Ⅶ－15 Effect of aeration conditions on adsorption of cationic and anionic metals ions onto activated sludge

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1. Introduction

To understand the effect of aeration conditions on metal uptake onto activated sludge, a set of laboratory adsorption experiments was carried out at pH7.0 during 12 hours under four alternated aeration conditions: aerated/aerated (A-A), aerated/non-aerated (A-NA), non-aerated/aerated (NA-A) and non-aerated/non-aerated (NA-NA) conditions. Metals used were Mn, Cu, Ni, Zn, Cd and Pb as cationic metal ions and Cr, As and Se as anionic metal ones.

2. Methods

Fresh activated sludge collected from the Tonan Wastewater Treatment Plant was washed three times with distilled water and centrifuged at 3500 rpm during 15min to separate liquid and solid phase. The supernatant was wasted and the solid phase was kept for the experiment.

Simultaneously, the pH of a prepared metal stock solution, separated in two shaking flasks, one for aerated experiment and the second for non-aerated conditions, was adjusted to 7.0. Before pH adjustment, dissolved oxygen present in the shaking flask was removed by purging with N_2 gas for non-aerated running.

At pH7.0, the solid phase of the activated sludge was mixed with the metal solution as about 1300 mg/L of SS and 1050 mg/L of VSS. The shaking flask was stirred on a shaker table at 120rpm. Then, 25mL of samples was collected after 1min, 10min, 30min, 1h, 2h, 3h and 6 hrs. After 6 hours, the solution contained in the two flasks were respectively separated into two flasks. The aeration condition of one flask was kept and that of another flask was alternated from aerated to non-aerated or from non-aerated to aerated. 25mL of samples was then collected after 8 hrs, 9 hrs, 10hrs and 12hrs, which is the end of the experiment. Initial metals concentrations were 0.1mg/L and to minimize the precipitation and to distinguish cationic and anionic metal ions adsorption, three metal stock solutions were prepared: one contained only Pb, a second contained Mn, Cu, Ni, Zn and Cd, and the last one contained Cr, As and Se.

Dissolved metals were analyzed with ICP-MS.

3. Results and discussion

Solubility of metals at pH7.0

Table 1 shows the concentrations of metals measured at pH7.0 without sludge addition. It seems that, in terms of percentage, the solubility of metals under aerated conditions is higher than in non-aerated conditions. At pH7.0, more metal precipitation may have occurred in non-aerated conditions. Actually, it was not possible to explain these differences.

Table 1. Metal solubility at pH7.0 (%)

		Mn	Ni	Cu	Zn	Cd	Pb	Cr	As	Se
A	Total (μg/L)	88.49	99.40	93.62	93.83	79.51	84.44	95.97	91.56	55.85
	Dissolved (μg/L)	85.19	94.84	91.66	92.64	71.51	75.82	95.83	82.27	62.86
	Soluble metal (%)	96.27	95.41	97.91	98.73	89.94	89.79	99.85	89.86	-
NA	Total (μg/L)	82.85	92.53	90.89	94.99	72.81	78.75	98.81	89.01	47.86
	Dissolved (μg/L)	74.89	82.13	66.79	86.10	61.74	54.22	98.97	78.17	36.88
	Soluble metal (%)	90.39	88.75	73.48	90.64	84.79	68.85	100.00	87.81	77.06

Behaviour of cationic and anionic metals ions

As shown in Figures 1-4, under both aerated and non-aerated conditions, the adsorption of cationic metals, except for Mn, is characterized by two phases: the first phase is a high rapid adsorption one within the first 10 min of sludge addition to the metal solution and the second phase is a slow one. Equilibrium under the conditions studied here was reached after two hours.

In contrast with cationic metals, the adsorption of anionic ions is relatively slow. The proportion of dissolved As and Cr remaining at the end of the experiments is high while dissolved Se remaining is low under aerated condition and very low in non-aerated condition. It should be noticed that initial dissolved Se at pH7.0 was already lower than those of other anionic metals.

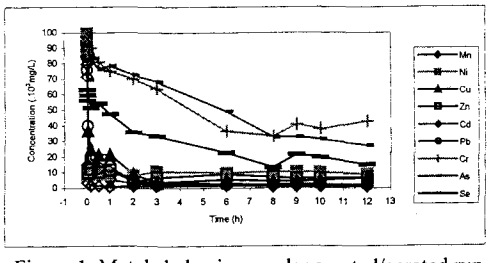

Figure 1. Metals behaviour under aerated/aerated run

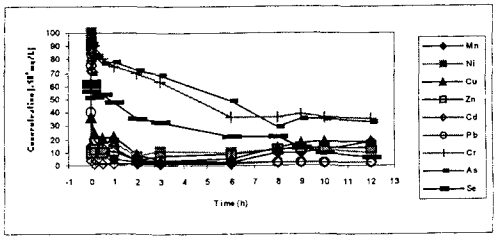

Figure 2. Metals behaviour under aerated/non-aerated run

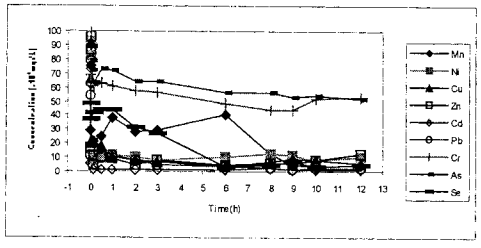

Figure 3. Metals behaviour under non-aerated/aerated run

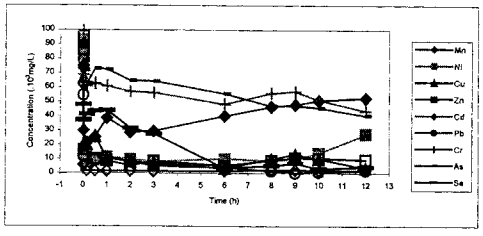

Figure 4. Metals behaviour under non-aerated/non-aerated run

Manganese behaviour

Among all the metals studied, Mn is the only metal that different aeration conditions have a significant effect on the adsorption onto activated sludge.

As shown in Figure 5, under initially aerated condition, the adsorption of Mn is very fast and high. When the aerated condition is kept after six hours, the dissolved concentration within the mixed liquor is maintained, while when non-aerated condition followed the aerated condition, an increase in dissolved Mn concentration is noticed.

On the other hand, when 12 hours of non-aerated condition is maintained, the concentration of dissolved Mn remains high during the length of the experiment. And when non-aerated condition was alternated with aerated condition, a great decrease in Mn solubility was immediately noticed during the following sampling time.

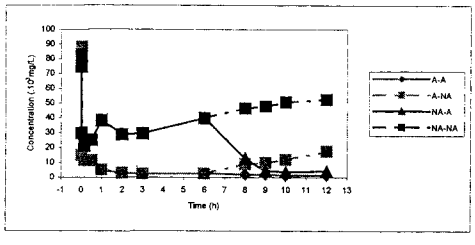

Figure 5. Mn behaviour under different aeration conditions

Under aerated conditions, the main mechanisms that affect the solubility of Mn may be the oxidation of Mn (II) to the insoluble instable Mn (IV) form and co-precipitation rather than adsorption onto sludge surfaces.

The increase in dissolved Mn concentration, when alternating non-aerated condition is probably due to the reduction of the previous Mn (IV) form to Mn (II). Or, desorption of Mn (II) from the sludge may have occurred. The rapid decrease in Mn solubility within the first ten minutes followed by continuous increase during non-aerated run is unclear because under this condition, no oxidation of Mn should occur.

Metals uptake under aerated and non-aerated conditions

Dissolved metals concentrations at pH7.0 before sludge addition, at T6=6hours and at T12=12hours were compared to evaluate the percentage of metal uptake under one aeration condition and alternated aeration conditions respectively. Results are shown in Tables 2-3.

Table 2. Cationic metal ions uptake (%)

	Time	Mn		Ni		Cu		Zn		Cd		Pb	
A	T6	96.8		89.8		94.3		90.7		97.8		97.2	
		A-A	A-NA	A-A	A-NA	A-A	A-NA	A-A	A-NA	A-A	A-NA	A-A	A-NA
	T12	98.5	79.2	90.8	89.5	92.8	79.4	92.8	85.8	98.7	96.6	96.6	97.4
NA	T6	39.9		87.8		95.1		94.2		98.0		93.0	
		NA-A	NA-NA	NA-A	NA-NA	NA-A	NA-NA	NA-A	NA-NA	NA-A	NA-NA	NA-A	NA-NA
	T12	94.5	29.8	87.2	66.8	85.0	95.0	85.9	89.2	98.0	96.9	95.5	97.0

Table 3. Anionic metal ions uptake (%)

	Time	Cr		As		Se	
A	T6	61.8		40.2		64.2	
		A-A	A-NA	A-A	A-NA	A-A	A-NA
	T12	55.5	62.5	66.9	60.5	76.2	90.5
NA	T6	51.4		28.8		90.6	
		NA-A	NA-NA	NA-A	NA-NA	NA-A	NA-NA
	T12	46.4	56.0	33.9	48.3	88.7	98.0

As indicated, uptake of Zn, Cd and Pb was not affected by the aeration condition. Whereas the uptake of Mn was very high in aerated condition compared with that in non-aerated condition. Uptake of Cr and As is also more pronounced in aerated condition than in non-aerated condition.

Last, non-aerated conditions decrease the solubility of Se and the change of aeration condition seems to have a small effect on Cu solubility while a long-period of non-aerated condition could lead to the increase of dissolved Ni.

4. Summary

Generally, the solubility of metals is higher in aerated condition than in non-aerated condition at pH7.0. The uptake of cationic metal ions by activated sludge is fast and high, while uptake of anionic metal ions is slow and low.

Aeration condition did not have a significant effect on metal uptake by activated sludge except for Mn and Se where Mn solubility greatly decrease in aerated conditions and increase in non-aerated conditions. On the other hand, removal of dissolved Se was higher in non-aerated conditions than in aerated conditions. Further investigations are needed to better understand these behaviours.