Research Article

pH Effect on Heavy Metal Release from a Polluted Sediment

Yanhao Zhang,1,2,3 Haohan Zhang,1 Zhibin Zhang,1,3 Chengying Liu,1 Cuizhen Sun,1 Wen Zhang,1,3 and Taha Marhaba1,3

1School of Municipal and Environmental Engineering, Shandong Jianzhu University, Jinan 250101, China
2Co-Innovation Center of Green Building, Jinan 250101, China
3Department of Civil and Environmental Engineering, New Jersey Institute of Technology, Newark, NJ 07102, USA

Correspondence should be addressed to Zhibin Zhang; zhazhb@163.com

Received 17 May 2018; Accepted 19 July 2018; Published 23 August 2018

Academic Editor: George Z. Kyzas

Copyright © 2018 Yanhao Zhang et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The performance of Cd, Ni, and Cu release from river sediment at different pH was investigated by a leaching test using deionised water and river water as leachants. Visual MINTEQ geochemical software was used to model the experimental results to predict heavy metal release from sediments. The distribution and speciation of heavy metals in the sediments after leaching test were analyzed by Tessier sequential extraction. Leaching test results showed that the release amounts of Cd, Ni, and Cu are in the range of 10.2–27.3 mg kg⁻¹, 80.5–140.1 mg kg⁻¹, and 6.1–30.8 mg kg⁻¹, respectively, with deionised water as leachant at different pH. As far as the river water was used as the leaching solution in the test, the results show similar metal leaching contents and tendencies to that of the deionised water as leaching solution. The results of Tessier sequential extraction indicate that Cd of residual fraction easily forms obvious precipitate under the acidic condition, especially in the range of pH 0–4 with the residual of Cd over 50% of the total Cd in the sediment. The exchangeable content of Ni decreases with the increase of pH under the range of 0–5. The Fe-Mn oxide fraction of Cu in the sediments changes significantly from pH 0 to pH 9. Based on the effect of pH on the leaching of Cd, Ni, and Cu from the polluted sediment in the tests, more accurate information could be obtained to assess the risk related to metal release from sediments once it is exposed to the changed acid/alkali water conditions.

1. Introduction

There is growing concern all over the world that a large amount of industrial wastewater and domestic sewage is discharged directly into rivers or other water bodies due to the rapid development of industrialization and urbanization [1–3]. Of all the pollutants in the discharges that endanger ecosystem, heavy metals play a significant role [4, 5]. When accumulated to some extent in sediment, heavy metals such as Cu, Cd, Pb, Zn, Ni, Hg, and Cr can be toxic to plants, animals, humans, and aquatic life due to the characteristic of bioaccumulation, persistence, and environmental toxicity [1, 2, 6].

The heavy metals discharged in the water bodies through different sources would finally be enriched in the sediments by adsorption, complexation, flocculation, and sedimentation [7, 8]. Once the water environmental conditions change, the dynamic equilibrium of the water sediment interface will be broken, so that the heavy metals in the sediment will be transferred and transformed, and released to the overlaying water, which will lead to pollution of water quality [9–12]. The mechanism of migration and transformation of heavy metals can be summarized as ion exchange, dissolution, and desorption [13, 14]. Among the numerous influencing factors, pH is one of the main factors, and the effect of pH on the speciation of heavy metals is of great significance to the migration and transformation of metals [15]. The change of pH conditions in the system will have a certain impact on the migration and distribution of heavy metals [16]. Yang et al. studied the effect of the change on the speciation of heavy metal Cd, and the result showed that the different speciation of Cd varies with the change of pH and Cd content of carbonate fraction and Fe-Mn oxides fraction increases with pH increasing in the range pH 4.5–9.5 [17]. Appel and Ma found that pH is the main factor affecting the adsorption characteristics of heavy metals, which controls the solubility.
of hydroxides, carbonates, and phosphates of heavy metals and also affects the hydrolysis of heavy metals in sediments and organic matter, dissolved clay surface charge changes, and the formation of ion pairs [18].

In this paper, the Cd-, Ni-, and Cu-contaminated sediments in Xiaofu River (Zibo, China) were selected as objects to investigate the performance of metal release from the sediments in different pH. Considering different acidification or alkalinisation conditions of the river due to the discharge of domestic/industrial wastewater with some extent of treatment, and the accidental chemical spills, the whole pH 0–14 was selected. On the other hand, Visual MINTEQ software was used to predict and explain the pH leaching behavior of contaminants. The influence of pH value on the speciation of heavy metal in the sediments after leaching tests at different pH was studied by Tessier Sequential extraction [19].

2. Materials and Experimental Method

2.1. Sediment Sample Collection. The sediment samples were collected in December 2015 from the middle of the Xiaofu River (Zibo city, China). There had been a lot of industrial factories including printing and ceramic factories along the River (Zibo city, China). Where had been a lot of industrial factories and the sampling and materials in the laboratory were washed by 10% HNO3 and rinsed with ultrapure water. All the sampling and materials in the laboratory were washed by 10% HNO3 and rinsed with ultrapure water.

2.2. Leaching Test. The study researches the effect of pH on the leaching of Cd, Ni, Cu, and DOC from the contaminated sediment in the fresh water river. The pH using in the leaching test is from pH 0 to 14, using river water and deionised water as leachants. The pH leaching test was done according to the test method standard for leaching toxicity of solid wastes (GB 5086.2, China) [20]. 2.0000 ± 0.0005 g of sediments was placed in a volume of 250 ml conical flasks, adding leaching solution at the solid/liquid ratio of 1:10 (S/L, g·ml⁻¹) and leached at the conditions of oscillation and stewed for 16 h at room temperature. Two sets of experiments with deionised water and river water were performed with predetermined amounts of acid (HNO3) or base (NaOH) added to subsamples at 1 mol·L⁻¹. We use the pH 0–14 to simulate potential environment risks situations, such as the acid water leakage by accidents or sewage discharge of dying factories.

Each leachate liquid got from the end of the leaching test was filtered through a 0.45 μm pore size nitrocellulose filtration membrane. DOC in the sample was measured by TOC-VCPH (Shimadzu Total Organic Carbon Analyzer, Japan), and the concentrations of Cd, Ni, and Cu in the filtering samples was determined by AAS (TAS-990, Beijing Puxi company, China).

2.3. Modeling of Metal Leaching. Geochemical modeling for the release of metals was performed using the software Visual MININEQ (version 3.1). The parameters needed for model inputting included the maximum concentrations obtained from test method standard for leaching toxicity of solid wastes (GB 5086.2, China) [20], CO3²⁻, as well as the major components (Al³⁺, Ba²⁺, Ca²⁺, and Fe³⁺) and metal-binding ligands (PO₄³⁻, SO₄²⁻, and SO₃²⁻) of the sediment [21, 22]. Surface complexation and bindings to organic matter were considered using the available models in the software. Adsorption on Fe- and Al-(hydr-) oxides was taken into consideration, and the NICA Donnan model and the SHM were used to assess metal binding to organic matter. The amounts of Fe- and Al-(hydr-) oxides were determined in duplicate by the system of sodium dithionite-sodium citrate with NaHCO3 buffer method [23]. The amounts of humic acids (HAs) and fulvic acids (FAs) in the sediments were determined by the method of selective chemical extractions [24, 25].

2.4. Tessier Sequential Extraction Experiment. Tessier extraction method was used to extract heavy metals from the sediments and to analyze the speciation of heavy metals in the sediment [19]. The method divides the heavy metals into five kinds of combined speciation including the fractions of exchangeable, carbonates, Fe-Mn oxides, organic, and residual. The sediment samples after the leaching test with deionised water as leachant was measured by Tessier to determine the speciation changes of the metals at different pH.

3. Results and Discussions

3.1. Characterization of the Sediment Sample. The selective chemical extractions performed on the sediment show that it contains 10.14 ± 0.24 mg·g⁻¹ of Fe (hydr) oxides, 1.46 ± 0.03 mg·g⁻¹ of Al-(hydr) oxides, 120.9 ± 27.2 mg·kg⁻¹ of HAs, 340.5 ± 10.2 mg·kg⁻¹ of FAs, 3.518 mg·L⁻¹ of Cd, 120.846 mg·L⁻¹ of Ni, and 5.307 mg·L⁻¹ of Cu.

Three oxid (oxyhydroxides) and anoxic (sulphide) phases normally coexist at the depths of 10 cm in the sediments [26, 27]. The sediment samples obtained from Xiaofu River are black color, and their redox potential is about −30 mV; therefore, the sediments were supposed to be reduced sediment.

3.2. Metal Release at Different pH. The release of cations from solid matrices normally has a close relationship with the release of DOC [28]. Figure 1 shows that there is little difference in the release of DOC with the deionised water and the river water as leaching solutions, respectively. The release amount of DOC at pH 2–4 is high for both of the solutions, which is probably due to the high solubility of FAs at low pH [29]. DOC increases rapidly with pH at basic pH condition just because the negative charges on both organic matter and soil inorganic solid surfaces.

Figures 2–4 shows the release of Cd, Ni, and Cu at the different pH with deionised water and river water, respectively. The results indicate that the heavy metal leaching with deionised water and river water as leachants presents similar tendencies, only with a slightly greater release in the case of deionised water.

Figure 2 shows the release curve of Cd in sediments at different pH. The release amounts of Cd is between 10.2 and
27.3 mg·kg\(^{-1}\) at the whole pH 0–14 with the deionised water as leachant. Cd release amounts decrease as the pH increases at acid condition, but the reduced amounts are not so much. And also at the basic conditions, the release amounts of Cd is not bigger, probably because that Cd is generally pyritised to a few percent as a consequence of the precipitation of metal sulphide phase [30].

From Figure 3, the maximum leaching amount for Ni is observed in the pH 0–4, which can be explained by that the solid surfaces are positively charged and metal sorption is not steady. The release amount of Ni is between 80.5 and 140.1 mg·kg\(^{-1}\) at the whole pH 0–14 with the deionised water as leachant. Between pH 5–10, the Ni release amounts are lower. After pH 10, the release amounts increases as the pH increases with the same reasons to Cu, that is, the release of the organometallic complexes with metals increases leads to the increase of metal release at high pH. It is noted that the release amounts of Ni is lower in the sediment with deionised water as leachant than that in river water, probably because of low concentration of DOC in deionised water [31].

From Figure 4, the release tendency of Cu is similar with the release of DOC. The release amounts of Cu is between 6.1 and 30.8 mg·kg\(^{-1}\) at the whole pH 0–14 with the deionised water as leachant. The sorption of Cu is weak in low pH and is becoming bigger as the pH increases under pH 9. At basic conditions, Cu sorption becomes stronger because of its complexation with the organic matter in sediments [32, 33]. Therefore, the low release amounts of Cu could be seen at pH 5–9.

3.3. Geochemical Modeling of the Metal Release. Figures 5–7 show the geochemical modeling results for the pH leaching test using recycled water deionised and water as leaching solutions at different pH. For modeling purposes, the sum of Fe- and Al- (hydr-) oxides, due to the absence of a database for adsorption on aluminum (hydr) oxides, was considered as solid adsorbent. According to Figure 5, the result shows that Cd is not affected significantly by pH with an increase in acidity. The geochemical modeling tendencies of Cd using river water and deionised water as leaching solutions are similar, but the pH value is different when the peak valley appears. Because Cd speciation is considerably much more than other elements, it is bound in lithogenic minerals depending on the different sediment matrix [34]. Figure 6 is the modeled result for Ni which shows that the curves are nearly coincident with the two media as leaching solutions. At pH 9, the Ni releasing is the minimum. Figure 7 shows that there is a minimum release of Cu at neutral pH, just because that the simulation used SHM model which includes the role of HAs and FAs. The organic complexation of HAs and FAs and the adsorption to Fe- and Al- (hydr-) oxides can influence the metal leaching behavior.
3.4. Metals Speciation in Sediment Analysis. Figures 8–10 show that the speciation distribution of the same kind of metal at different pH values is similar in proportion and the distributions of different metal elements are different.

Figure 8 shows the contents of the various speciation of Cd at different pH after leaching tests with deionised water as leachants: residual > carbonate > Fe-Mn oxides > organic > exchangeable. At neutral pH, the content of residual fraction in the sediments is 238 mg·kg⁻¹, with the proportion of over 50%. It is originally slight toxic to the ecosystem. However, with the decrease of pH value, the speciation of Cd is easily transferring to the unsteady fractions. Compared to alkaline conditions, the residual fraction for Cd is obvious easily to form precipitate under acidic condition, especially in the range of pH 0–4. The results indicate that it is likely to cause water pollution due to heavy metal release when acidic liquid is discharged into the river due to wastewater drainage or accidents. Ca²⁺, Mg²⁺, K⁺, Na⁺, and other alkaline ions in sediment colloid adsorption are displaced due to the strong exchangeable capacity of H⁺ in leaching solution. Content of exchangeable fraction is almost close to 0, which indicates that the exchangeable speciation of Cd could enter the overlaying water in the leaching experiment.

The contents of different speciation of Ni at different pH after leaching tests with deionised water as leachants are shown in Figure 9. The exchangeable fraction is adsorbed on the surface of the sediment mainly by diffusion and outer complexation of nonobligatory, which is also easy to form insoluble precipitate of carbonate, and then fixed in the sediment. The exchangeable content of Ni decreases with the increase of pH value in the range of 0–5, and in the range of pH 6–14, the exchangeable fraction of Ni becomes larger indicating that strong acid condition is beneficial to improve Ni content of exchangeable in sediment. As the pH value decreases, the content of carbonate and Fe-Mn oxides fractions increases. Residual fraction is relatively stable in the sediments at different pH.

Figure 10 shows the change of speciation of Cu at different pH after leaching tests with deionised water as leachants. The speciation of Cu in the sediments changes significantly at pH 0–9, especially for Fe-Mn oxides fraction. With the increase of pH, the content of Fe-Mn oxides fraction increases, while carbonate and organic fractions decrease slightly and residual fraction is relatively stable. The result indicates that it is likely to cause Cu release from the sediments due to the discharge of acid wastewater from industries or incidents.

4. Conclusions

The leaching performance of heavy metal-contaminated sediments at different pH was investigated using river water and deionised water as leaching solutions. The results show that the release of DOC is significantly affected by pH. The change curve of leaching contents of heavy metal from sediments at different pH has a similar tendency with river water and deionised water as leachants. It is slightly greater when using deionised water at high pH values.

The separation contents of different metals in sediments are different at different pH. Under acidic conditions, Cd, Ni, or Cu are more likely to be released into the overlaying water. Modeling of metal leaching from sediments by Visual MINTEQ indicated that the metal leaching behavior by modeling fits well with the experimental values, so Visual MINTEQ is a useful model to determine metal species in
Figure 8: Contents of the various speciation of Cd at different pH after leaching tests with deionised water as leachant (5 fractions: S1-exchangeable, S2-Carbonate, S3-Fe-Mn oxides, S4-organic, S5-residual).

Figure 9: Contents of the various speciation of Ni at different pH after leaching tests with deionised water as leachant (5 fractions: S1-exchangeable, S2-Carbonate, S3-Fe-Mn oxides, S4-organic, S5-residual).

Figure 10: Contents of the various speciation of Cu at different pH after leaching tests with deionised water as leachant (5 fractions: S1-exchangeable, S2-Carbonate, S3-Fe-Mn oxides, S4-organic, S5-residual).
solution over a large pH range. The results would be helpful to risk assessment of the metal release in the heavy metal-contaminated sediments in rivers or lakes at some conditions such as emergency wastewater drainage or accidental spill.

Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments
This research was supported by Natural Science Foundation of Shandong Province (no. ZR2018ME045), Shandong Provincial Department of Housing and Urban Rural Construction (no. 2017-K2-002), Foundation of Remediation of Contaminated Sediment in Shandong Province (nos. 2017-HC2BLY-003 and SDHBYF-2012-14), Shandong Key Scientific and Technical Innovation Project (no. 2018YFJH0902), and Research Project of Shandong Environmental Protection Department (no. SDDPPS2018C(402001)006). Yanhao Zhang was very grateful for the support of China Scholarship Council.

References


