Adsorption of Amine and Paints on H-Form Resin from Electrodeposition Wastewater

Wastewater of electrodeposition painting process contained diisopropanolamine, unknown three paints, and solvents (butylcellosolve and/or ethylcellosolve). The recovery of the amine and paints from the real wastewater by adsorption on an H-form strong acid ion exchanger appeared feasible technically and economically.

Equilibrium isotherms and breakthrough curves have been determined experimentally. The selectivity for the amine adsorption on the resin was fairly high. Solvents were not adsorbed on the resin. The components of the wastewater showed typical breakthrough curves for multicomponent system. Theoretical breakthrough curves and intraparticle effective diffusivities of the amine were determined from the analytic solution for rectangular isotherm in the single-component system. Experiments of adsorption, elution and regeneration also have been repeated. The amine and paints adsorbed on the resin were eluted completely by NaOH aqueous solution. The adsorption capacity of the amine did not change with repeat times, and the intraparticle effective diffusivity of the amine was constant after the second cycle.

Hiroyuki Yoshida
Kazuyuki Shimizu
Takeshi Kataoka
Department of Chemical Engineering
University of Osaka Prefecture
Sakai 591, Japan

Introduction

Organic amines are used commonly as the dispersing agents for water-soluble paints in the electrodeposition painting process, which is used widely to paint metal panels with complicated shapes, such as car bodies, 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 meeting environmental standards. Since no efficient treatment methods for such effluents have been developed, they have been treated by the activated sludge process, in which the amines and paints are expected to be destroyed by bacterial oxidation. The process is inefficient and does not recover amines and paints.

An H-form 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). It makes it possible to have an alternative process that has the advantages of amine recovery and higher removal efficiency.

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

$$R \cdot \mathrm{H} + R' - \mathrm{NH_2} \rightarrow R \cdot \mathrm{NH_3} - R' \qquad (1)$$

where $R' - \mathrm{NH_2}$ denotes the amine and $R \cdot \mathrm{NH_3} - R'$ is the amine-H-form resin complex. The amine is desorbed almost irreversibly by the following neutralization reaction:

$$R \cdot \mathrm{NH_3} - R' + \mathrm{NaOH} \rightarrow R \cdot \mathrm{Na} + R' - \mathrm{NH_2} + \mathrm{H_2O} \qquad (2)$$

and the resin is finally regenerated by acid:

$$R \cdot \mathrm{Na} + \mathrm{H}X \rightleftarrows R \cdot \mathrm{H} + \mathrm{Na}X \qquad (3)$$

In this paper, the above method was applied for the recovery of amine and paints from the wastewater of the electrodeposition painting process. The wastewater used contained diisopropanolamine, solvents, three paints, and Fe^{2+}. We measured the equilibria for adsorption of the amine on H-form strong acid ion

Correspondence concerning this paper should be addressed to H. Yoshida.

exchanger and show how coexistent components affect the adsorption isotherm of the amine. Experimental breakthrough curves for the adsorption of each component of the wastewater on the virgin H-form resin and for repeat experiments demonstrate that it is feasible for the proposed process to recover the amine and paints from the wastewater of the electrodeposition painting process.

Electrodeposition Painting Process

The electrolytic cell contains various paints, amines, and solvents that are dissolved in distilled water. Amines are used as a dispersing agent for water-soluble paints. A metal panel is set at 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 heavy paints can be recovered from the UF, the amine, light 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 the accumulation of the contents in the solution of the washing process, 10% of the solution is exchanged for distilled water. This is the wastewater of the electrodeposition painting process.

Table 1 shows their contents and concentrations in the three wastewaters. The wastewater contained diisopropanolamine, one or two solvents, three paints, and Fe^{2+}. Concentration of each component of the three wastewaters differed slightly. Concentration of diisopropanolamine was relatively high and it had to be removed. Concentration of Fe^{2+} was very low. The three paints are not identified here because they are proprietary information.

Physical Properties

Table 2 shows the experimental physical properties of the resin and the wastewater. The ion exchanger used is a strong acid gel type with sulfonic acid groups (H-form), because intraparticle effective diffusivities of the amine in gel-type resin were about five times greater than those in MR-type resin (Yoshida and Kataoka, 1987). d_{pH}, d_{pA}, and d_{pW} are the particle

Table 1. Real Wastewater of the Electrodeposition Painting Process

Byproduct	Component	Concentration
No. 1 (June, 1984)		
Amine	Diisopropanolamine	0.026 mol/dm^3
Solvent	Butylcellosolve(S1)	About 2 vol. %
Paints	Unknown: P1, P2, P3	Unknown
Others	Fe^{2+}	About 9×10^{-6} mol/dm^3
No. 2 (June, 1985)		
Amine	Diisopropanolamine	0.0293 mol/dm^3
Solvents	Butylcellosolve(S1) and ethylcellosolve(S2)	About 2 vol. %
Paints	Unknown: P1, P2, P3	Unknown
Others	Fe^{2+}	About 9×10^{-6} mol/dm^3
No. 3 (November, 1986)		
Amine	Diisopropanolamine	0.033 mol/dm^3
Solvents	Butylcellosolve(S1) and ethylcellosolve(S2)	About 2 vol. %
Paints	Unknown: P1, P2, P3	Unknown
Others	Fe^{2+}	About 9×10^{-6} mol/dm^3

Table 2. Basic Physical Properties (298 K)

Resin: DIAION SK1B	
Gel-type	
Sulfonated stylene-divinylvenzene	
Degree of crosslinking	8 wt. %
Exchange capacity (Q)	2.85 mol/dm^3 wet resin
Ratio of particle diameters	
d_{pW}/d_{pH}	1.006
d_{pA}/d_{pH}	0.9821
Wastewater	
Viscosity	9.56×10^{-4} kg·m^{-1}·s^{-1}
Liquid-phase diffusivity of diisopropanolamine	7.34×10^{-10} m^2·s^{-1}
Diisopropanolamine Aqueous Solution (C_o = 0.026 mol/dm^3)	
Viscosity	9.20×10^{-4} kg·m^{-1}·s^{-1}
Liquid-phase diffusivity of diisopropanolamine	7.20×10^{-10} m^2·s^{-1}

diameters of H-form resin in water, diisopropanolamine-form resin in 0.026 mol/dm^3 diisopropanolamine aqueous solution, and wastewater-form resin in the wastewater, respectively. They were determined by averaging the diameters of 50 particles. Particle diameters of the three different forms differed slightly. The components in the wastewater do not affect the viscosity significantly. The liquid-phase diffusivity of diisopropanolamine was estimated using Wilke–Chang's equation (1955) and the experimental viscosity listed in Table 2.

Experimental Studies

Equilibria were measured by the batch method. The H-form resin particles were brought into contact with the wastewater no. 1. To confirm the effects of the components in the wastewater on the equilibrium isotherm of the diisopropanolamine, we also measured the equilibria for adsorption of the amine from the aqueous solution of the amine (single-component system) and two model wastewaters that consist of (diisopropanolamine + butylcellosolve) and (diisopropanolamine + butylcellosolve + Fe^{2+}). Concentrations of those components were the same as the wastewater no. 1. The solution and the resin particles were well mixed. The equilibrium was fully reached in four days. The resin-phase concentration of the amine was calculated according to the following equation:

$$q^* = \frac{V(C_o - C^*)}{W} \tag{4}$$

The systems and conditions used in an experimental study for the breakthrough curve are shown in Table 3. Breakthrough curves (runs 1–6) 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 0.2, 0.4 and 0.8 m. The flow rates are shown in Table 3. The repeat experiments of adsorption, elution and regeneration were carried out by using wastewater no. 2. The first adsorption cycle was run 3 in Table 3. The molecules adsorbed were eluted by 0.5 mol/dm^3 NaOH aqueous solution (Eq. 2). Na-form resin particles were finally regenerated by 0.5 mol/dm^3 HCl aqueous solution (Eq. 3). The flow rates of the wastewater, NaOH solution and HCl solution were about $Re' = 3.6\sim3.9$, $0.95\sim1.0$, and $1.1\sim1.3$, respectively. The periods of time of adsorption,

Table 3. Experimental Conditions for Breakthrough Curve (Virgin H-Form Resin) and Model Parameters for Calculating Theoretical Breakthrough Curve for Rectangular Isotherm in Single-Component System*

Run	Solution	$C_{o,\text{amine}}$ mol/dm³	$q_{o,\text{amine}}$ mol/dm³	$q_{o,\text{amine}}/Q$	H m	Re'	$d_p \times 10^4$ m	δ	k_f 1/s	$k_p \times 10^4$ 1/s	$D_{\text{eff}} \times 10^{12}$ m²/s
1	W(No. 1)	0.026	2.27	0.80	0.2	1.99	8.69	9.13	0.207	2.6	3.27
2	W(No. 1)	0.026	2.16	0.76	0.8	4.36	8.69	11.1	0.267	2.9	3.65
3	W(No. 2)	0.0293	2.43	0.85	0.35	3.76	7.73	8.97	0.312	4.2	4.18
4	W(No. 2)	0.0293	2.38	0.84	0.36	3.79	7.73	8.20	0.313	4.7	4.68
5	W(No. 3)	0.033	2.60	0.91	0.79	4.1	7.73	21.5	0.321	1.9	1.89
6	S	0.025	2.85	1	0.2	8.74	8.53	1.09	0.322	28	35.2

*Yoshida et al. (1984)
H = bed length; W = real wastewater; S = single-component system of diisopropanolamine; $d_p = 0.5\,(d_{pW} + d_{pH})$

elution and regeneration processes were 185, 60 and 50 min, respectively.

Concentrations of the amine, paints and solvents were determined by gas chromatography with an FID detector (Schimadzu GC-7A). Since the names of the paints were unknown, we could not measure the absolute concentrations of the paints but determined the concentration ratio of the effluent and the influent of the column according to the following equation:

$$X_{Pi} = \frac{C_{Pi}}{C_{Pi,o}} = \frac{S_{Pi}}{S_{Pi,o}}$$

where $S_{Pi,o}$ and S_{Pi} denote the areas of chromatogram of paint Pi (i = 1, 2, 3) determined by the gas chromatography for the influent solution (real wastewater) and for the effluent solution, respectively.

All experiments were carried out at 298 K.

Results and Discussion

Equilibrium isotherm

Compared in Figure 1 are the equilibrium isotherms for adsorption of diisopropanolamine from the wastewater no. 1, the aqueous solution of diisopropanolamine, and two model wastewaters. In the case of the single-component system, the maximum amount of the amine adsorbed coincided with the exchange capacity of the resin. The solid line represents the theoretical line calculated from Eqs. 7 and 8 that are derived from applying the mass action law to Eqs. 5 and 6.

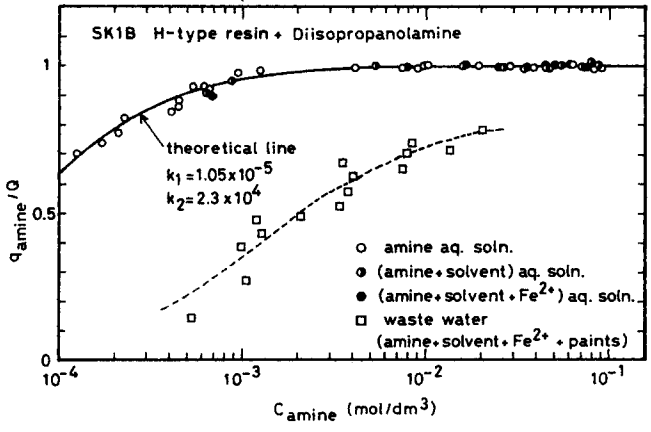

Figure 1. Equilibrium isotherms for adsorption of diisopropanolamine on H-form resin.

———, Eqs. 7 and 8, Q = 2.85 mol/dm³ wet resin; -----, Eq. 9, q_o = 2.38 mol/dm³ wet resin, R = 0.050

$$R' - NH_2 + H_2O \overset{K_1}{\rightleftharpoons} R' - NH_3^+ + OH^- \quad (5)$$

$$R \cdot H + R' - NH_2 \overset{K_2}{\rightleftharpoons} R \cdot NH_3 - R' \quad (6)$$

$$\frac{q}{Q - q} = K_2 a \quad (7)$$

$$a = C + 0.5\{K_1 - \sqrt{K_1(4C + K_1)}\} \quad (8)$$

where C denotes the total amine concentration in the liquid phase ($=[R' - NH_2] + [R' - NH_3^+]$) (mol/dm³). The value of K_1 was determined from independent experimental measurements of pH in the amine solution. Since the equilibrium isotherms for the model wastewaters coincide with the single-component system, we may conclude that the solvent and Fe^{2+} do not affect the adsorption of the amine from the real wastewater but the paints influence it. The dotted line shows the Langmuir isotherm calculated from Eq. 9 for the wastewater.

$$\frac{q}{q_o} = \frac{x}{R + (1 - R)x} \quad (9)$$

Although the selectivity for the amine adsorption in the wastewater is lower than the single-component system, the Langmuir coefficient is still small (R = 0.050). That is, the selectivity is relatively high even in the wastewater. In the case of the wastewater, the amount of the amine adsorbed, which is in equilibrium with C_o ($=$0.026 mol/dm³), q_o, is about 79% of the exchange capacity of the resin, Q. These results may suggest that the three paints are adsorbed on the H-form resin, and the maximum total amount of the paints adsorbed is about 20% of the exchange capacity of the resin.

Breakthrough curve (virgin H-form resin)

Figures 2–4 show typical experimental breakthrough curves for the adsorption of each component of the wastewaters of nos. 1–3 on virgin H-form resin particles. The amine is removed well by 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, especially in wastewater no. 2 (Figure 3), the amine and paint 3 have almost identical affinities

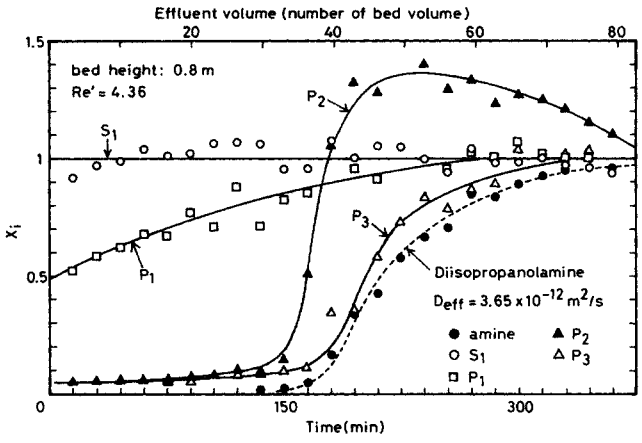

Figure 2. Breakthrough curves for adsorption of components in wastewater no. 1 on virgin H-form resin (run 2).

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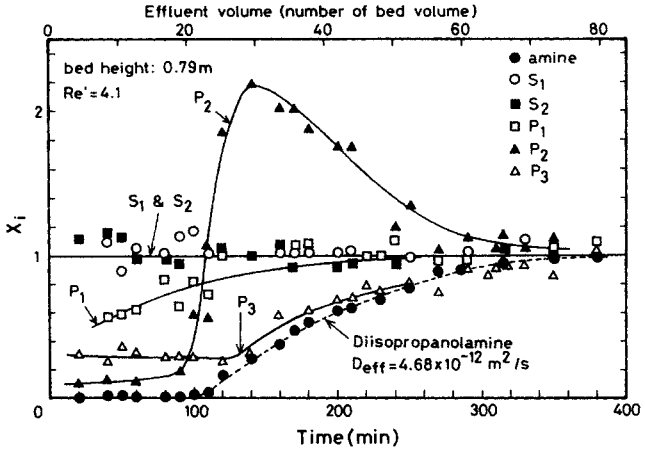

Figure 4. Breakthrough curves for adsorption of components in wastewater no. 3 on virgin H-form resin (run 5).

-------, theoretical line calculated from the analytical solution for rectangular isotherm in single component system

to the H-form ion-exchange resin and have almost the same intraparticle diffusivities. Because paint 2 has lower affinity than paint 3 and the amine, paint 2 shows chromatographic elution effect where the effluent concentration of paint 2 during column runs becomes significantly greater than its influent concentration. Paint 1 has the smallest intraparticle diffusivity or unfavorable equilibrium relation, because it breaks through quite early but does not show chromatographic elution effect. The effluent concentrations of the solvents [butylcellosolve ($S1$) and ethylcellosolve ($S2$)] do not change with time ($X_{S1} = 1$ and $X_{S2} = 1$). This means that the solvents are not adsorbed on H-form resin and flow through the bed. This can be understood from the equilibria shown in Figure 1. Since the concentration of Fe^{2+} was significantly lower than the other components, we did not measure the breakthrough curve of Fe^{2+}.

Many researchers have presented experimental and theoretical breakthrough curves for the multicomponent system (Helferich and Klein, 1970; Thomas and Lonbardi, 1971; Gariepy 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; Balzi 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). They have shown that the most weakly adsorbed species breaks through first with concentration rising above the feed concentration and that the most strongly adsorbed species breaks through last without chromatographic elution effect. These results support the above discussion on the experimental breakthrough curves.

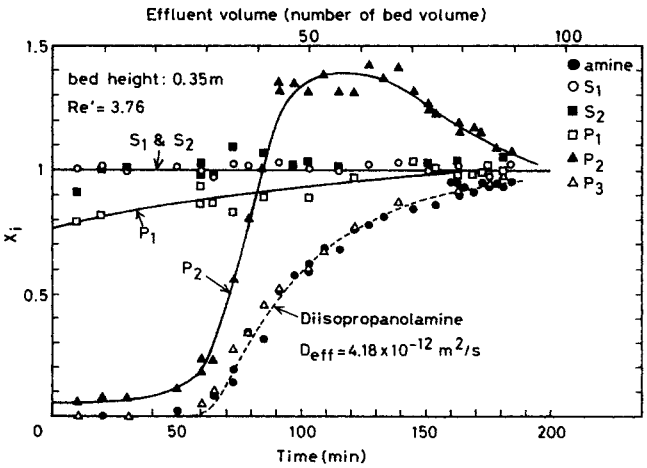

Figure 3. Breakthrough curves for adsorption of components in wastewater no. 2 on virgin H-form resin (run 3).

-------, theoretical line calculated from the analytical solution for rectangular isotherm in single component system

Since the names of the paints were unknown, we could not quantitatively determine the equilibrium isotherms for the paints and could not calculate the theoretical breakthrough curve for each component. Therefore, we tried to get the theoretical breakthrough curve only for the most strongly adsorbed species diisopropanolamine. As mentioned earlier, the experimental Langmuir coefficient R for diisopropanolamine in wastewater is 0.050. This value is small enough to approximate the equilibrium isotherm as rectangular when the breakthrough curve for the single-component system is calculated theoretically as discussed by Yoshida et al. (1984). However, it has not been proven yet that the assumption can be applied for the multicomponent system.

Figure 5 shows theoretical breakthrough curves for strongly adsorbed species (component 2) in the binary system calculated from Eqs. A1 to A10 in the Appendix. Solid and dotted lines show the breakthrough curves for β ($=k_{p1}/k_{p2}$) = 1 and 10, respectively. The value of k_p is given by $k_p = 15\ D_{eff}/r_o^2$. The difference between the breakthrough curves of strongly adsorbed species, $\beta = 1$ and 10, is minimal. Open circles show the theoretical breakthrough curve for strongly adsorbed species calculated from the analytical solution for rectangular isotherm in the single-component system, which was described by Yoshida et al. (1984). The basic equations of the analytic solutions are Eqs. A5 and A6, in which the mass transfer rate is controlled by the combined effects of external film and internal homogeneous diffusion (or surface diffusion). Yoshida et al. (1984) offer more

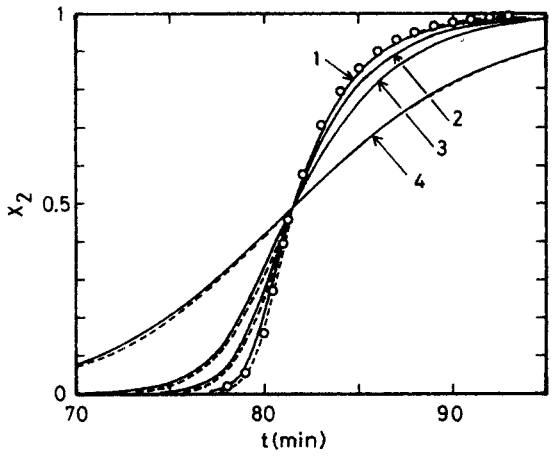

Figure 5. Theoretical breakthrough curve of strongly adsorbed species (component 2) in binary system.

$\delta_2 = 3$; $k_{f1} = k_{f2} = 0.732\ s^{-1}$; $C_{o1} = C_{o2} = 0.05$ mol/dm^3; $q_{o1}/q_{o2} = 1/30$; $q_{o2} = 2$ mol/dm^3
———, $\beta = k_{p1}/k_{p2} = 1$; ------, $\beta = 10$; O, theoretical values calculated from the analytical solution for rectangular isotherm in single-component system (Yoshida et al., 1984)
1. $\zeta_1 = 0.01, \zeta_2 = 0.99$; 2. $\zeta_1 = 0.1, \zeta_2 = 0.9$; 3. $\zeta_1 = 0.2, \zeta_2 = 0.8$; 4. $\zeta_1 = \zeta_2 = 0.5$

detailed information about the model. The values of the parameters used for the calculation of the analytical solutions are the same as those for the strongly adsorbed species in the binary system: $\delta = \delta_2$, $C_o = C_{o2}$, $q_o = q_{o2}$, $k_f = k_{f2}$, and $k_p = k_{p2}$. The smaller the value of ζ_1 and the larger the value of ζ_2, the steeper the breakthrough curve of the strongly adsorbed species and the closer to the analytical solution it becomes. When $\zeta_1 < 0.1$ and $\zeta_2 > 0.9$, that is, the equilibrium isotherm of component 2 is very favorable, the breakthrough curve of the strongly adsorbed species (component 2) agrees with the theoretical values calculated from the analytic solution for the single-component system with the rectangular isotherm system. This result may be useful. When the equilibrium isotherm of the strongly adsorbed species in the multicomponent system is very favorable ($R < 0.1$), the breakthrough curve can be estimated from the analytical solution for rectangular isotherm in the single-component system (Yoshida et al., 1984) without any complicated calculations for multicomponent system.

The dotted lines in Figures 2–4 show the theoretical breakthrough curve of diisopropanolamine (the very strongly adsorbed species, $R = 0.05$) calculated from the analytical solution for rectangular isotherm in the single-component system (Yoshida et al., 1984). Intraparticle effective diffusivity values [D_{eff} (m^2/s)] were determined by matching the data with the analytical solution. First of all, the external mass transfer coefficient k_f (s^{-1}) was estimated from the following correlation (Kataoka et al., 1972):

$$\left(\frac{1-\epsilon}{\epsilon}\right)^{1/3} \frac{k_f' Sc^{2/3}}{v} = 1.85\, Re'^{-2/3} \qquad (10)$$

$$k_f = 6k_f'/d_p$$

The liquid-phase diffusivity of the amine listed in Table 2 was used for the calculation of Eq. 10. 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. It is evident from Figures 2–4 that in general the theoretical curves give a good prediction of the experimentally obtained behavior of the amine. The value of k_p was calculated from that of δ obtained by matching. The intraparticle effective diffusivity value was obtained from $k_p = 15\, D_{eff}/r_o^2$.

The model parameters determined by the above procedure are summarized in Table 3. The intraparticle effective diffusivities of diisopropanolamine for the wastewater are 10–20 times smaller than those for the single-component system of the amine (run 6), perhaps because the diisopropanolamine combines with paint 3 in the wastewater to become a larger molecule. The intraparticle effective diffusivities of wastewaters of nos. 1–3 differ slightly due possibly to the difference in concentrations of the three paints from each wastewater. The value of $q_{o,amine}$ (mol/dm^3 wet resin), which is the adsorbed capacity of the amine in equilibrium with the concentration of the amine in the wastewater, was determined by integrating the breakthrough curve. $q_{o,amine}$ increases with influent concentration of the amine. In the case of wastewater no. 1 (runs 1 and 2), the ratio of $q_{o,amine}$ and the exchange capacity of the resin Q (mol/dm^3 wet resin) are almost the same as that determined from the experimental equilibrium isotherm for the wastewater (Figure 1).

Effect of repeat times

To test the possibility of using this method to cyclic operation, repeat experiments were carried out. The first adsorption cycle was run 3 in Table 3. The amine and paints were completely eluted by the aqueous solution of 0.5 mol/dm^3 NaOH. The details of the experimental elution curves for the amine and three paints will be reported in the subsequent paper. The resin particles, which became Na form during the elution process, were regenerated to H form by the aqueous solution of 0.5 mol/dm^3 HCl. Figure 6 shows the experimental breakthrough curves for the fifth adsorption cycle. These breakthrough curves are similar to those for the first cycle (Figure 3). The dotted line shows the theoretical breakthrough curve calculated from the analytical solution (Yoshida et al., 1984). Figure 7 shows the

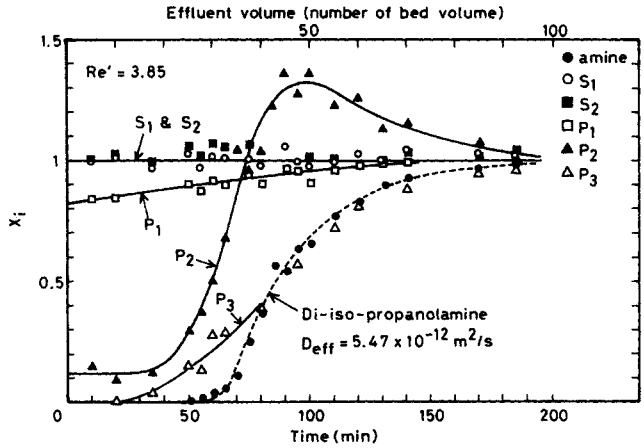

Figure 6. Breakthrough curves for fifth adsorption cycle in repeat experiment using wastewater no. 2.

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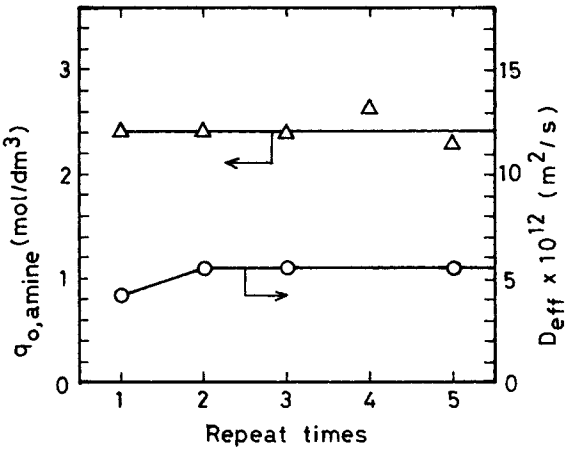

Figure 7. Effect of repeat time on adsorption capacity and intraparticle effective diffusivity of diisopropanolamine.

experimental adsorption capacity and intraparticle effective diffusivity of the amine with repeat time. The adsorption capacity of the amine does not change with repeat time, and the intraparticle effective diffusivity is constant after second cycle. 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 and economically for the recovery of amine and paints from the wastewater of the electrodeposition painting process.

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Notation

a = constant in Langmuir isotherm, dm^3/mol
b = constant in Langmuir isotherm, dm^3/mol
C = fluid-phase concentration, mol/dm^3
C^* = fluid-phase concentration in equilibrium with resin phase, mol/dm^3
C_o = fluid-phase concentration at bed inlet (breakthrough curve) or initial concentration of fluid phase (equilibrium), mol/dm^3
D_{eff} = intraparticle effective diffusivity, m^2/s
d_p = $0.5(d_{pW} + d_{pH})$, m
d_{pA} = diameter of a resin particle saturated by amine in the amine solution, m
d_{pH} = diameter of an H-form resin particle in water, m
d_{pW} = diameter of a resin particle saturates by the wastewater components of electrodeposition painting in the wastewater, m
K_1 = equilibrium constant of Eq. 5, mol/dm^3
K_2 = equilibrium constant of Eq. 6, dm^3/mol
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/dm^3 wet resin
$\bar{q}$ = resin-phase concentration averaged over a resin particle, mol/dm^3 wet resin
q^* = resin-phase concentration at fluid–solid interface, mol/dm^3 wet resin
q_o = resin-phase concentration in equilibrium with feed, mol/dm^3 wet resin
R = Langmuir coefficient (Eq. 9)
Re' = $d_p v\rho\epsilon/\mu(1-\epsilon)$
r_o = radius of a resin particle, m
t = time, s
V = volume of solution, dm^3
v = interstitial fluid velocity, m/s
W = weight of resin particles, kg
x = C/C_o
x^* = C^*/C_o
$\bar{y}$ = $\bar{q}/q_o$
z = distance through bed, m

Greek letters

α = ratio of fluid-phase mass transfer coefficients, k_{f1}/k_{f2}
β = ratio of intraparticle mass transfer coefficients, k_{p1}/k_{p2}
γ = $(C_{o2}/q_{o2})/(C_{o1}/q_{o1})$
δ = diffusion resistance parameter in single-component system, $k_f C_o/k_p q_o$
δ_2 = diffusion resistance parameter in binary system, $k_{f2}C_{o2}/k_{p2}q_{o2}$
ϵ = void fraction of bed
ζ_i = dimensionless equilibrium constant in Langmuir isotherm, $(1 + b_i C_{oi})/(1 + b_1 C_{o1} + b_2 C_{o2})$
ξ = bed length parameter, $(1-\epsilon)k_f z/\epsilon v$ for single-component system and $(1-\epsilon)k_{f2} z/\epsilon v$ for binary system
ρ = density, kg/dm^3
τ = time parameter, $C_o k_f (t - z/v)/q_o$ for single-component system and $C_{o2}k_{f2}(t - z/v)/q_{o2}$ for binary system

Subscripts

1 = less strongly adsorbed species
2 = strongly adsorbed species

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Appendix

A differential mass balance for a point in the column, neglecting axial dispersion, gives the familiar fixed-bed equation:

$$v\frac{\partial C_i}{\partial z}+\frac{\partial C_i}{\partial t}+\left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial \bar{q}_i}{\partial t}=0 \qquad (i=1,2) \qquad \text{(A1)}$$

For simplicity, mass transfer rate is represented by a linear driving force expression:

$$\frac{\partial \bar{q}_i}{\partial t}=k_{fi}(C_i-C_i^*)=k_{pi}(q_i^*-\bar{q}_i) \qquad \text{(A2)}$$

Miura et al. (1979) have shown that this approximation gives sufficient accuracy for surface diffusion kinetics and homogeneous diffusion in the binary system.

Expressed in dimensionless form, Eqs. A1 and A2 become:

$$\frac{\partial x_1}{\partial \xi}+\gamma\frac{\partial \bar{y}_1}{\partial \tau}=0 \qquad \text{(A3)}$$

$$\frac{\partial \bar{y}_1}{\partial \tau}=\frac{\alpha}{\gamma}(x_1-x_1^*)=\frac{\beta}{\delta_2}(y_1^*-\bar{y}_1) \qquad \text{(A4)}$$

$$\frac{\partial X_2}{\partial \xi}+\frac{\partial \bar{y}_2}{\partial \tau}=0 \qquad \text{(A5)}$$

$$\frac{\partial \bar{y}_2}{\partial \tau}=x_2-x_2^*=\frac{y_2^*-\bar{y}_2}{\delta_2} \qquad \text{(A6)}$$

where $\delta_2=k_{f2}C_{o2}/k_{p2}q_{o2}$, which shows the ratio of external and intraparticle mass transfer resistance of component 2, $\tau=C_{o2}k_{f2}(t-z/v)/q_{o2}$, $\xi=(1-\epsilon)k_{f2}z/\epsilon v$, $\alpha=k_{f1}/k_{f2}$, $\beta=k_{p1}/k_{p2}$, and $\gamma=(C_{o2}/q_{o2})/(C_{o1}/q_{o1})$. When the equilibrium is expressed by Langmuir form:

$$q_i^*=\frac{a_iC_i^*}{1+b_1C_1^*+b_2C_2^*} \qquad \text{(A7)}$$

$$y_1^*=\frac{x_1^*}{\zeta_1+\zeta_2-1+(1-\zeta_2)x_1^*+(1-\zeta_1)x_2^*} \qquad \text{(A8)}$$

where $\zeta_i=(1+b_iC_{oi})/(1+b_1C_{o1}+b_2C_{o2})$.

We considered an initially clean bed subjected at time zero to a step increase of the sorbate concentration at the bed inlet. Initial and boundary conditions are:

$$IC: \quad \bar{y}_i=0, \quad \text{at} \quad \tau=0 \qquad \text{(A9)}$$

$$BC: \quad x_i=1, \quad \text{at} \quad \xi=0 \qquad \text{(A10)}$$

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