Adsorbing-Particle Flotation of Hg^{2+} by Combined Use of Charcoal, Polyacrylamide, and Cationic Surfactant

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Adsorbing-particle flotation of Hg^{2+} ions by using active charcoal as an adsorbent, Polyacrylamide (PAA) as a coagulant, and hexadecyltrimethylammonium chloride (HTAC) as a frother was carried out. The floatability exceeded 90% in a wide range of pH and nearly 98% of Hg^{2+} ions was floated from 2.1×10^{-4} mol dm^{-3} solution by adding 2500 ppm of active charcoal, 24 ppm of PAA, 81 ppm of HTAC and with shaking. Stepwise and double flotations were further attempted which proved to distinctly increase the floatability, while sodium sulfide treatment of active charcoal showed only a slight increase and the coexistence of chloride ions showed no effect. The mechanism of adsorbing-particle flotation was discussed.

The adsorbing-particle or colloid flotation has been known as one of the effective methods to remove or concentrate dissolved ions in solution, because it enables the flotation of various organic and inorganic ions and molecules by selecting suitable adsorbent, coagulant, and surfactant as a collector and/or a frother. With regard to the practical application of such a technique, Grieves[1] published a general review in which we confirm that adsorbents mainly used are oxides, hydroxides or sulfides of Fe^{3+}, Al^{3+}, Cd^{2+}, Hg^{2+}, Mn^{4+}, and Th^{4+}. However, one of the present authors has drawn attention to different group of ion adsorbents of particulate or powder type, such as bentonite,[2,3] charcoal,[4] and poly(ethyleneimine),[5] confirming that these effectively remove inorganic and organic anions and cations. Among them charcoal is particularly promising since it can be used widely as an adsorbent. But published reports are rather scanty although the possibility of its application has been suggested.[6]

In the present study, removal of Hg^{2+} ions was attempted by using charcoal as an adsorbent, Polyacrylamide as a coagulant, and hexadecyltrimethylammonium chloride (HTAC) as a surfactant. The stepwise and double flotations were worked out to improve the flotation efficiency.

Experimental

Materials. Active charcoal mainly used as an adsorbent was the product of Wako Pure Chemicals, labelled "Chemical Activated." Some other charcoals of different origin were used for comparison. Polyacrylamides mainly used as coagulants were the products of Mitsubishi Chemical Industries, DCLE MA-3000L (DL), DCLE MA-3000H (DH), and DCLE MA-3000-3H (D3H), molecular weight being about 10^7 and the content of sodium polyacrylate 10, 20, and 30% respectively. Other coagulants used were the products of Toagosei Chemical Industries, sodium polyacrylate (AR) of molecular weight of $2—6\times10^6$ and PAA derivatives of Sanyokasei Industries, anionic Sanfloc AH (SA), nonionic Sanfloc N (SN), and cationic Sanfloc CH (SC) of molecular weight of 1.7×10^7 for the former two and 7×10^6 for the latter. Surfactants used were the commercial products of cationic HTAC and anionic sodium dodecyl sulfate (SDS).

Measurement. To carry out the flotation measurement, 20 cm^3 of an aqueous solution of nitric acid containing 2.1×10^{-4} mol dm^{-3} Hg^{2+} ions, 2500 ppm charcoal of different origins, coagulant and surfactant in different amounts, and NaOH for controlling the pH, was introduced into a stoppered test tube of 1.6 cm in inner diameter and 29 cm in length, equipped with a stopcock at the bottom. The test tube was gently turned upside down repeatedly for 2 min and then vigorously shaken ten times by hand to complete the flotation.

Concentration of Hg^{2+} ions in the underlying solution was determined by Hitachi Atomic Absorption Spectrometer 508 at wavelength of 248.3 nm. The floatability F (%) was calculated by the following equation:

$$F = \frac{C_0 - C}{C_0} \times Fc \times 100\%, \qquad (1)$$

where C_0 and C express concentrations of solution before and after the flotation respectively, and Fc fraction of active charcoal floated.

The stepwise flotation was worked out similarly to the previous study[2] to improve the flotation efficiency. In this technique, charcoal was added to the solution at a time but coagulant and surfactant were added in two steps. After the first addition of coagulant and surfactant, flotation was carried out and the suspension below the scum was transferred to another test tube, into which remaining portions of coagulant and surfactant were added and the second flotation was conducted. From the concentration of Hg^{2+} and the amount of active charcoal in the solution after the second flotation, floatability of Hg^{2+} was calculated. A similar stepwise flotation but without transferring the solution to another test tube was carried out to simplify the operation. This procedure is called the double flotation to distinguish it from the stepwise flotation.

All the measurements were done at room temperature.

Results and Discussion

According to the preliminary measurements and the former study,[4] concentrations of coagulant and surfactant favorable for charcoal flotation were pre-

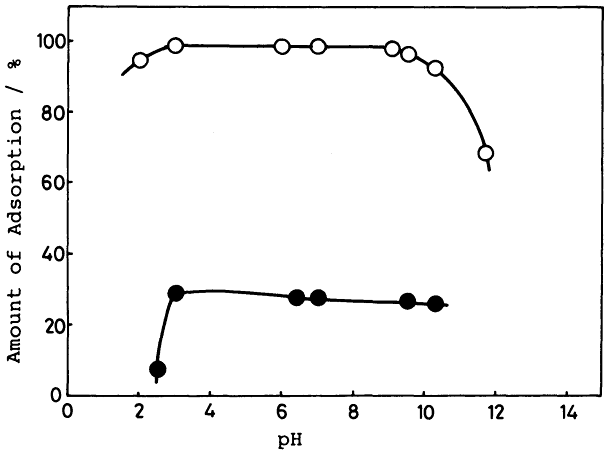

Fig. 1. Adsorption of Hg^{2+} by charcoal. Hg^{2+}: 2.1×10^{-4} mol dm^{-3}. Charcoal ○: 2500 ppm, ●: 400 ppm.

sumed to be in the ranges of 20 to 200 ppm and 50 to 500 ppm, respectively, for 2500 ppm of charcoal. The optimum concentration range varies with the adsorbent to be used and ions to be floated.[2–5]

Adsorption of Hg^{2+} Ions by Charcoal. In order to confirm the proper amount of active charcoal required for the Hg^{2+}-ion flotation, adsorption of Hg^{2+} ions by active charcoal was measured for the solution containing various amounts of charcoal and at different pH. Figure 1 shows two such instances. Here the amount of Hg^{2+} ions adsorbed is expressed not as per unit weight of charcoal but conventionally as percent of initial Hg^{2+} concentration in agreement with $(C_0-C)/C_0$ term in Eq. 1. The figure shows a flat maximum of adsorption exceeding 98% for a wide range of pH at charcoal concentration of 2500 ppm. From this result, the concentration of charcoal was kept constant to 2500 ppm throughout the present study. It should be noted that although all of the charcoals used in the present study which are not listed here exhibited a good adsorption towards Hg^{2+} and most of them also showed a good floatability as reported in a previous paper,[4] the floatability of Hg^{2+}-adsorbed charcoal was often unsatisfactory. In the present study, the product of Wako, Charcoal Activated, was eventually used exclusively.

Adsorbing-Particle Flotation of Hg^{2+} (Simple Flotation). Adsorbing particle flotation of Hg^{2+} ions was carried out for various combinations and compositions of charcoal, coagulant, and surfactant. Figure 2 shows some results of floatability of Hg^{2+} plotted against pH. Floatability appeared to exceed 90% in a wide range of pH for the coagulant of various types of Polyacrylamide and 98% floatability was seen for the system using D3H as a coagulant. Wide pH range of high floatability is seen which is favorable because the flotation of Hg^{2+} ions has been often conducted under the conditions of excess chloride ions and low pH.[7]

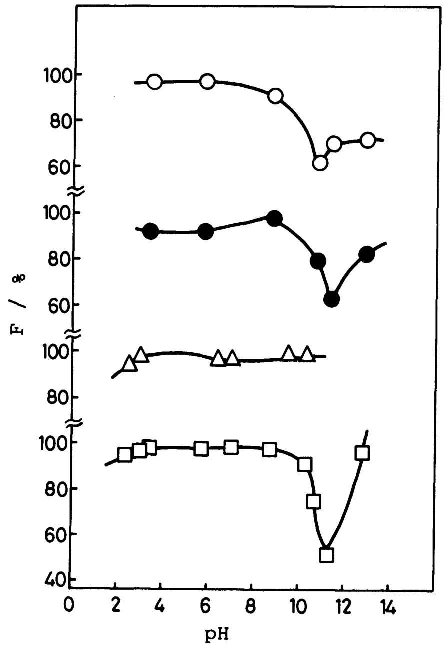

Fig. 2. Flotation of Hg^{2+} by different coagulants. Hg^{2+}: 2.1×10^{-4} mol dm^{-3}. Charcoal: 2500 ppm. HTAC: 540 ppm. Coagulants ○: DL 210 ppm, ●: DH 160 ppm, △: D3H 210 ppm, □: SA 210 ppm.

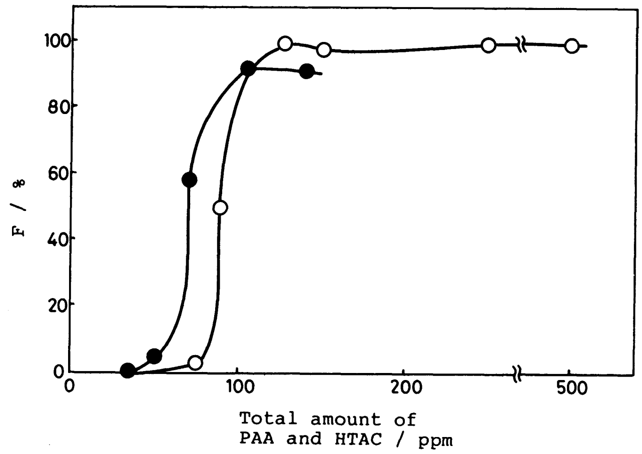

Fig. 3. Floatability vs. concn of PAA+HTAC. Hg^{2+}: 2.1×10^{-4} mol dm^{-3}. Charcoal: 2500 ppm. ○: DL-HTAC system, weight ratio of DL/HTAC=0.388 ●: DH-HTAC system, weight ratio of DH/HTAC=0.296.

The floatability seems to increase as a whole with the degree of both the polymerization and hydrolysis of Polyacrylamide as far as the present study is concerned.

We further attempted to reduce the amount of coagulant and surfactant without considerable decrease in the floatability. Figure 3 shows the results for DL-HTAC and DH-HTAC systems. The figure expresses the relation between the floatability of Hg^{2+} ions and the total concentration of coagulant and surfactant at a constant ratio between them and at constant pH. As seen in Fig. 3, amounts of both coagulant and surfactant could be reduced to 35 and 90 ppm respectively for DL–HTAC system and 24 and 81 ppm respectively for DH–HTAC system without noticeable decrease in floatability.

Effects of Na_2S-Treatment of Charcoal and Coexistence of Chloride Ions on Floatability. In order to enhance the floatability of Hg^{2+}, active charcoal was immersed in an aqueous solution of 1 mol dm^{-3} sodium sulfide for 6 h, then washed with distilled water until the supernatant became neutral and dried. An instance of the floatability of Hg^{2+} ions using Na_2S-treated charcoal is shown in Fig. 4, together with the result using charcoal without the Na_2S-treatment. The increase of floatability due to the treatment was observed, but the effect was not so distinct as had been expected. Further the effect of the coexistence of chloride ions upon the floatability was examined, because halogen ions have been reported to increase the adsorption of Hg^{2+} ions by charcoal.[7,8] But such an effect did not appear as far as the present study is concerned.

Dependence of Floatability on Hg^{2+} Concentration. The effect of Hg^{2+} ion concentration upon the floatability was examined and the result is shown in Fig. 5. The coagulant AR used there was somewhat different in the degree of polymerization from that used in the previous experiments, so the results were unable to compare strictly with each other but general tendency is seen that the floatability increases slightly in the concentration range of 10^{-5} to 10^{-6} mol dm^{-3} of Hg^{2+} ions.

Ionic Interaction Between Coagulant and Surfactant. In order to examine the ionic interaction between coagulant and surfactant, which supposedly contributes to the flotation, the floatability of Hg^{2+} ions was further measured by using SA, SN, and SC as anionic, nonionic, and cationic coagulants respectively and HTAC and SDS as cationic and anionic surfactants. The results are shown in Fig. 6. As seen in Fig. 6, among the systems using cationic surfactant HTAC, the system with anionic coagulant SA exhibited most pronounced floatability in a wide range of pH, the value was distinctly small for nonionic coagulant SN and zero for cationic coagulant SC in a wide range of pH. Thus the ionic interaction between coagulant and surfactant is evident. Large floatability shown by the system of SC–SDS also confirms this fact.

Stepwise and Double Flotations. Some of the results of stepwise and double flotations are shown in Table 1, together with the simple one-step flotation hitherto mentioned. In this table we can see a general tendency of enhanced floatability of stepwise and double flotations compared with that of simple foltation, similarly to the case of stepwise flotation using bentonite as an adsorbent.[2] It is noted that the floatability increases as a whole in the order of double flotations applying stepwise additions for surfactant alone, coagulant alone and for both of them, and

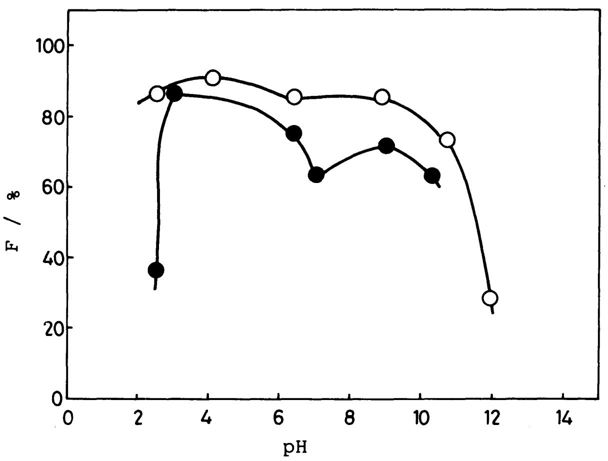

Fig. 4. Effect of Na_2S treatment on floatability.
Hg^{2+}: 2.1×10^{-4} mol dm^{-3}. Charcoal: 2500 ppm. DL: 24—25 ppm. HTAC: 63—64 ppm. ○: Na_2S-treated charcoal, ●: charcoal without treatment.

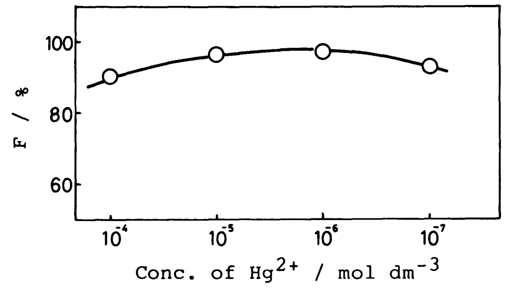

Fig. 5. Floatability vs. Hg^{2+} concentration.
Hg^{2+}: 2.1×10^{-4} mol dm^{-3}. Charcoal: 2500 ppm. AR: 60 ppm. HTAC: 540 ppm. pH: 6—7.5.

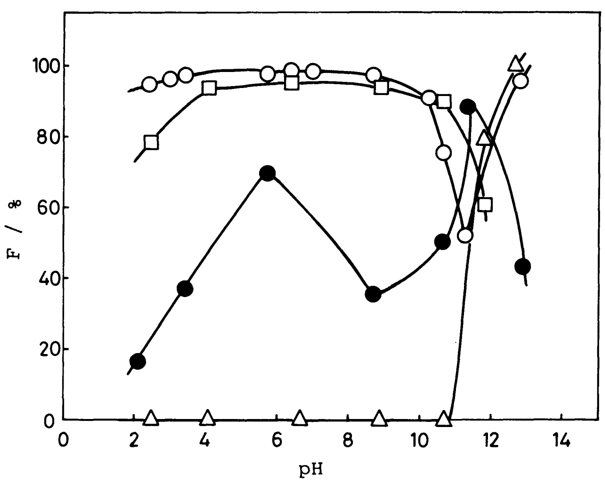

Fig. 6. Ionic interaction between coagulant and surfactant.
Hg^{2+}: 2.1×10^{-4} mol dm^{-3}. Charcoal: 2500 ppm. ○: SA 210 ppm, HTAC 540 ppm. ●: SN 210 ppm, HTAC 540 ppm. △: SC 210 ppm, HTAC 540 ppm. □: SC 210 ppm, SDS 450 ppm.

Table 1. Simple, Double, and Stepwise Flotations

SA added/ppm[a] First	SA added/ppm[a] Second	HTAC added/ppm First	HTAC added/ppm Second	F(%)
		Simple flotation		
250	0	300	0	91.7
		Double flotation		
250	0	240	60	94.8
200	50	300	0	98.5
200	50	240	60	99.3
		Stepwise flotation		
200	50	240	90	99.7

a) Amount of addition is expressed by the increase of concentration. Hg^{2+}: 2.1×10^{-4} mol dm^{-3}, charcoal: 2500 ppm, pH: 7.5—9.5.

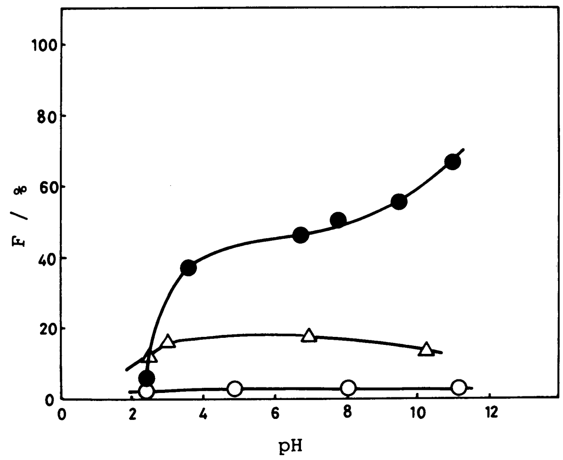

Fig. 7. Flotation without charcoal and/or coagulant. Hg^{2+}: 2.1×10^{-4} mol dm^{-3}. ○: Charcoal 2500 ppm, DL 0, HTAC 540 ppm. ●: Charcoal 0 ppm, DL 210, HTAC 540 ppm, △: Charcoal 0 ppm, DL 0, HTAC 540 ppm.

stepwise flotation. Thus, both the stepwise and double flotations are confirmed to be equally effective compared with the simple flotation. In the case of practical application, the double flotation is considered preferable compared with the stepwise one.

Mechanism of Adsorbing-Particle Flotation. In order to confirm the action of each component contributing to the adsorbing-particle flotation, flotation measurement of Hg^{2+} using HTAC without the

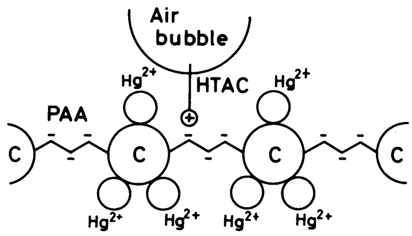

Fig. 8. Structure of scum consisting of Hg^{2+}, charcoal, PAA and HTAC. C: Charcoal.

addition of charcoal and/or coagulant was carried out. The results are show in Fig. 7. It is evident in this figure that charcoal, coagulant, and surfactant is indispensable for the adsorbing-particle flotation of Hg^{2+} ions, because the absence of any one of them results in a poor flotation. Thus the mechanism of adsorbing-particle flotation of Hg^{2+} ions is considered to be similar to the case of flotation using poly(ethyleneimine) as an adsorbent reported in a preceding paper.[5] Figure 8 illustrates the scum structure composed of Hg^{2+} ions, charcoal, anionic coagulant, and cationic surfactant together with an air bubble to which the sum is attached.

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