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Removal of Thallium from Waste Water by Using the Iron Metal and Hydrogen Peroxide

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Thallium in waste water can be removed effectively by DOWA Iron Powder Method which uses Fe metal powder and H_2O_2. The concentration of Tl in waste water was decreased by a factor of about 100 from the initial concentration with each treatment.

Thallium (Tl) is a poisonous metallic element. Although there are few industrial uses, it is used widely in laboratory.1) Especially Tl has recently been used to make superconductive ceramics.2) In these experiments, Tl or Tl compounds inevitably mix into waste water, because the tools used to treat them must be washed with water. There is, however, no established technique to remove Tl from waste water. In this work, we report the removal of Tl from the waste water by DOWA Iron Powder Method3,4) which removes inorganic materials and decreases COD (chemical oxygen demand), by using Fe powder and H_2O_2.

The procedure of this method is as follows: first, the waste water is adjusted to pH 3-4, and then 12.5 g of Fe metal powder per 1 dm^3 of waste water is added and suspended through strong agitation. Second, 50-100 cm^3 of H_2O_2 30wt.% aqueous solution per 1 dm^3 of waste water is gradually injected, which takes 10-15 min. Third, alkali (NaOH or $Ca(OH)_2$ etc.) is added to adjust the pH to 10-11, and the agitation is continued for 2-5 min. Finally, flocculant is added and the precipitation is separated by filtration.

From the analysis of the precipitate with X-ray microanalyser, the metallic element which presented in the waste water, was found to be at the surface of the Fe metal particles or in the iron hydroxide polymer. Therefore the removal mechanism of this process is thought to be as follows: (I) at low pH, Fe metal corrodes and generates Fe^{2+} ion. At this time, Fe metal reduces the metal ions (M^{n+}) with standard electrode potential of $M^{0/n+}$ couple being more anodic than that of $Fe^{0/2+}$ couple (-0.44 V vs. NHE). The surfaces of the Fe particles are very active because they are washed with acid and are polished with each other. Thus, ions and metal particles are adsorbed chemically and/or physically on the Fe particles. Moreover, Fe^{2+} and H_2O_2 react each other to make ·OH radical (Fenton's reaction). This ·OH radical is very active and works as a strong oxidant; it oxidizes the reducing species in the solution and decreases COD. (II) After the alkali has been added and the pH of the solution has been adjusted to 10-11, Fe^{3+} ions form poly-nuclear complex. The complex polymerizes and precipitates. During this reaction, various ions and particles are trapped in the precipitate. Tl^+, which is stable in the solution, is oxidized to Tl^{3+} by $\cdot OH$, and insoluble $Tl_2O_3 \cdot nH_2O$ is presumably formed. In addition, Tl^+ and $Tl_2O_3 \cdot nH_2O$ are removed through adsorption to the surface of the Fe particles or inclusion in the polymerized Fe complex.

We used two types of model waste water; one contained 100-500 ppm Tl^+ as Tl_2SO_4 and the other contained 0.1-1 vol.% acetic acid besides Tl_2SO_4. We also used real waste water which contained ca. 500 ppm Tl and Zn, pyridine, quinone etc. The concentration of Tl in the solution was determined with atomic absorption spectrometry. One mol dm^{-3} NaOH aqueous solution or solid $Ca(OH)_2$ was used to increase pH of the solution, and Accofloc N100S (Mitsui-Cyanamid, Ltd.) was used as a flocculant.

Table 1 shows the concentration of remaining Tl ($[Tl]_R$) before and after treatment. It became ca. 1/100 of the initial concentration after the treatment when there was no organic impurity. The existence of organic impurity made $[Tl]_R$ larger, because the oxidation of the organic chemicals competed with the oxidation of Tl^+ to Tl^{3+}. These results show that $[Tl]_R$ can be decreased by repeating this operation. Figure 1 shows the results of the repeated operation with the actual waste water and the solution containing 0.1 vol.% acetic acid and 100 ppm Tl. The $[Tl]_R$ decreased exponentially with the number of the treatments, and finally it became below 0.1 ppm. However, we could not ascertain the limit of this method, since the detection limit of Tl with atomic absorption spectrometry was in the order of 0.01 ppm.

These results indicate that the concentration of Tl can be decreased below 0.01 ppm with repeated operation. Therefore this method can be applied for the practical use.

Table 1. The concentration of Tl before and after treatment

Initial concentration of Tl/ppm	$[Tl]_R$/ppm
500 (no organic chemicals)	3
200 (no organic chemicals)	3
100 (no organic chemicals)	0.4
100 (contains 0.1vol.% AcOH)	1
500 (real waste water)	20

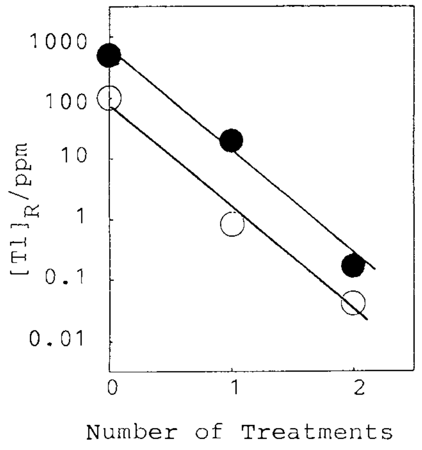

Fig. 1. The decrease in $[Tl]_R$ due to repeated treatment. ○:model solution contains 0.1vol.% AcOH ●:real waste water

References

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