Foamy Complex Formation for Removing and Recovering of Heavy Metal Ions in Dilute Solutions with *N*-Monodecanoyl Diethylenetriamine

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In order to highly selectively remove and recover heavy metals, usually harmful, from wastewater, a modified foam-separating method using a fatty compound, *i.e.* *N*-monodecanoyl diethylenetriamine, was investigated on real and model wastewater, containing several kinds of metals. This agent forms soluble and foamy complexes with the metals.

As methods for removing harmful heavy metals from wastewater, precipitation, floatation after deposition, absorption, extraction, *etc.* have been employed. However, these methods are accompanied by difficult problems, especially, in the case where a small amount of heavy metals is dissolved in a large quantity of wastewater.[1] Therefore, in order to solve these problems, the authors proposed an effective method[2] based on the foam-separating principle.[3]

Generally, such compounds as fatty acid amidoamines which contain amino- or imino-groups in the molecule react with heavy metal salts and produce organic complexes.[4] The authors have found that, if a fatty acid amino-amine having a suitable structure is added to an aqueous solution of heavy metal salts, even in a very dilute solution, the amido-amine reacts instantly with the metal ions and produces complexes which are considerably water-soluble, very foamy and very absorbable in bubbles.[2,5] Also, the authors have successfully applied this to the removal and recovery of harmful heavy metals from wastewater.[2] In the present paper, the results for an effective typical amido-amine type agent, *N*-monodecanoyl diethylenetriamine hydrochloride, are reported.

Experimental

N-Monodecanoyl diethylenetriamine hydrochloride (C_{10}-ODT) was prepared by the direct aminolysis of methyl decanoate with diethylenetriamine and neutralization with hydrochloride.

After C_{10}ODT was added to the aqueous solution containing heavy metal ions, the pH of the solution was adjusted. Then, the foam treatment was carried out by bubbling air, passed through a water-washing bottle, into the solution at a constant flow rate (200—250 ml/min) until foaming almost ceased.

The batch foaming column consisted of a glass tube (28 mm i.d., 500 mm long) with a glass filter (2G, 20 mm i.d.) fixed in a rubber stopper at the bottom of tube. Into this column, 50 ml of the solution for foam treatment was poured. The foam which ran over the top of the column was recovered and the amount of metal ions in the residual water was analysed after the treatment.

The continuous multistage foam treatment was carried out using a trial apparatus (Fig. 1). After the treatment, the amount of metal ions in the residual water was analyzed.

Solutions containing 10 ppm of single metal ions were prepared with sulfates, chlorides or acetates of copper, lead, zinc and iron.

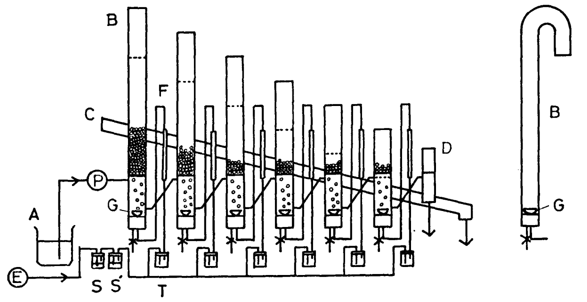

Fig. 1. The trial apparatus for the multistage foam treatment.

C_{10}ODT was added into the wastewater and the pH of the solution was adjusted. This solution was sent by the fluid pump P from the beaker A to the first foaming column B. Every column also consists of glass tube (ϕ 32, L 360—220 mm) with a glass filter G fixed in the rubber stopper at the bottom of tube, and the top of the column is bent in a shape of a half circle and is connected to the foam assembling pipe C. The six foaming columns are all connected in series and the last column is connected to the fluid level meter D. Air is blown into B at the flow rate of about 300 ml/min through the blower E, the humidity chamber S, S′, the trap T, the flow meter F and G. The water is sent at the flow rate of 23—25 ml/min.

Solutions containing mixtures of 10 ppm of each metal ion were prepared with copper sulfate, lead nitrate, zinc sulfate, and calcium sulfate or with copper sulfate, zinc sulfate, lead nitrate, cadmium chloride, cobalt sulfate, and manganese sulfate.

For application to real wastewater, several kinds of wastewater were sampled at non-ferrous metal mines, an electroplating factory, a spinning factory and an antiseptic factory.

The amounts of heavy metals in the solutions were analyzed for hydrochloric acidity with an atomic absorption spectrophotometer (Shimadzu-AA600).

Results

The result of the elementary analysis of C_{10}ODT is as follows. Found: C, 51.00; H, 9.94; N, 12.44%. Calcd for $C_{14}H_{33}N_3OCl_2$: C, 51.00; H, 10.33; N, 12.60%.[5]

Foaming Ability of the Solution Containing a C_{10}ODT–Metal Complex. An aqueous solution of C_{10}ODT has little foaming ability, but when C_{10}ODT is added to a dilute aqueous solution containing heavy metal ions, the foaming ability of the solution greatly increases due to the rapid formation of water-soluble and foaming C_{10}ODT–metal complex over a suitable pH range (Fig.

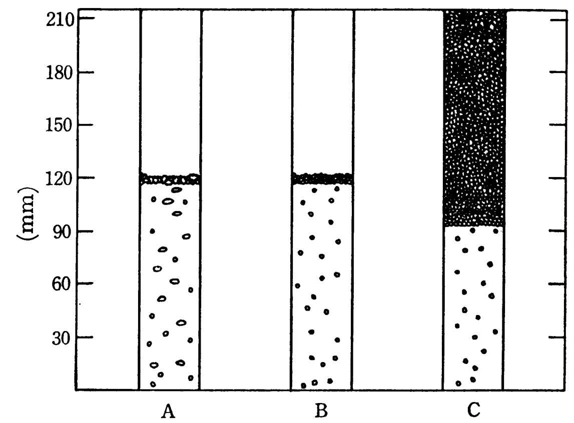

Fig. 2. The foaming ability of the solution of C_{10}ODT–metal complex.
A: Air was blown at the flow rate of 250 ml/min into the aqueous solution of ferrous sulfate at pH 7.
B: Air was blown into the aqueous solution of C_{10}-ODT on the same conditions as A.
C: After C_{10}ODT was added to the aqueous solution of ferrous sulfate at the addition ratio of 2 mol of C_{10}ODT/ gram-atom of iron, air was blown into this solution on the same conditions as A.

2). The foaming ability of the C_{10}ODT–metal complex differs according to the kind of heavy metal, with the C_{10}ODT–copper complex having a particularly high foaming ability.

The effect of the addition of C_{10}ODT to an aqueous solution containing an amount of ferrous sulfate equivalent to 10 ppm of iron is shown in Fig. 2. C_{10}ODT and ferrous sulfate solutions have little foaming ability separately, but a solution of the C_{10}ODT–iron complex has a great foaming ability.

Foam Treatment of Prepared Solution. As an example of batch foam treatment of solutions containing a single kind of metal ion with C_{10}ODT, the case of a solution containing copper ions is shown in Fig. 3.$^{5)}$

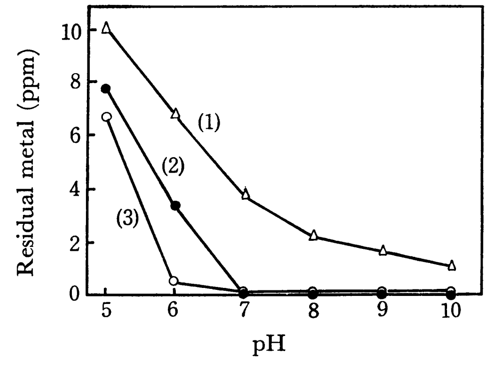

Fig. 3. The result of the batch foam treatment of the aqueous solution of copper sulfate equivalent to 10 ppm of copper with C_{10}ODT.
(1): 1/1; (2): 2/1; (3): 3/1 (C_{10}ODT/Cu).

For the foam treatments of aqueous solutions of copper sulfate, copper chloride, and copper acetate, there was no significant difference between the removing and recovering effects of copper ions. In each case, with a proportional addition of 2 mol of C_{10}ODT/gram-atom of copper, the residual copper after foam treatment at pH 7—10 was 0.05—0.4 ppm.

In the case of zinc, at a proportional addition ratio of more than 2 mol of C_{10}ODT/gram-atom of zinc, the residual zinc after foam treatment at pH 9—10 was less than 1 ppm (Fig. 4).

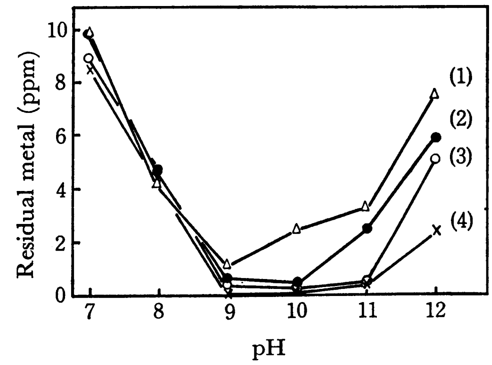

Fig. 4. The result of the batch foam treatment of the aqueous solution of zinc sulfate equivalent to 10 ppm of zinc with C_{10}ODT.
(1): 1/1; (2): 2/1; (3): 3/1; (4): 4/1 (C_{10}ODT/Zn).

As is shown in the above instances, it is seen that the optimum pH value for foam treatment with C_{10}ODT is considerably different for each heavy metal.

In the case of an equimolar mixed solution of several kinds of heavy metal ions, the metal ion content in the residual water after foam treatment differed for each metal (Figs. 5—7).

The results of Figs.5—7suggest that, if the proportional addition of C_{10}ODT to metal ions is selected properly, the specific metal may be removed and recovered over a definite pH range. Thus, by utilizing such properties of C_{10}ODT, the specific metal ion can be removed and recovered selectively (Fig. 8). Thus,

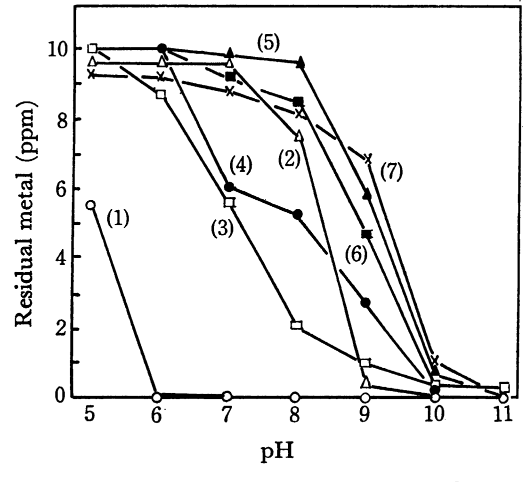

Fig. 5. The result of the foam treatment of the mixed aqueous solution of heavy metal ions.
After C_{10}ODT was added to the solution at the addition ratio of 0.5 mol of C_{10}ODT/ gram-atom of each metal, the pH of the solution was adjusted and the foam treatment was carried.
(1): Cu; (2): Zn; (3): Pb; (4); Ni; (5): Cd; (6): Co; (7): Mn.

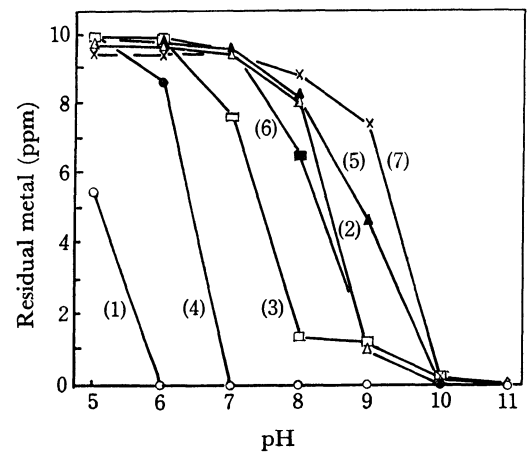

Fig. 6. The result of the foam treatment of the mixed aqueous solution of heavy metal ions.
The similar treatment, at the addition ratio of 1 mol of C_{10}ODT/ gram-atom of each metal, was carried.
(1): Cu; (2): Zn; (3): Pb; (4): Ni; (5): Cd; (6): Co; (7): Mn.

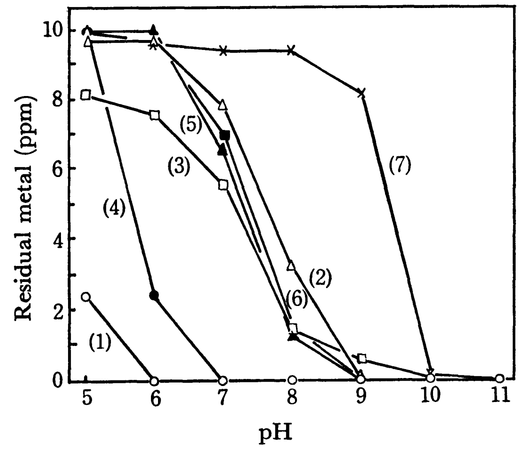

Fig. 7. The result of the foam treatment of the mixed aqueous solution of heavy metal ions.
The similar treatment, at the addition ratio of 2 mol of C_{10}ODT/ gram-atom of each metal, was carried.
(1): Cu; (2): Zn; (3): Pb; (4): Ni; (5): Cd; (6): Co; (7): Mn.

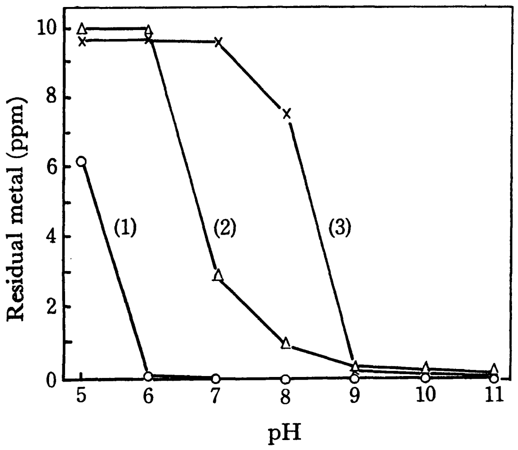

Fig. 8. The selective foam treatment of the mixed aqueous solution of heavy metal ions.
(1): Cu; (2): Pb; (3): Zn.

after 200 ppm of C_{10}ODT was added to a mixed solution of copper sulfate, lead nitrate, and zinc sulfate which was equivalent to a mixture of 10 ppm of each metal ion, batch foam treatment was carried at various pH values of the solution. Consequently, at first, nearly 100% of the copper ions at pH 6, next, about 70% of the lead ions at pH 7 and finally, about 98% of the zinc ions at pH 9 were selectively removed and recovered. However, for a foam treatment beginning at pH 9 resulted in the simultaneous recovery of more than 96% of all heavy metal ions. Calcium sulfate (equivalent to 200 ppm of calcium) did not influence these results.

Foam Treatment of Real Wastewater. Batch foam treatment was carried out on wastewater from a mine A (Table 1), after the addition of C_{10}ODT to the water at ratios of 0.5, 1.0 or 2.0 mol/gram-atom of zinc and copper with the pH of the solution adjusted. The result is shown in Table 1. 100% of the copper and zinc were removed and recovered by the foam treatment at pH 9 for a proportional addition of 1—2 mol of C_{10}ODT/gram-atom of copper and zinc.

TABLE 1. BATCH FOAM TREATMENT OF A SAMPLE FROM A NON-FERROUS METAL MINE A

Sample	pH	Addition ratio (C_{10}ODT/ Metal)	(ppm)		
			Zinc	Copper	Iron
A	2.9	—	30.78	8.84	5.60
Treated A	9.0[a)]	1/1	0.15	0.00	0.00
		2/1	0.00	0.00	0.00

a) pH directly before foam treatment.

The batch foam treatment was carried on wastewater from a mine B (Table 2) for a proportional addition of 0.1 mol of C_{10}ODT/gram-atom of zinc and the results are shown in Table 2. All heavy metals were completely removed and recovered within limited values, and moreover, no reduction of the efficiency of the treatment by the coexisting abundant calcium ions was observed.

TABLE 2. BATCH FOAM TREATMENT OF SAMPLES FROM A NON-FERROUS METAL MINE B

Sample	pH	(ppm)					
		Zinc	Cadmium	Copper	Lead	Iron	Calcium
B	2.3	679.39	4.02	0.18	1.29	111.69	250.0
Treated B	8.0[a)]	6.64	0.17	0.00	0.00	0.00	
	9.0[a)]	1.46	0.07	0.00	0.00	0.00	
	10.0[a)]	8.54	0.07	0.00	0.00	0.00	

Addition Ratio (C_{10}ODT/Zinc)=0.1/1.
a) pH directly before foam treatment.

After C_{10}ODT was added to the wastewater from a mine C (Table 3) for a proportional addition of 1 mol of C_{10}ODT/gram-atom of each metal, the foam treatment was carried at pH 6. As shown in Table 3, about 99% of the copper was removed and recovered selectively. The cadmium and zinc in the residual water were removed and recovered within limited values by

Table 3. Batch foam treatment of samples from a non-ferrous metal mine C

Sample	pH	(ppm) Copper	Zinc	Cadmium	Iron
C	6.2	9.5	68.5	3.2	0.9
1 (Treated C)	6.0[a]	0.1	63.6	3.2	0.2
Treated 1	9.0[a]	0.1	0.5	0.1	0.1

Addition Ratio (C_{10}ODT/Each Metal) = 1/1.
a) pH directly before foam treatment.

the form treatment of the residual water at pH 9 (Table 3).

After C_{10}ODT was added to the wastewater of an electroplating factory E (Table 4) for a proportional addition of 1 or 1.5 mol of C_{10}ODT/gram-atom of each metal, the pH of the solution was adjusted and continuous multistage foam treatment was carried out. A better removal and recovery yield of the metal ions was obtained when 1.5 mol of C_{10}ODT was added (Fig. 9). When the foam treatment was applied at pH 6, 99.5% of the copper was removed and recovered selectively, but 90.1% of the zinc and 100% of the nickel remained in the residual water. When the foam treatment was carried out initially at pH 9, the copper, zinc and nickel were removed and recovered simultaneously with a yields of 100, 93.6, and 93.7%, respectively.

Table 4. Analysis of wastewater from an electroplating factory E and a spinning factory S

Sample	pH	(ppm) Copper	Zinc	Nickel	Calcium
E	1.9	50.46	24.88	3.15	—
S	1.9	—	128.7	—	1.1

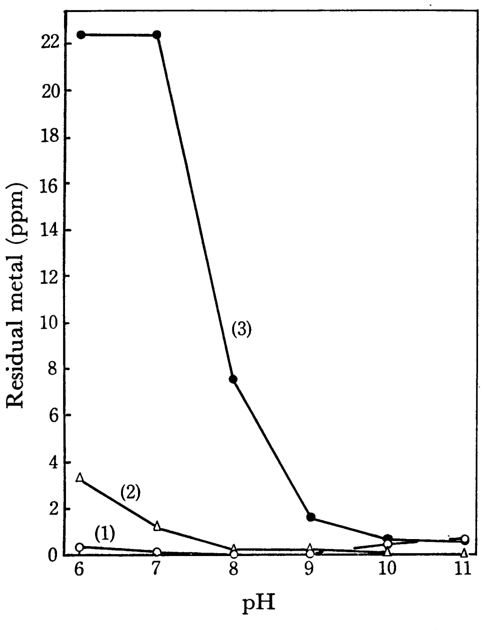

Fig. 9. The result of the continuous multistage foam treatment of the wastewater of an electroplating factory.
(1): Cu; (2): Ni; (3): Zn.

When C_{10}ODT was added to the wastewater from a spinning factory S (Table 4) for a proportional addition of 0.5 mol of C_{10}ODT/gram-atom of zinc and continuous multistage foam treatment was applied at pH 10, 99.7% of the zinc ions were removed and recovered.

Of course, by bubbling air into the real wastewater and the model solution, both without C_{10}ODT, almost no foam was produced, and consequently, none of the metal dissolved in the water could be removed and recovered.

Discussion

For the foam treatment of aqueous solutions containing heavy metal ions, the optimum pH for good foaming varies with the metal. This may be due to the differences of the conditional stability constant[6] of the C_{10}ODT–metal complex.

Also, when the C_{10}ODT addition ratio was varied, even when good foaming was observed upon the application of the foam treatment, in some cases the residual metal concentration varies considerably. For instance, for the foam treatment of copper sulfate (Fig. 3), at pH values above about 6.5, good foaming was observed. But in this foam treatment for a proportional addition ratio of 1 mol of C_{10}ODT/gram-atom of copper, the removal and recovery yield of the copper was lower in comparison with other cases. Such differences due to the variation of the C_{10}ODT ratio were similarly observed in cases involving other heavy metals and were thought to be due to the structural differences of the complexes.

When a tridentate ligand co-ordinates over a suitable pH range to a copper ion having a co-ordination number of four, one of two types of complexes, *i.e.*, a 1: 1 hydroxo chelate (A) or a 2: 1 chelate (B), is obtained[7] and one of the copper co-ordination bonds in the former complex A co-ordinates with the water.[7] Thus, C_{10}ODT, a tridentate ligand, may co-ordinate with copper ions similarly in the above-mentioned case. The authors have previously determined that when C_{10}ODT was added exessively to a solution containing copper ions, a 2: 1 chelate was produced.[5] The difference in the structures of the complexes which are formed by adding 1 or 2 mol of C_{10}ODT per gram-atom of copper may be inferred by the fact that the colors of the solutions in these two cases are considerably different from each other, that is, the color in the former case is blue and that of the latter is purple. However, concerning the structures of the complexes, no further investigation was attempted.

As mentioned above, in the case of a small amount of harmful heavy metals dissolved in a large quantity of wastewater, by applying the usual methods, especially, the precipitation method, it is not easy to remove effectively the metals. But, by the present simple method utilizing complex formation of the amidoamines, the problem can be solved.

If necessary, from the complexes recovered by this method, almost all the amido-amine can be easily regenerated by electrolysis.[8]

The structure of the ligand of a metal complex has influence on not only the solubility,[7] but also the effect of the foam treatment. The authors found that among the acyl groups of C_8–C_{12} involved in these water-soluble metal complexes, the decanoyl group acted as the most desirable hydrophobic group for the foam treatment.[9]

It is interesting that for wastewater containing a high concentration of heavy metal ions, even with a small amount of C_{10}ODT, the foam treatment can be applied (Table 2). The reason for this may be that the complexes formed by the co-ordination of the metal ions with C_{10}ODT are also water-soluble and foamy, and the foam absorbs not only the dissolved complexes but also the deposited particles consisting of the hydroxides of the heavy metals and the complexes which have formed beyond their solubilities.

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