electrodeposition painting process. The affinity of the amine may be the highest, because the breakthrough time of the amine is the longest. However, since the breakthrough curve of paint 3 (P3) is almost the same as that of the amine, the amine and paint 3 have almost identical affinities to the H-form resin and have almost the same intraparticle diffusivities. Because paint 2 has lower affinity than paint 3 and the amine, paint 2 shows a chromatographic elution effect where the effluent concentration of paint 2 during the column run becomes greater than its feed concentration. Paint 1 has the smallest intraparticle diffusivity or unfavorable equilibrium relation, because it breaks through quite early but does not show a chromatographic elution effect. Since the effluent concentrations of the solvents are the same as those feed concentrations, they are not adsorbed on H-form resin and flowed through the bed.

5.3. Elution Curve (Virgin Wastewater-H-Form Resin Complex). Elution curve is defined as the concentration history of the components desorbed from the virgin wastewater-H-form resin complex using NaOH

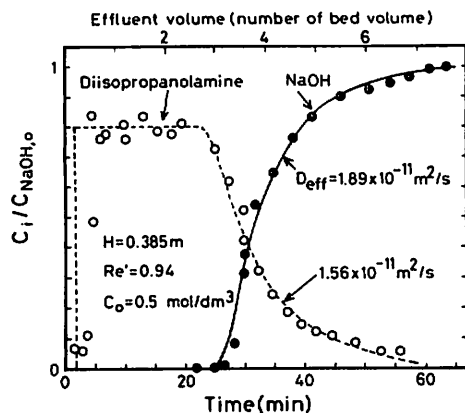


Figure 3. Elution curve of diisopropanolamine and breakthrough curve of NaOH (run 2). (—, ---) Theoretical line calculated from the analytic solution for a rectangular isotherm in a single-component system.

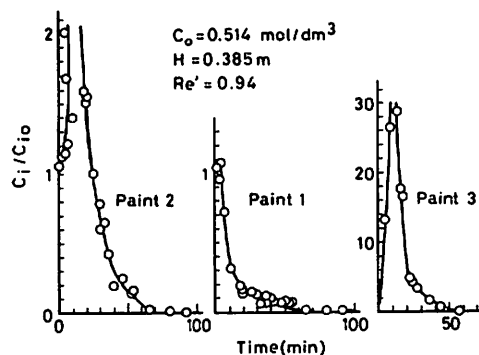


Figure 4. Elution curves of paints 1, 2, and 3 (run 2).

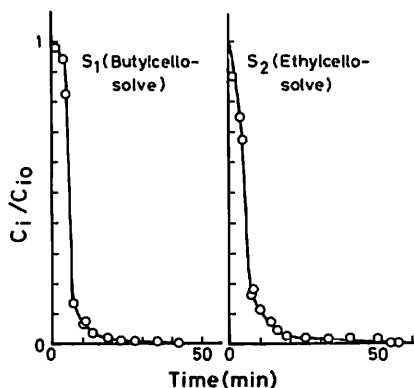


Figure 5. Elution curves of solvents (run 2).

aqueous solution. Since the elution is accomplished by eq 2, NaOH is adsorbed by the resin during the elution cycle. Therefore, the concentration history of NaOH is called the breakthrough curve.

Figures 3–5 show typical experimental elution curves of diisopropanolamine, three paints, and solvents, from the wastewater (no. 2)–H-form resin complex (run 2 in table III), respectively. The concentration of the eluent, aqueous NaOH solution, was 0.5 mol/dm³. The components in the resin phase are desorbed well by the aqueous NaOH solution. This can be understood from the equilibrium isotherm shown in Figure 1. Figure 3 shows that the flat region exists in the elution curve of diisopropanolamine and the value of $X_{\text{amine}} (=C_{\text{amine}}/C_{\text{NaOH},0})$ is about 0.8 (C_{amine} is about 0.4 mol/dm³). This is because the initial concentration of the amine in the resin phase is about 80% of the exchange capacity of the resin as mentioned earlier. When the eluent NaOH breaks through, the concentration of the amine in the effluent starts to decrease. Figure 4

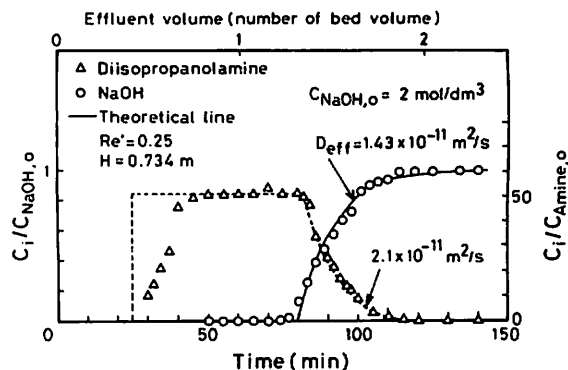


Figure 6. Elution curve of diisopropanolamine and breakthrough curve of NaOH (run 5). (—, ---) Theoretical line calculated from the analytic solution for a rectangular isotherm in a single-component system.

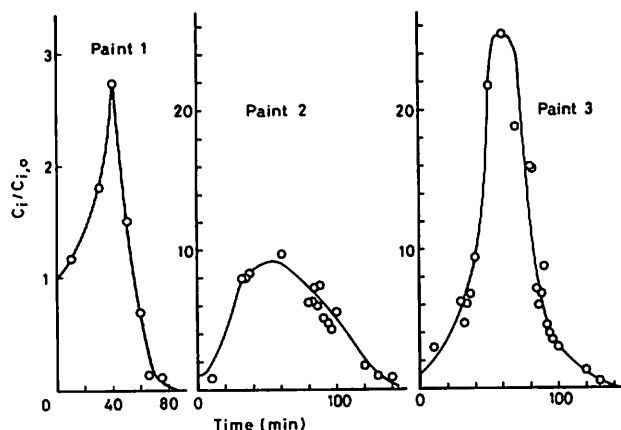


Figure 7. Elution curves of paints 1, 2, and 3 (run 5).

shows the elution curves of paints 1–3. Since the three paints were not identified, we could not determine those absolute concentrations. Therefore we determined the value of C_i/C_{i0} according to eq 7. Since the elution curves show sharp peaks, the paints are desorbed well by the aqueous NaOH solution. Since the peak of paint 3 is the highest, paint 3 may be the main component in the three paints. Paint 1 may be a minor component, because the peak is much lower than the others. Figure 5 shows that the solvents are eluted without a peak and the elution finished faster than the amine and paints. This is because the solvents were not adsorbed on the H-form resin as mentioned earlier and they only existed in the void of the bed before the elution. All components are eluted almost completely in about 60 min.

In order to test whether we can increase the concentration of the amine eluted or not, we changed the concentration of the eluent NaOH from 0.5 mol/dm³ (Figures 3–5) to 2 mol/dm³ (run 5). Figures 6 and 7 show the elution curves of diisopropanolamine and the three paints, respectively. Figure 6 shows that X_{amine} of the flat region is about 0.84 (C_{amine} is about 1.7 mol/dm³). This is similar to the result in Figure 3. Since the concentration of the amine of the flat region is about 80–84% of the concentration of the eluent because of the reason as mentioned earlier, it is possible to recover the concentrated amine by using concentrated eluent NaOH. Figure 7 shows that the peaks of the elution curves of paints 1 and 2 become higher than those for run 2 (Figure 4). All components were eluted almost completely in about 120 min. In addition, we measured the elution curves for run 4. Since Re' of run 4 was about twice that of run 5, the flat region of the elution of the amine did not appear. As the longer the flat region of the elution curve is, the higher the concentration

Table IV. Summary of the Analytic Solution of the Breakthrough Curve for a Rectangular Isotherm and a Single-Component System in the Homogeneous Model

general solution	range of τ and ξ	
$x = 1 - \frac{\xi}{\delta} \exp(-\tau/\delta), \quad y = 1 - \exp(-\tau/\delta)$	$\delta \geq 1$ $\tau \geq 0, \quad 0 \leq \xi \leq \delta - 1$	(9)
$x = \frac{1}{\delta} \exp(\delta - 1 - \xi), \quad y = \tau \exp(\delta - 1 - \xi)$	$0 \leq \tau \leq \frac{1}{\delta}, \quad \xi \geq \delta - 1$	(10)
$x = y = 1 - \left\{1 - \frac{1}{\delta} \exp(\delta - 1 - \xi)\right\} \exp\left(\left(\frac{1}{\delta} - \tau\right)/\delta\right)$	$\tau \geq \frac{1}{\delta}, \quad \delta - 1 \leq \xi \leq \delta - 1 + \ln\left(\frac{\delta + 1}{\delta}\right)$	(11)
$x = y = \frac{1}{\delta} \exp\left(\tau - \xi + \delta - 1 - \frac{1}{\delta}\right)$	$\frac{1}{\delta} \leq \tau \leq \xi - \delta + 1 + \frac{1}{\delta} - \ln\left(\frac{\delta + 1}{\delta}\right), \quad \xi \geq \delta - 1 + \ln\left(\frac{\delta + 1}{\delta}\right)$	(12)
$x = y = 1 - \frac{\delta}{\delta + 1} \exp\left[\left(-\tau + \xi - \delta + 1 + \frac{1}{\delta} - \ln\left(\frac{\delta + 1}{\delta}\right)\right)/\delta\right]$	$\tau \geq \xi - \delta + 1 + \frac{1}{\delta} - \ln\left(\frac{\delta + 1}{\delta}\right), \quad \xi \geq \delta - 1 + \ln\left(\frac{\delta + 1}{\delta}\right)$	(13)
$x = \exp(-\xi), \quad y = \tau \exp(-\xi)$	$\delta \leq 1$ $0 \leq \tau \leq 1, \quad \xi \geq 0$	(14)
$x = y = 1 - \{1 - \exp(-\xi)\} \exp[(1 - \tau)/\delta]$	$\tau \geq 1, \quad 0 \leq \xi \leq \ln(1 + \delta)$	(15)
$x = y = \exp(\tau - \xi - 1)$	$1 \leq \tau \leq \xi + 1 - \ln(1 + \delta), \quad \xi \geq \ln(1 + \delta)$	(16)
$x = y = 1 - \frac{\delta}{\delta + 1} \exp\{[-\tau + \xi + 1 - \ln(\delta + 1)]/\delta\}$	$\tau \geq \xi + 1 - \ln(1 + \delta), \quad \xi \geq \ln(1 + \delta)$	(17)
constant pattern solution	range of τ and ξ	
$x = y = \frac{1}{\delta} \exp\left(\tau - \xi + \delta - 1 - \frac{1}{\delta}\right)$	$\delta \geq 1$ $\tau - \xi \leq -\delta + 1 + \frac{1}{\delta} - \ln\left(\frac{\delta + 1}{\delta}\right)$	(18)
$x = y = 1 - \frac{\delta}{\delta + 1} \exp\left[\left(-\tau + \xi - \delta + 1 + \frac{1}{\delta} - \ln\left(\frac{\delta + 1}{\delta}\right)\right)/\delta\right]$	$\tau - \xi \leq -\delta + 1 + \frac{1}{\delta} - \ln\left(\frac{\delta + 1}{\delta}\right)$	(19)
$x = y = \exp(\tau - \xi - 1)$	$\delta \leq 1$ $\tau - \xi \leq 1 - \ln(1 + \delta)$	(20)
$x = y = 1 - \frac{\delta}{\delta + 1} \exp\{[-\tau + \xi + 1 - \ln(\delta + 1)]/\delta\}$	$\tau - \xi \geq 1 - \ln(1 + \delta)$	(21)

of the amine recovered becomes, Re' should be selected carefully.

Since the paints were not identified, we could not determine the equilibrium isotherms for desorption of the paints quantitatively and could not calculate the theoretical elution curve for each component. The above results may suggest that the key components for controlling the column operation are NaOH and the amine. In order to reuse the amine and the paints for electrodeposition painting, it is important to know the breakthrough time of NaOH. Further, if aqueous NaOH solution flows through the bed until X_{amine} becomes smaller than about 0.05, the other components are desorbed almost completely as shown in Figures 3–7. Therefore, we tried to get the theoretical breakthrough curve of NaOH and the elution curve of the amine.

A number of investigators have presented experimental and theoretical breakthrough curves for a multicomponent system (Helfferich and Klein, 1970; Klein and Vermeulen, 1970; Thomas and Lombardi, 1971; Garipey and Zweibel, 1971; Cooney and Strusi, 1972; Rhee and Amundson, 1974; Zweibel et al., 1974; Carter and Husain, 1974; Bradley and Sweed, 1975; Liapis and Rippin, 1978; Balzli et al., 1978; Takeuchi et al., 1979; Miura et al., 1979; Miura and Hashimoto, 1979; Santacesaria et al., 1982; Ruthven, 1984; Takeuchi and Furuya, 1989). However, when unknown components exist, the way in which the theoretical breakthrough curves are obtained has not been studied.

Yoshida et al. (1990) have shown that when the equilibrium isotherm of the strongly adsorbed species in a multicomponent system is very favorable, its breakthrough curve can be estimated from the analytic solution for a

rectangular isotherm in the single-component system (Yoshida et al., 1984) shown in Table IV without any complicated calculations for a multicomponent system. This method may be directly used to determine the theoretical breakthrough curve of NaOH because the equilibrium isotherm for sorption of NaOH on wastewater-H-form resin complex is very favorable as shown in Figure 1. Since when NaOH coexists, the equilibrium isotherm for adsorption of the amine is very unfavorable as shown in Figure 1, the elution curve of the amine can be also calculated from the theoretical equation for irreversible desorption in the single-component system (Yoshida and Kataoka, 1989) shown in Table V. These are explained briefly in the Appendix.

The solid lines in Figures 3 and 6 show the theoretical breakthrough curve of NaOH (the very strongly adsorbed species) calculated from the analytic solution for a rectangular isotherm in a single-component system (Yoshida et al., 1984). The dashed lines in Figures 3 and 6 show the theoretical elution curve of diisopropanolamine calculated from the analytic solution for a very unfavorable isotherm (irreversible desorption) in a single-component system (Yoshida and Kataoka, 1989). Intraparticle effective diffusivity values [$D_{\text{eff}}(\text{m}^2/\text{s})$] were determined by matching the data with the analytic solutions. First of all, the external mass-transfer coefficient $k_f(\text{s}^{-1})$ was estimated from the following correlation (Kataoka et al., 1972):

$$\left(\frac{1 - \epsilon}{\epsilon}\right)^{1/3} \frac{k_f Sc^{2/3}}{v} = 1.85 Re'^{-2/3} \quad (35)$$

$$k_f = 6k'_f/d_p$$

Table V. Summary of the Analytic Solution of the Elution Curve for Irreversible Desorption in the Homogeneous Model

general solution	range of τ and ξ	
	$\delta \geq 1$	
$x = \frac{\xi}{\delta} \exp(-\tau/\delta), \quad y = \exp(-\tau/\delta)$	$\tau \geq 0, \quad 0 \leq \xi \leq \delta - 1$	(22)
$x = 1 - \frac{1}{\delta} \exp(\delta - 1 - \xi), \quad y = 1 - \tau \exp(\delta - 1 - \xi)$	$0 \leq \tau \leq \frac{1}{\delta}, \quad \xi \geq \delta - 1$	(23)
$x = y = \left\{1 - \frac{1}{\delta} \exp(\delta - 1 - \xi)\right\} \exp\left(\left(\frac{1}{\delta} - \tau\right)/\delta\right)$	$\tau \geq \frac{1}{\delta}, \quad \delta - 1 \leq \xi \leq \delta - 1 + \ln\left(\frac{\delta + 1}{\delta}\right)$	(24)
$x = y = 1 - \frac{1}{\delta} \exp\left(\tau - \xi + \delta - 1 - \frac{1}{\delta}\right)$	$\frac{1}{\delta} \leq \tau \leq \xi - \delta + 1 + \frac{1}{\delta} - \ln\left(\frac{\delta + 1}{\delta}\right), \quad \xi \geq \delta - 1 + \ln\left(\frac{\delta + 1}{\delta}\right)$	(25)
$x = y = \frac{\delta}{\delta + 1} \exp\left[\left(-\tau + \xi - \delta + 1 + \frac{1}{\delta} - \ln\left(\frac{\delta + 1}{\delta}\right)\right)/\delta\right]$	$\tau \geq \xi - \delta + 1 + \frac{1}{\delta} - \ln\left(\frac{\delta + 1}{\delta}\right), \quad \xi \geq \delta - 1 + \ln\left(\frac{\delta + 1}{\delta}\right)$	(26)
	$\delta \leq 1$	
$x = 1 - \exp(-\xi), \quad y = 1 - \tau \exp(-\xi)$	$0 \leq \tau \leq 1, \quad \xi \geq 0$	(27)
$x = y = \{1 - \exp(-\xi)\} \exp\{(1 - \tau)/\delta\}$	$\tau \geq 1, \quad 0 \leq \xi \leq \ln(1 + \delta)$	(28)
$x = y = 1 - \exp(\tau - \xi - 1)$	$1 \leq \tau \leq \xi + 1 - \ln(1 + \delta), \quad \xi \geq \ln(1 + \delta)$	(29)
$x = y = \frac{\delta}{\delta + 1} \exp\{[-\tau + \xi + 1 - \ln(\delta + 1)]/\delta\}$	$\tau \geq \xi + 1 - \ln(1 + \delta), \quad \xi \geq \ln(1 + \delta)$	(30)
constant pattern solution	range of τ and ξ	
	$\delta \geq 1$	
$x = y = 1 - \frac{1}{\delta} \exp\left(\tau - \xi + \delta - 1 - \frac{1}{\delta}\right)$	$\tau - \xi \leq -\delta + 1 + \frac{1}{\delta} - \ln\left(\frac{\delta + 1}{\delta}\right)$	(31)
$x = y = \frac{\delta}{\delta + 1} \exp\left[\left(-\tau + \xi - \delta + 1 + \frac{1}{\delta} - \ln\left(\frac{\delta + 1}{\delta}\right)\right)/\delta\right]$	$\tau - \xi \geq -\delta + 1 + \frac{1}{\delta} - \ln\left(\frac{\delta + 1}{\delta}\right)$	(32)
	$\delta \leq 1$	
$x = y = 1 - \exp(\tau - \xi - 1)$	$\tau - \xi \leq 1 - \ln(1 + \delta)$	(33)
$x = y = \frac{\delta}{\delta + 1} \exp\{[-\tau + \xi + 1 - \ln(\delta + 1)]/\delta\}$	$\tau - \xi \geq 1 - \ln(1 + \delta)$	(34)

The liquid-phase diffusivity of the amine was estimated from Wilke and Chang's equation (1955). The values of τ and ξ can be calculated according to the definitions and the estimated value of k_f . To match the theoretical breakthrough curve with the experimental breakthrough curve, the value of δ was assumed. The value of k_p was calculated from the value of δ obtained by matching. The intraparticle effective diffusivity value was obtained from $k_p = 15D_{\text{eff}}/r_0^2$.

The intraparticle effective diffusivities of diisopropanolamine and Na^+ determined by the above procedure are summarized in Table III. In the case of diisopropanolamine-H-form resins (runs 6–8), there is little difference between the intraparticle effective diffusivities of diisopropanolamine and Na^+ . These values are almost the same as those obtained from the experimental breakthrough curve for adsorption of the amine (single-component system) on H-form resin (Yoshida et al., 1990). The intraparticle effective diffusivity of diisopropanolamine for the wastewater-H-form resin complex (runs 2, 3, and 5) are about half that for the diisopropanolamine-H-form resin complex (runs 7 and 8), perhaps because the paints coexisted in the resin phase.

5.4. Effect of Repeat Times. In order to test the possibility of using this method to cyclic operation, repeat experiments were carried out. The first elution cycle was run 2 in Table III. Figure 8 shows the experimental elution curve of diisopropanolamine and the breakthrough curve of NaOH for the fifth elution cycle. They are similar to those for the first cycle (Figure 3). The solid and dashed lines show the theoretical breakthrough curve of Na^+ and the elution curve of diisopropanolamine, respectively, calculated as mentioned earlier.

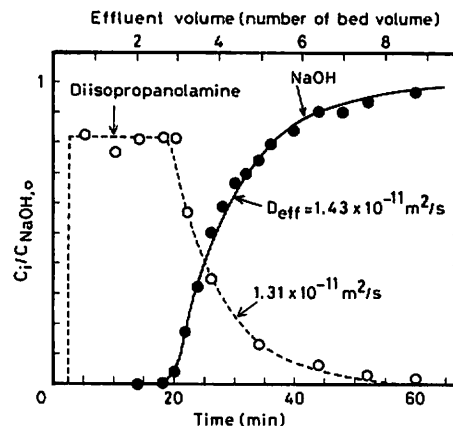


Figure 8. Elution curve of diisopropanolamine and breakthrough curve of NaOH for fifth elution cycle in repeat experiment using wastewater no. 2. (—, ---) Theoretical line calculated from the analytic solution for a rectangular isotherm in a single-component system.

Figure 9 shows the experimental adsorption capacity of diisopropanolamine and intraparticle effective diffusivities of the amine and Na^+ with repeat time. In the elution cycle, the intraparticle effective diffusivities of Na^+ and the amine decrease with repeat time until the third cycle, but are constant after the third cycle. In the case of the adsorption cycle, the intraparticle effective diffusivity of the amine increases in the second cycle and is constant after the second cycle. The steady-state intraparticle effective diffusivities of Na^+ and the amine in the elution process are about 2.6 and 2.4 times larger than the steady-state intraparticle diffusivity of the amine in the

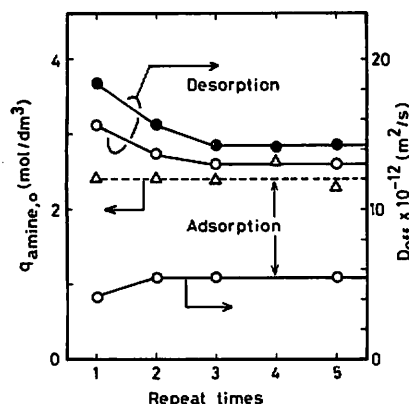


Figure 9. Effects of repeat time on adsorption capacity and intraparticle effective diffusivity of diisopropanolamine and Na^+ : (O, Δ) diisopropanolamine; (●) Na^+ .

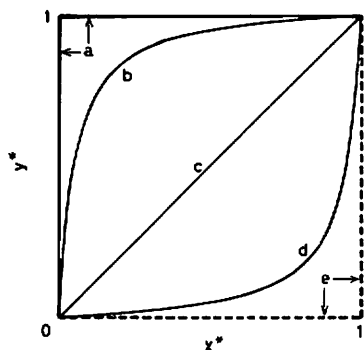


Figure 10. Equilibrium isotherms. (a) Rectangular isotherm (for adsorption); (b) very favorable; (c) linear; (d) very unfavorable; (e) rectangular isotherm (for desorption).

adsorption process, respectively, although, in the single-component system, the intraparticle effective diffusivity of diisopropanolamine in the elution cycle is almost the same as that in the adsorption cycle as mentioned earlier. The adsorption capacity of the amine does not change with repeat time. Any cracks did not appear within the resin particles. These results suggest that the paints and the solvents do not harm the resin, and the proposed method may be feasible technically for recovery of the amine and paints from the wastewater of electrodeposition painting process. Furthermore, distilled water or deionized water is used in the electrodeposition painting process. Such relatively expensive water is also recovered in the adsorption cycle, and it can be reused in the electrodeposition painting process. This may increase the economical feasibility of this method.

6. Conclusion

In order to develop a treatment method of the wastewater of the anodic electrodeposition painting process, the possibility of using an H-form strong acid ion exchanger for adsorption of the components in the wastewater and also the desorption method using aqueous NaOH solution have been investigated. The following conclusions were drawn.

1. The desorption method using aqueous NaOH solution appears feasible technically.
2. The experimental equilibrium isotherm for the amine and paints in wastewater-H-form resin complex + NaOH system was very unfavorable, and they were exchanged for Na^+ almost completely according to eq 2.
3. The experimental elution curves of the amine showed that the amine was desorbed well by using aqueous NaOH

solution. The elution curves of three paints showed sharp peaks. The time to elute each component completely was short and almost the same.

4. Experiments of adsorption, elution, and regeneration also have been repeated. The adsorption capacity of the amine did not change with repeat times. The intraparticle effective diffusivities of the amine and Na^+ in elution process were constant after the third cycle, and the intraparticle effective diffusivity of the amine in adsorption process was constant after the second cycle. The paints and solvents did not harm the resin.

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Nomenclature

- C = fluid-phase concentration, mol/dm³
 C^* = fluid-phase concentration at fluid-solid interface, mol/dm³
 C_0 = fluid-phase concentration at bed inlet (breakthrough curve) or initial concentration of fluid phase (equilibrium), mol/dm³
 D_{eff} = intraparticle effective diffusivity, m²/s
 $d_p = 0.5(d_{\text{PW}} + d_{\text{PH}})$, m
 d_{PA} = diameter of resin particle saturated by amine in the amine solution, m
 d_{PNa} = diameter of Na-form resin particle in NaOH solution, m
 d_{PW} = diameter of resin particle saturated by the components of wastewater of electrodeposition painting in the wastewater, m
 H = bed height, m
 K = equilibrium constant
 k_f = fluid-phase mass-transfer coefficient, 1/s
 k'_f = fluid-phase mass-transfer coefficient, m/s
 k_p = intraparticle mass-transfer coefficient, 1/s
 Q = exchange capacity of resin, mol/dm³ wet resin
 q = resin-phase concentration, mol/dm³ wet resin
 \bar{q} = resin-phase concentration averaged over an adsorbed particle, mol/dm³ wet resin
 q^* = resin-phase concentration at fluid-solid interface, mol/dm³ wet resin
 q_0 = resin-phase concentration in equilibrium with feed, mol/dm³ wet resin
 $Re' = d_p v \rho \epsilon / \mu (1 - \epsilon)$
 R = Langmuir coefficient (eq A-3)
 r_0 = radius of a resin particle ($=0.5d_p$), m
 t = time, s
 V = volume of solution, dm³
 v = interstitial fluid velocity, m/s
 W = volume of resin particles, dm³
 $X = C/C_0$
 $X^* = C^*/C_0$
 $Y = q/Q$
 $y = q/q_0$
 $\bar{y} = \bar{q}/q_0$
 $y^* = q^*/q_0$
 z = distance through bed, m

Greek Symbols

- β = Freundlich coefficient (eq A-4)
 δ = diffusion resistance parameter, $k_f C_0 / k_p q_0$
 ϵ = void fraction of bed
 ξ = bed length parameter, $(1 - \epsilon) k_f z / v$
 ρ = density, kg/dm³
 τ = time parameter, $C_0 k_f (t - z/v) / q_0$

Appendix

A differential mass balance, neglecting axial dispersion, gives the familiar fixed-bed equation:

$$\frac{\partial X}{\partial \xi} + \frac{\partial \bar{y}}{\partial \tau} = 0 \quad (\text{A-1})$$

for simplicity, the mass-transfer rate is represented by a linear driving force expression:

$$\frac{\partial y}{\partial \tau} = X - X^* = \frac{y^* - \bar{y}}{\delta} \quad (\text{A-2})$$

Figure 10 shows the equilibrium isotherms. We have presented the analytic solutions for eqs A-1 and A-2 for a rectangular isotherm in a single-component system [Yoshida et al. (1984) for adsorption (Table IV); Yoshida et al. (1989) for desorption (Table V)]. Yoshida et al. (1984) have also investigated the effect of the form of the equilibrium isotherms (Langmuir isotherm, eq A-3, and Freundlich isotherm, eq A-4, respectively) on the break-

$$y^* = \frac{X^*}{R + (1 - R)X^*} \quad (\text{A-3})$$

$$y^* = X^{*\beta} \quad (\text{A-4})$$

through curve, and have shown that when $R < 0.05$ and $\beta < 0.1$ (over the line b in Figure 10), the deviation from the analytic solutions for rectangular isotherm (Table IV) is negligibly small. Yoshida et al. (1989) have presented that the deviation from the analytic solution (Table V) may be negligible from the analytic solution (Table V) when the isotherm is under the line d in Figure 10.

Registry No. DIAION SK1B, 39346-62-8; $\text{NH}(\text{CH}_2\text{CH}(\text{OH})\text{CH}_3)_2$, 110-97-4.

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