



THE INFLUENCE OF NITRILOTRIACETIC ACID (NTA) ON METAL MOBILIZATION FROM A CONTAMINATED RIVER SEDIMENT

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ABSTRACT

Sediment samples and river water used in this study were collected from a contaminated river, namely, the Lau-Che river located in northern Taiwan, in order to investigate the mobilization of heavy metals from river sediment influenced by NTA in a simulated continuous-flow channel reactor. Concurrently, the kinetic model was applied to describe the mobilization of heavy metals from sediments. When the NTA was first discharged into the reactor, the initial adsorption of NTA by the sediment decreased the mobilization of heavy metals and changed the released behavior of heavy metals. It made bad agreement between models and experimental data. Due to the bacteria were completely acclimated to degrade NTA in the former experiment, the release of heavy metals was significant at the initial addition of NTA and the concentrations of heavy metals in the liquid phase decreased after that the NTA was degraded by bacteria. The maximum mobilization of heavy metals increased with the increase of concentration of NTA. According to the experimental data, the mobilization of heavy metals by NTA appeared to follow multiple first-order reaction model, two constant model, or diffusion model. © 1998 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Contaminated sediment, kinetics, metal, mobilization, nitrilotriacetic acid (NTA), release.

INTRODUCTION

High industrialization and related human activities result in the increase of the concentrations of heavy metals in water bodies in Taiwan. Heavy metals discharged into rivers, are rapidly transferred from surface waters to bottom sediments by adsorption and precipitation processes (Förstner and Wittmann, 1979). However, heavy metals can be remobilized from sediments by changes in pH-Eh or complexing with complexing agents, such as soluble humic substances, NTA (nitrilotriacetic acid), and EDTA (ethylenediaminetetraacetic acid) (Samanidou and Fytianos, 1990).

In order to control the eutrophication of rivers and lakes, nitrilotriacetic acid (NTA) has been widely used to substitute sodiumtripolyphosphate (STPP) in detergents. However, because of the strong chelating capacity, NTA may result in the mobilization of heavy metals from aquatic sediments in receiving waters, and pose a risk to an aquatic ecosystem or to supplies of potable water. Thus, it is important to examine the effects of

NTA on sediments in receiving waters, particular to the area, such as Taiwan, not popularly served by wastewater treatment system. In the countries using NTA to replace STPP including USA, Canada, Finland, Germany, Netherlands, Norway, Sweden, and Switzerland, concentrations of NTA in domestic sewerage are between 10 and 20 mg/l, even as great as 35 mg/l in areas of hard water (Rossin *et al.*, 1982; Perry *et al.*, 1984).

Many desorption kinetic models of metals have been applied to soils. The kinetics of metal desorption in various soil systems have been shown to conform to first-order kinetics and to the parabolic model (Sivasubramaniam and Talibudeen, 1972; Sparks and Jardine, 1981; Jardine and Sparks, 1984). Kuo and Lotse (1974) investigating phosphate release from lake sediment with various anionic solutions (EDTA^{2-} , OH^- , F^- and HC_2O_4^-), found that the kinetics of phosphate desorption also conformed to first-order kinetics and to a diffusion model. The kinetics of Zn desorption by DTPA (diethylenetriaminepentaacetic acid) and Cu desorption by EDTA from soils indicated that desorption process could be explained by the two constant model (Kuo and Mikkelsen, 1980; Jopony and Young, 1987). The purposes of this study are to investigate the influence of NTA on metal mobilization from a contaminated river sediment. In addition, the kinetic model, multiple first-order reaction model, diffusion model and two constant model are applied to describe the mobilization of heavy metals from sediments.

MODELING OF MOBILIZATION KINETICS

Two first-order reaction model

This model assumes that there are two concurrent reactions differing in reaction rates and these two different first-order reactions are attributed to discrete types of binding sites, with the following additional assumption. The faster reaction proceeds to completion before the slower reactions begin (Yu and Klarup, 1994). If the rates of desorption of heavy metals from the sediment particulates follow the first-order reactions. It can be described as follows:

$$\frac{dC_1}{dt} = k_1(C_1^0 - C_1) \quad (1)$$

and

$$\frac{dC_2}{dt} = k_2(C_2^0 - C_2) \quad (2)$$

where, C_i is the concentration of desorbed metal from site i in solution at time t , C_i^0 is the equilibrium concentration of desorbed metal caused by complexation of NTA from site i , and k_i is the rate coefficient of the first-order reaction for each reactive site i . Reaction (1) is fast and reaction (2) is slow. The initial conditions given in this model are $C_1|_{t=0} = 0$ and $C_2|_{t=0} = 0$. Integrating equations (1) and (2) and rearranging the solutions, the final solution, equation (3) can be obtained.

$$C = C_0\alpha(1 - e^{-k_1t}) + C_0(1 - \alpha)(1 - e^{-k_2t}) \quad (3)$$

where C_0 represents the total amount of heavy metal which could be released at equilibrium ($C_0 = C_1^0 + C_2^0$) and α represents the fraction of the total amount of heavy metal which could be released resulting from the fast reaction ($\alpha = C_1^0/C_0$).

Two-constant model

This kinetic model can be given as follows:

$$C = At^B \quad (4)$$

In equation (4), C is the concentration of desorbed metal in the solution, and A and B are constants. The agreement between the model and the experimental data is always good, but the physico-chemistry meanings

of A and B are ambiguous (Yu and Klarup, 1994). Kuo and Mikkelsen (1980) had tried to derive this model with a multiple order kinetic equation to simulate the rate of zinc desorption by DTPA (diethylenetriaminepentaacetic acid), but the physical meanings of A and B did not become clearer after this study. Therefore, it was considered a more empirical model.

Diffusion or parabolic model

Diffusion or parabolic model assumes that among the sediment particulates, the complexing reactions of metals with NTA are fast and their product diffusion are slow. In the diffusion or parabolic model, intraparticle diffusion or surface diffusion is considered to be the limiting step for the release of the metal (Crank, 1976). This model is based on Fick's law of diffusion that can be displayed as follows (Sivasubramaniam and Talibudeen, 1972; Jarine and Sparks, 1984):

$$\frac{M_t}{M_\infty} = \left(\frac{4}{\pi^{1/2}}\right) \left(\frac{Dt}{a^2}\right)^{1/2} - \frac{Dt}{a^2} \quad (5)$$

where M_t is the concentration in the solution at time t , M_∞ is the equilibrium concentration, D is the coefficient of diffusion, and a is the radius of the particle. Hence this model has important physical meaning. Crank (1976) indicated that there would be a linear relationship between the amount of desorption of a sorbate and the square root of time in the initial phase of diffusion if the reaction conforms to the Fickian diffusion. Thus, it would be lean to the axis of $t^{1/2}$, and in the initial phase of diffusion, equation (5) can be simplified to equation (6).

$$\frac{M_t}{M_\infty} = k(t)^{1/2} \quad (6)$$

MATERIALS AND METHODS

Sediment samples and river water used in this study were collected from a contaminated river, namely, the Lau-Che river located in northern Taiwan. All gravel and litter were removed from the sample. The pretreatment of the sample was naturally dried at room temperature and screened with a 20 mesh (0.84 mm) sieve. The moisture and volatile solids of the sediment were determined with Standard Method 2540G (APHA, 1992) and the contents of heavy metals in the sediment was examined by a HF-HNO₃-HCl microwave digestion method (CEM, 1991). The contents of heavy metals in river water were determined with Standard Method 3030K (APHA, 1992). The concentrations of Pb, Cu, Zn and Cr were analyzed by a flame atomic absorption spectrometer (Hitachi, model Z-8100).

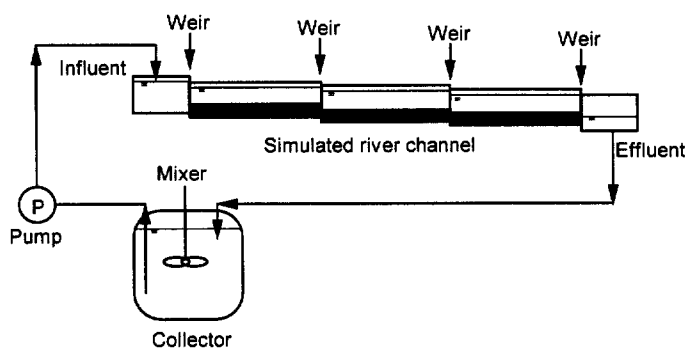


Fig. 1. Schematic diagram of experimental apparatus.

A acrylic simulated river channel reactor (length 150 cm × width 20 cm × depth 6 cm), as shown in Figure 1, was used in this investigation. At first, 6 kg of the prepared sediment was filled into the reactor (average depth 2 cm) and filled up the reactor with 1.5 liters of deionized water. Then, blend the 10 liters of river water, 40 liters of deionized water and various amount of Na₃NTA to obtain different concentrations of NTA

solutions (5, 10, 50, and 100 mg/l). The NTA of concentration of 10 mg/l was first added into the continuous-flow reactor to simulate the effects of NTA on the mobilization of heavy metals (Cu, Zn, Pb, and Cr) from sediment in natural waters. Following this test, the experiment was orderly respiked 100, 50, 10 and 5 mg/l NTA into the reactor, respectively. At selected time intervals, an aliquot of about 15 ml of the river water from the reactor was collected and immediately filtered through a 0.45 μm filter membrane. Then came the digestion of the filtered river water with Standard Method 3030K (APHA, 1992). The concentrations of Pb, Cu, Zn and Cr of digested supernatants were analyzed by a flame and graphite atomic absorption spectrometer (Hitachi, model Z-8100). The concentration of NTA was determined with the Zinc-Zincon method which is a compleximetric, colorimetric procedure (Thompson and Duthie, 1968).

RESULTS AND DISCUSSION

Properties of Sediment

The content of moisture, content of volatile solids and concentrations of heavy metals of the dried sediment and river water in this research are shown in Table 1. The content of zinc was the highest and the content of chromium was lowest in the sediment and river water.

Table 1. The properties of sediment and water of Lau-che creek.

Item	Sediment*	River water*
Moisture	0.39 \pm 0.08 %	-
Volatile solids	1.81 \pm 0.09 %	-
Pb	106.74 \pm 8.54 $\mu\text{g/g}$	0.13 \pm 0.03 mg/l
Cu	92.96 \pm 6.69 $\mu\text{g/g}$	0.08 \pm 0.01 mg/l
Zn	832.40 \pm 24.68 $\mu\text{g/g}$	0.22 \pm 0.08 mg/l
Cr	57.04 \pm 2.81 $\mu\text{g/g}$	0.03 \pm 0.01 mg/l

*: mean (n=4).

Effects of NTA on metal mobilization

The mean concentration of Pb released by NTA at the first addition of 10 mg/l NTA in simulated river channel was shown in Figure 2(a). It appeared that Pb was visibly released from the sediment during the first day but the concentration of Pb decreased on the second day. It should result from the initial adsorption of NTA on the sediment particles (as shown in Figure 3(a)). Sanchez and Lee (1973) indicated that NTA complexes may be adsorbed by the sediments and the amounts of released metal might decrease. A similar result was also observed in Garnett *et al.* (1985). After 2 days of reaction time, the concentrations of Pb increased (Figure 2(a)) with increasing concentrations of NTA (Figure 3(a)) and it reached the maximum released concentration of 29.67 $\mu\text{g/l}$ (0.1 % of total Pb) on the 37th day. Due to the degradation of Pb-NTA complexes by microorganisms and following change in the form of Pb in water, Pb was adsorbed by sediments and the concentration of Pb in water decreased after 37 days of reaction time. Banat *et al.* (1974) found that the concentration of Pb would decrease after a long reaction time caused by the biodegradation of Pb-NTA complexes. It suggests that the acclimation time of Pb-NTA is about 37 days.

Figure 2(b) is the concentration of Cu released by NTA at the first addition of 10 mg/l NTA. In the initial stage, the rate of Cu released from the sediment was slow, which was resulted from the initial adsorption of NTA on the sediment. Due to the desorption of NTA from the sediment (Figure 3(a)), the rate of Cu released by NTA increased after 10 days of reaction time. Then it decreased after 40 days. The reason why the release rate of Cu decreased was the same as that of Pb. It also implies that Cu-NTA needs about 40 days for acclimation of microorganisms. The concentration of Zn mobilized by NTA at the first addition of 10 mg/l NTA was displayed in Figure 2(c). The rate of Zn released by NTA was fast in first 7 days. Then it slowed down and reached the equilibrium state after 20 days of reaction time. In Figure 2(d), there were no obvious release of Cr (1-3 $\mu\text{g/l}$) in the sediment. This result is the similar to those of Chen *et al.* (1996), because of the very small solubility of $\text{Cr}(\text{OH})_3$ ($\text{pK}_{\text{sp}}=30$). The maximum mobilization percentages of heavy metals from the sediment by NTA in the experiment of first addition of 10 mg/l NTA

were shown in Table 2. It was found that the mobilization tendency of heavy metals followed the order: $Zn > Cu > Pb > Cr$ in the first addition of 10 mg/l NTA. Comparing the results shown in Table 2, it appears that there are much difference between the mobilization percentage of this study and those of other researches. Because of complete mixing of NTA solutions with sediments in the batch shaking experiments, they would cause much more mobilization. Therefore, the results obtained from this research can approach more closely to the real conditions.

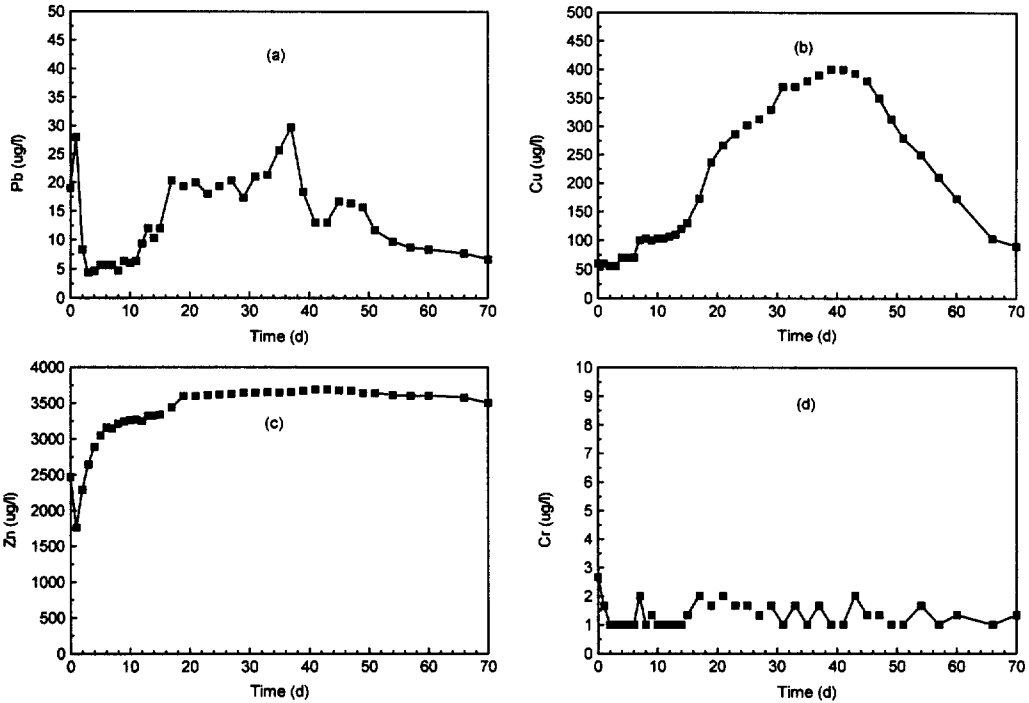


Figure 2. The concentration of heavy metals (a) Pb, (b) Cu, (c) Zn, and (d) Cr released by NTA in the experiment of the first addition of 10 mg/l NTA.

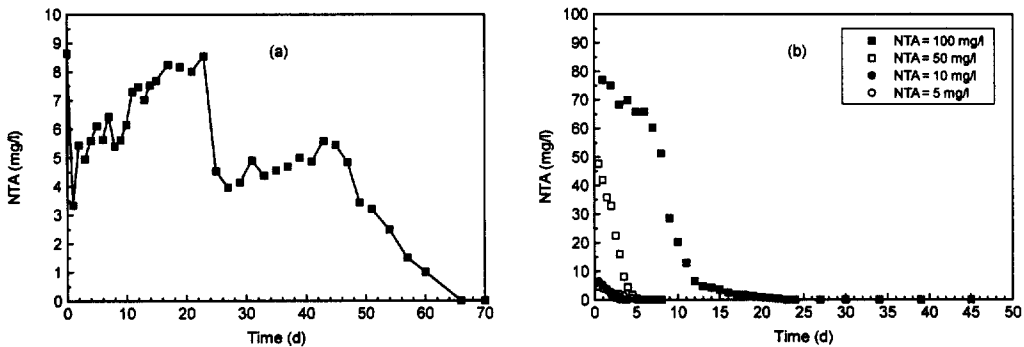


Figure 3. Changes in concentration of NTA in the liquid phase (a) first addition experiment (b) respiking experiment.

The concentrations of heavy metals released by NTA in the respiking experiment of NTA were indicated in Figure 4. Due to the bacteria were completely acclimated to degrade NTA in the previous experiment, the release of heavy metals was significant at the initial addition of NTA. The maximum mobilization of heavy metals (Pb, Cu, and Zn) appeared at the same time for various concentrations of NTA, respectively. The maximum concentrations of released heavy metals increased with the increase of concentration of NTA.

However, the concentrations of heavy metals in the liquid phase decreased after that the NTA was degraded by bacteria, as shown in Figure 3(b), and heavy metals would be adsorbed on the sediment again. The maximum mobilization percentages of heavy metals from the sediment by NTA in the respiking experiment of NTA were also shown in Table 2.

Table 2. The maximum mobilization (%) of heavy metals from sediment by NTA.

Experiment	Pb	Cu	Zn	Cr
1st addition (NTA=10 mg/l)	0.10	3.55	3.68	-
1st respiking (NTA=5 mg/l)	0.08	0.67	0.49	-
2nd respiking (NTA=10 mg/l)	0.11	0.92	1.34	-
3rd respiking (NTA=50 mg/l)	0.32	2.76	2.38	-
4th respiking (NTA=100 mg/l)	1.74	7.27	4.90	0.28
Banat <i>et al.</i> (1974)*	55.00	20.00	70.00	-
Samanidou and Fytianos (1990)*	4.80	37.50	-	2.00
Lo and Huang (1993)*	50.26	34.10	36.03	-
Chen <i>et al.</i> (1996)*	48.08	49.77	81.86	4.70

*: results of batch shaking experiment with 100 mg/l of NTA.

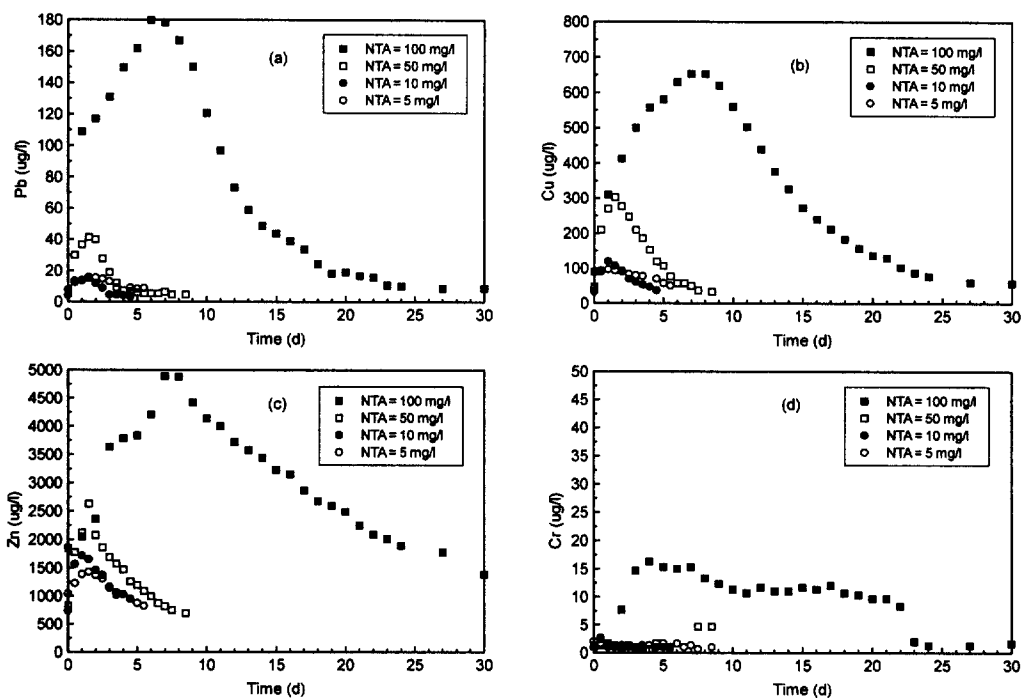


Figure 4. The concentration of heavy metals (a) Pb, (b) Cu, (c) Zn, and (d) Cr released by NTA in the respiking experiment of NTA.

Mobilization kinetics

Since NTA began to be biodegraded and the concentrations of released heavy metals decreased in the first addition and respiking experiments of NTA, the kinetic models were only used to simulate the mobilization of heavy metals from sediment in the initial stage of release. The kinetic models were fitted with selected data for Zn and Cu, as shown in Figure 5 and Figure 6. The curve of the two first order model can approximate the experimental data but it had more errors for Zn and Cu in the initial time. The fitting results of the kinetic models were listed in Table 3. It was visible that k_1 was much greater than k_2 , and k_2 could not be obtained in the experiment which did not reach equilibrium. α meant that the fast reaction accounted for a considerable proportion of the total heavy metal released. The linear coefficient of determination (R^2) were greater than 0.94 for Pb, Cu and Zn.

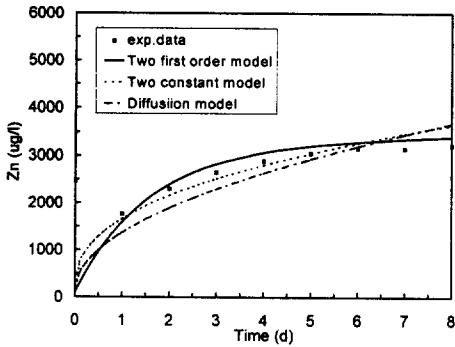


Figure 5. The results of fitting the kinetic models to the experimental data of Zn in the first addition experiment of 10 mg/l NTA.

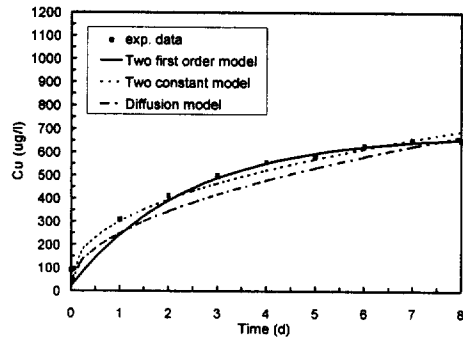


Figure 6. The results of fitting the kinetic models to the experimental data of Cu in the respiking experiment of 100 mg/l NTA.

Table 3. Fitting results of the kinetic models for Pb, Cu and Zn.

Model		Parameters					T-test
Two first model		C_0 ($\mu\text{g/l}$)	k_1	k_2	α	R^2	$1-\alpha$
Zn	first addition of 10 mg/l NTA	3,545	0.654	0.084	0.83	0.97	
Pb	respiking 100 mg/l NTA	195	0.476	-	1	0.95	0.950 - 0.980
Cu	respiking 100 mg/l NTA	680	0.412	-	1	0.99	0.980 - 0.990
Zn	respiking 100 mg/l NTA	5,685	0.28	-	1	0.94	0.998 - 0.999
Two constant model		A	B			R^2	$1-\alpha$
Zn	first addition of 10 mg/l NTA	1,217.14	0.395			0.98	
Pb	respiking 100 mg/l NTA	98.60	0.301			0.98	0.998 - 0.999
Cu	respiking 100 mg/l NTA	280.67	0.420			0.99	0.998 - 0.999
Zn	respiking 100 mg/l NTA	1,249.27	0.608			0.93	0.998 - 0.999
Diffusion model		k				R^2	$1-\alpha$
Zn	first addition of 10 mg/l NTA	986.87					
Pb	respiking 100 mg/l NTA	65.06				0.96	0.990 - 0.995
Cu	respiking 100 mg/l NTA	229.40				0.98	0.995 - 0.998
Zn	respiking 100 mg/l NTA	1,549.92				0.96	0.995 - 0.998

The agreement between the model and the experimental data was good for Zn and Cu with two constant model. In Table 3, R^2 , generally was very high for the metals in this study. It is obvious that the two constant model is an useful equation to predict the mobilization kinetics of heavy metals from the sediment. Unfortunately, it is not consistent with the facts that C approaches the limit infinity as $t \rightarrow \infty$ hence this model applies only within a certain time scale. In addition, the physico-chemical meanings of the two parameters (A and B) are indeterminate.

In Equation (6), k is a function of diffusion coefficient and the difference in ionic activity between the two phases which leads to diffusion across the phase boundary. Thus, the difference in ionic activity between the solid and solution phase has a tendency towards zero when diffusion is approaching equilibrium (Jopany and Young, 1987). Therefore, the diffusion model can employ only within a certain time before k is not constant again. The diffusion model had more error to the experimental data than others shown in Figure 5 and Figure 6 and it was not conformable after 6 days in Figure 6. The linear coefficient of determination, R^2 , was very high for Pb, Cu, and Zn as shown in Table 3. Application of diffusion model indicated that the mobilization of heavy metals from sediments by NTA exhibited a diffusion-controlled process.

CONCLUSIONS

When the river first receives wastewater containing NTA, the initial adsorption of NTA by the sediments reduces the amounts of released metal. The behavior of metal released will be changed, and it can not be

simulated with the kinetic models. After a certain period, bacteria were completely acclimated to degrade NTA, thus NTA was degraded by the bacteria. Then the released heavy metals in the liquid phase will be adsorbed by the sediment again. However, the release of heavy metals was significant at the initial addition of NTA. According to the experimental data, the mobilization of heavy metals by NTA appeared to follow two first-order reaction model, two constant model, or diffusion model. The two first-order reaction model was suitable to describe the mobilization of heavy metals from the sediment to the liquid phase as the reaction of mobilization reached an equilibrium; whereas, the two constant model and diffusion models were only suitable for the initial period of the mobilization.

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