BEHAVIOUR OF METAL ANION SPECIES IN ACTIVATED SLUDGE TREATMENT PROCESS

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Introduction

The behaviour of metal anions in alternated aerobic and anoxic activated sludge, based on total dissolved concentration analysis, was previously studied [1]. Since metal anions can exist in various species on which their toxicity and chemistry depend, new experiments, based on speciation analysis, were conducted to investigate the transformations of different metal anion species during the activated sludge treatment process and to get more information on their removal mechanisms.

Methodology

Fresh activated sludge collected from the Tonan Wastewater Treatment Plant in Iwate Prefecture was washed three times with deionized water. After settling and centrifugation of the washed sludge, the liquid phase was wasted and the solid phase was kept for the experiments.

Simultaneously, the pH of two solutions containing Cr(VI), As(III), As(V), MMA, DMA, Se(IV) and Se(VI) was adjusted to 7. The concentration of each species in the solution was 100 μg l^{-1}. One solution was used for aerobic experiment were the DO concentration was maintained higher than 2 mg l^{-1}, and the second for anoxic experiment. The anoxic condition was obtained by purging the solution with N_2 gas until the DO concentration was dropped to less than 0.2 mg l^{-1} and kept to this value during the experiments.

At pH 7, samples were collected to determine the initial concentration of each species. Then, appropriate volume of the washed sludge was added to the solution and the mixture was agitated on a shaker table at 120 rpm. Next, samples were collected after 0.17, 0.5, 1, 3, 6, 9 and 12 hours of sludge addition and were filtrated with a 0.45 μm membrane filter.

By following the same experimental procedure, two blank experiments were performed to determine the nature of the reactions among the metal anion species, sludge and water. One was carried out with no sludge addition during 12 hours, and the other with addition of autoclaved sludge. Before the experiments, the autoclaved sludge was washed three times to remove remaining soluble components.

Dissolved Cr [D-Cr], dissolved As [D-As] and dissolved Se [D-Se] were analyzed with an ICP-MS. Dissolved Cr(VI), As(III), As(V), MMA, DMA, Se(IV) and Se(VI) were determined by an HPLC-ICP-MS system based on the method developed by Martinez-Bravo et al.[2]. This method allows the simultaneous determination of all species described above in 20 min. The chromatogram of the standard solution containing all the anion species is represented in Figure 1.

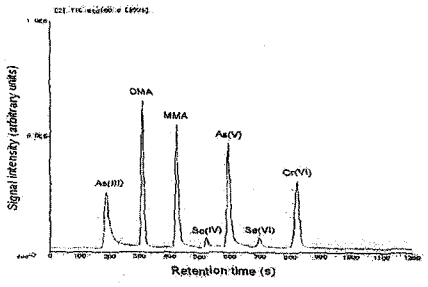

Figure 1. Chromatogram of a standard solution containing Cr(VI), As and Se species as 100 μg l^{-1} each species.

Results and discussion

Effect of autoclaved sludge and no sludge addition

Figures 2 and 3 show the behaviour of the metal anion species in autoclaved sludge under aerobic and anoxic conditions respectively. Under both aerobic and anoxic conditions, only Cr(VI) concentration was slowly decreased respectively to 66 μg l^{-1} and 50 μg l^{-1} after 12 hours. A small decrease in other species concentration was noticed immediately after the addition of the autoclaved sludge. Then, no change in the form and the concentration was observed until the end of the experiments under both aerobic and anoxic conditions.

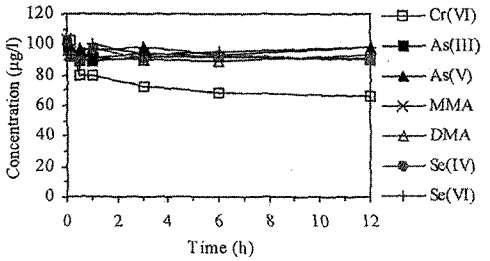

Figure 2. Metal anion species behaviour in aerobic autoclaved sludge (SS= 700 mg l^{-1})

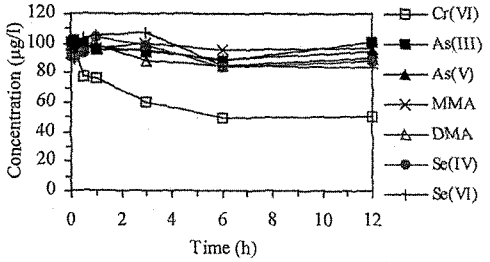

Figure 3. Metal anion species behaviour in anoxic autoclaved sludge (SS= 700 mg l^{-1})

Results obtained from experiments with no sludge addition (data not reported) were similar to those with autoclaved sludge except that no significant change in the form and the concentration of Cr(VI) were observed and the small decrease in other metal species at the beginning of the experiments did not occur.

The immediate decrease of a small concentration of As and Se species could be due to their adsorption onto sludge surfaces by physico-chemical reactions. On the other hand, the decrease in Cr(VI) concentration under the two aeration conditions may be due to its reduction to Cr(III) since it was reported that Cr(VI) is not be adsorbed onto activated sludge surfaces [3].

Effect of aerobic activated sludge

As shown in Figure 4, the concentration of Cr(VI) was rapidly decreased to about 50 μg l^{-1} within one hour after sludge addition, then slowly decreased and finally dropped to 10 μg l^{-1}. The concentration of As(III) and MMA were gradually decreased, and no more As(III) was detected after 9 hours while final concentration

of MMA was 16 μg l^{-1}. On the other hand, As(V) and DMA were gradually increased respectively to 186 μg l^{-1} and 120 μg l^{-1}. Last, Se(IV) was decreased to around 80 μg l^{-1} after 1 hour and then stabilized to this value while Se(VI) was slowly decreased to about 60 μg l^{-1} after 12 hours.

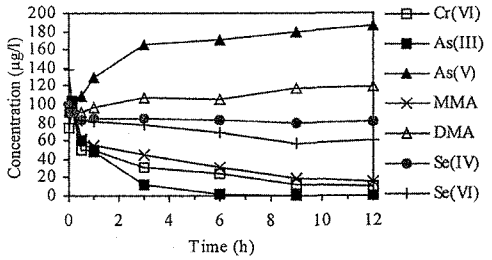

Figure 4. Metal anion species behaviour in aerobic activated sludge (SS= 1100 mg l^{-1})

As previously stated, the decrease in Cr(VI) concentration was due to its reduction to Cr(III). The decrease in As(III) associated with the increase in As(V) concentration could be explained by the oxidation of As(III) to As(V). The small increase of DMA combined with the decrease of MMA suggests that a part of MMA was methylated to DMA. The decrease in Se species concentration was not clarified. Since no significant reaction occurred during the blank experiments (Figures 2 and 3), it is then shown that the changes in As and Se species concentration (Figure 4) are mediated by living microorganisms. The microbial oxidation of As was reported by Frankenberger [4].

Effect of anoxic activated sludge

As shown in Figure 5, within 1 hour after the sludge addition, the concentration of Cr(VI) was dropped to less than 1 μg l^{-1}. As(V) was gradually decreased during the first 6 hours and then was dropped to less than 10 μg l^{-1} while As(III) was increased to around 155 μg l^{-1} during the first 6 hours and then was stabilized to this value. MMA and DMA were slowly decreased in 3 hours and were stabilized to 75 μg l^{-1}. Next, Se(VI) was decreased to around 70 μg l^{-1} in 3 hours and was stabilized to this value. Last, Se(IV) was decreased to 83 μg l^{-1} in 1 hour, was decreased to 68 μg l^{-1} after 6 hours and then was finally dropped to less than 10 μg l^{-1}.

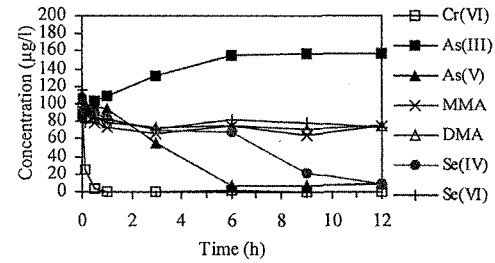

Figure 5. Metal anion species behaviour in anoxic activated sludge (SS= 1100 mg l^{-1})

In anoxic activated sludge, the reduction of Cr(VI) is much faster than that under aerobic condition. Similar observations were reported by Stasinakis et *al.* (2004). As(V) could be reduced to As(III) and Se(IV) was reduced to the insoluble elemental Se. The reactions among As and Se species and activated sludge are also shown to be biologically mediated. Literatures has reported the biological reduction of As and Se [4]-[5].

Metal anions removal in activated sludge

The concentrations and the removal efficiencies reported in Table 1 are based on the dissolved concentration analysis (ICP-MS).

As shown, the removal efficiencies of Cr and Se under anoxic condition, respectively 92.9% and 53.6%, were higher than those under aerobic one (65.1% for Cr and 16.7% for Se). The removal efficiency of As was low compared with other metals. And the As removal efficiency under anoxic condition (12.5%) was lower than that under aerobic one (26.0%).

Table 1. Dissolved Cr, As and Se removal in activated sludge.

Metal	Aeration	Initial conc. (μg l^{-1})	Final conc. (μg l^{-1})	Removal (%)
D-Cr	Aerobic	80.8	28.2	65.1
	Anoxic	72.3	5.1	92.9
D-As	Aerobic	390.9	289.2	26.0
	Anoxic	423.4	371.1	12.4
D-Se	Aerobic	202.8	168.9	16.7
	Anoxic	252.2	116.9	53.6

Under anoxic condition, the reduction rate of Cr(VI) to Cr(III) was higher than that under aerobic condition (Figures 4 and 5). The positively charged Cr(III) ion is reported to be easily adsorbed onto the activated sludge surfaces [3]. Therefore higher Cr(VI) removal occurred under anoxic condition.

Higher removal of Se was also observed under anoxic condition because more reduction of Se(IV) to elemental Se occurred.

Last, the removal of As seems to be mainly due to the removal of MMA (Figure 4) probably by specific anion adsorption onto sludge surfaces.

Summary

The Cr(VI) concentration was always decreased under both arobic and anoxic conditions and with either autoclaved or activated sludge. As and Se species transformations were mostly due to biological reactions between the metal anion species and the sludge. These transformations were immediate and achieved within the 12 hours. Under anoxic condition, Se species could be reduced to the elemental Se while under aerobic condition Se(IV) was not oxidized to Se(VI). Last, it seems evident that under aerobic condition, As(III) was oxidized to As(V) and some MMA was methylated to DMA, and under anoxic condition, As(V) was reduced to As(III). However, more investigations, such as the separate study of each species, are needed to confirm the suggestions obtained from the present study.

Under different aeration conditions, the least removable metal anion was always As followed by Se. Cr was the most removable with a removal efficiency exceeding 90% under anoxic condition.

References

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