In-situ stabilization of Pb, Zn, Cu, Cd and Ni in the multi-contaminated sediments with ferrihydrite and apatite composite additives

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ABSTRACT

Three additives were evaluated for their effectiveness in the attenuation of Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+} in contaminated sediments. Apatite, ferrihydrite and their composite were applied to the sediments. For the remediation, BCR, SEM/AVS and TCLP were adopted as the evaluating method and comparison of their results were used for the first time to test in-situ stabilization effect. The results showed that after 5 months composite treatment, more than 70% Pb^{2+}, 40% Zn^{2+}, 90% Cu^{2+}, 50% Cd^{2+} and 80% Ni^{2+} was immobilized in oxidizable and residual phases, respectively. Compared to untreated sediment, Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+} in residual fraction increased 20%, 10%, 10%, 10% with composite treatment after 5 months, respectively. ΣSEM/AVS ratio declined from 12.6 to 9.3, in addition, composite treatments reduced the leaching of Pb^{2+} and Zn^{2+} from $10.6\,mg\,L^{-1}$ and $42.5\,mg\,L^{-1}$ to $5.4\,mg\,L^{-1}$ and $24.1\,mg\,L^{-1}$ in the sediment by TCLP evaluation. Meanwhile, apatite and ferrihydrite composite additives lowered the bioavailability and toxicity of sediments as well. Ferrihydrite had a positive effect in controlling the bioavailability and toxicity of heavy metals because it effectively retarded the oxidation of AVS in sediment.

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1. Introduction

Sediments are often the sinks of metal contaminants in aquatic systems [1]. Contamination of sediments by metals and organic compounds is now widespread and well documented in numerous Chinese rivers and coastal waters [2,3]. Using mineral additives to remediate the contaminated sediments is getting increasingly public recognition as the cost of cleaning and the number of contaminated sediments has steadily increased over the past decades [4,5].

In situ stabilization is a technique whereby an additive is incorporated and mixed with a contaminated soil or sediment. Just like other in-situ methods (e.g. natural attenuation, in-situ capping and in-situ confinement), it has many advantages such as reducing the risk of worker exposure during the remediation process as well as being less expensive and disruptive to ecosystems than conventional ex-situ methods [5]. Toxic metals are bound to the additive, which changes the chemical speciation of trace metals, thus reducing their leaching and bioavailability.

As an additive, mineral apatite has been shown to be the most economical and effective choice for the remediation of contaminated sites due to their ready availability and low cost. Its stabilization mechanisms include precipitation, surface complexation, ion exchange and the formation of amorphous solids [6,7]. However, its disadvantages and limitations in remediation process also appeared: (1) apatite is extremely effective at immobilizing Pb^{2+} but less effective for Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+} [8–12]; (2) apatite addition to sediment possibly induces the desorption of contaminants and enhances the mobility of non-target heavy metals [13]. In fact, many contaminated sites contain manifold heavy metals simultaneously, which commonly posses different chemical properties controlling their mobility and toxicity. As such, no single additive is expected to immobilize all inorganic contaminants. Therefore, a composite additive besides apatite is needed to immobilizing co-existed heavy metals in multi-contaminated sediment. Iron is an excellent metallic material for environmental remediation because it is a strong reducer, non-toxic and inexpensive and their reaction rates are limited by mass transport [14]. Ferrihydrite is an iron oxy-hydroxide known to play an important role in the natural environment. Its large surface area, strong adsorptive properties, high adsorptive capacity and low cost make it an attractive material, which may enhance contaminant removal by co-precipitation and adsorption [15–19]. A range of metals sorbed onto ferrihydrite by formation of inner-sphere sorption

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complexes or co-precipitated with the Fe(II/III)-oxyhydroxide., as verified for Cr, As, Se, Cd, Zn, Cu and Pb [20–23]. This removal or stabilization process is generally more desirable than adsorption onto the surfaces.

Having more than one stabilizing additives acting on a contaminant in the sediment would lead to a gradual and lower contaminant release. This would diminish the tendency of the amended sediments from releasing the contaminants in response to a drastic environmental change. For instance, apatite and zero-valent iron have been taken as a composite additive to immobilize the metals of sediments in previous studies, which significantly reduced the aqueous Ce^{2+}, Co^{2+} and Pb^{2+} concentrations [24]. With respect to the characteristic of apatite and ferrihydrite, the author imagined that, if we could combine apatite with ferrihydrite to remove heavy metals without any negative effect on each other, thus a synergistic and superposition effect on stabilizing of Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+} in the multi-contaminated sediments would be anticipated.

The USEPA guidelines of Sediment Quality Guideline for remediation of metal contaminated sediments are based on total metal concentrations [25]. This can be misleading because digestion techniques are too powerful to actually represent the portion of metals or to indicate the mobility of metals in the sediment that may be re-suspended to the overlying water. Metals are bound with different geochemical fractions in sediment, including the operationally defined carbonate, reducible, organic matter and sulfide phase and residual phases [26–29]. The eco-toxicity and mobility of metals in the environment depends strongly on their speciation or methods of binding rather than the total element contents [30]. Therefore, the objective of this paper is: (1) evaluate the effect of immobilization on heavy metals in the sediments of Suzhou creek by using apatite and ferrihydrite composite additives; (2) use BCR speciation analysis, SEM (Simultaneously Extracted Metals)/AVS (Acid Volatile Sulfide) ratio and TCLP results as the evaluating methods to test the effect of additives on controlling the mobility and toxicity of heavy metals in sediment and to compare the short- and long-term durability of their effects in the process of in-situ stabilization.

2. Materials and methods

2.1. Sediment sample

Sediment grab samples were collected by hand from the top 10–15 cm of the sediment and placed into plastic containers immediately with an airtight cover sealing. The samples were then taken to the lab within 2 h and cooled at 4 °C in a refrigerator.

A particle size distribution of sediment was carried out by sieving the sediment through the sieves ranging from the sizes of 14 mm to 425 μm. The soil fraction that passed through the 425 μm sieve was further collected for particle size analysis using Malvern Microplus Mastersizer. The weight percentage of organic matter and carbonate content in sediment were estimated by the means of LOI (Loss On Ignition). The element contents of C and N were determined by CHNS/O Elementary Analyzer (PerkinElmer 2400 Series II). Physical and chemical properties of the sediments are summarized in Table 1.

2.2. Background of contamination in Suzhou Creek

Suzhou creek is a typical tidal river in Shanghai, China. Due to past industrial activities, sediment is heavily contaminated with metal cations, mainly Pb^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+} and Cu^{2+}. The contaminants of Suzhou creek mainly existed in the middle reach and all of the samples investigated in this study were taken from it. The total

Table 1
Physical and chemical properties of sediments.

Sediment property	
Water content (%)	32
Particle size distribution (%)[*]	
Sand	15.6
Silt	80.9
Clay	3.5
pH[*]	7.01 ± 0.10
ORP (mV)[*]	−121 ± 27
Organic matter content (%) 450 °C[*]	2.95 ± 0.03
Inorganic matter content (%) 850 °C[*]	3.62 ± 0.05
C[*] (%)	2.04 ± 0.23
N[*] (%)	3.01 ± 0.01
CEC (cmol/kg) at natural pH[*]	11.48 ± 0.14
AEC (cmol/kg) at natural pH[*]	4.69 ± 0.37

[*] Average ± standard deviation (n = 3).

concentration of Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+} in sediment sample was 2647 mg kg^{-1}, 2053.4 mg kg^{-1}, 246 mg kg^{-1}, 23.4 mg kg^{-1} and 217.8 mg kg^{-1}, respectively.

2.3. Experimental procedure

All solutions were prepared with ultrapure DI water and reagent-grade chemicals. All filters were polycarbonate unless otherwise stated. Three replicates of all batch equilibrations were conducted to estimate variability. The amount with 600-g (dry wt) samples of field-moist sediment was placed in 2 L batch reactors.

Considering the high contamination of Pb and Zn in sediment and according to previously fundamental study on the adsorption capacity of apatite and ferrihydrite, we choose 5% as dosage rate in our study. Three proportions of immobilizing additives were added to each reactor, 5 wt% apatite, 5 wt% ferrihydrite, 5 wt% apatite + 5 wt% ferrihydrite.

2.4. Sequential extraction and SEM/AVS analysis procedure

The speciation of trace metals in sediment was quantified using a modified BCR. The detailed procedure for the sequential extraction has been described by Rauret et al. [28,29]. SEM (Simultaneously Extracted Metals)/AVS (Acid Volatile Sulfide) had been endorsed as the best technology for assessing the bioavailability of five important toxic metals (Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}). The procedures for AVS and SEM analysis were adopted from the method described by Allen et al. [31].

2.5. TCLP procedure

TCLP is commonly used either to determine whether a waste is hazardous or to determine whether a treated waste meets the treatment standards for land disposal. This test provides useful information on the potential leachability of metals in sediments under moderately (pH 4.9) or strongly (pH 2.9) acid conditions. In general, the amounts of metals extracted with the solution were greater than those obtained under less acidic conditions. In order to test the potential leachability of metals in treated sediment and to evaluate the long-term stable effect of additives on in-situ stabilization, strongly acid solutions (pH 2.9) was chosen in this study. TCLP tests were performed using US EPA Method 1311 [32]. This procedure uses a 5.7-ml aliquot of glacial acetic acid (pH 2.97 ± 0.03) in 500 ml of deionized water and 64.3 ml of 1N NaOH, diluting to a volume of 1 L. A 100-ml aliquot of this solution was used to extract Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+} from the sediment samples, each weighing 5 g.
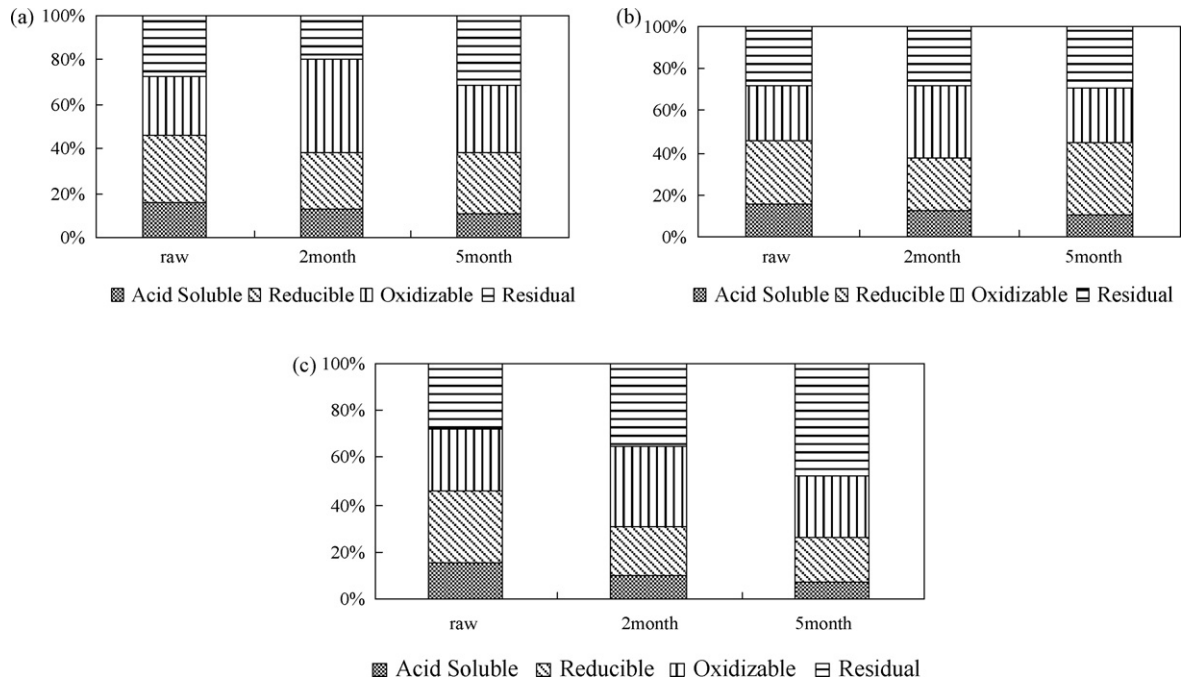
Fig. 1. Pb^{2+} speciation after the treatment of different additives (a) apatite; (b) ferrihydrite; (c) apatite + ferrihydrite.

3. Results and discussion

3.1. Speciation evolvement of heavy metals by composite additives

Because of the historically industrial pollutants discharge, contamination of heavy metals in sediments of Suzhou Creek is a tough problem. The previous studies have proved that Pb, Zn, Cu, Cd and Ni were the main metal pollutants in the sediment and the speciation changed with their location, depth and season [33]. Thus, speciation analysis of heavy metals after using additives will be necessary, and the effect of three additives (ferrihydrite, apatite and composite additives) is compared as below.

3.1.1. Lead

From Fig. 1, it can be found that the effects of single and composite additives on the speciation transformation were quite different.

When the apatite was used as the additive, acid soluble fraction maintained at about 16.0%. Reducible fraction reached the 24.6% after 2 months, but its proportion had nearly changed during 2–5 months. Oxidizable fraction increased to 41.5% and kept steady at last 5 months. This variation was related with the increase of Eh. Residual fraction initially maintained stable and it continued to increase to 21.8% after 5 months. The increasing of residual fraction was mainly from the decreasing of reducible fraction and oxidizable fraction.
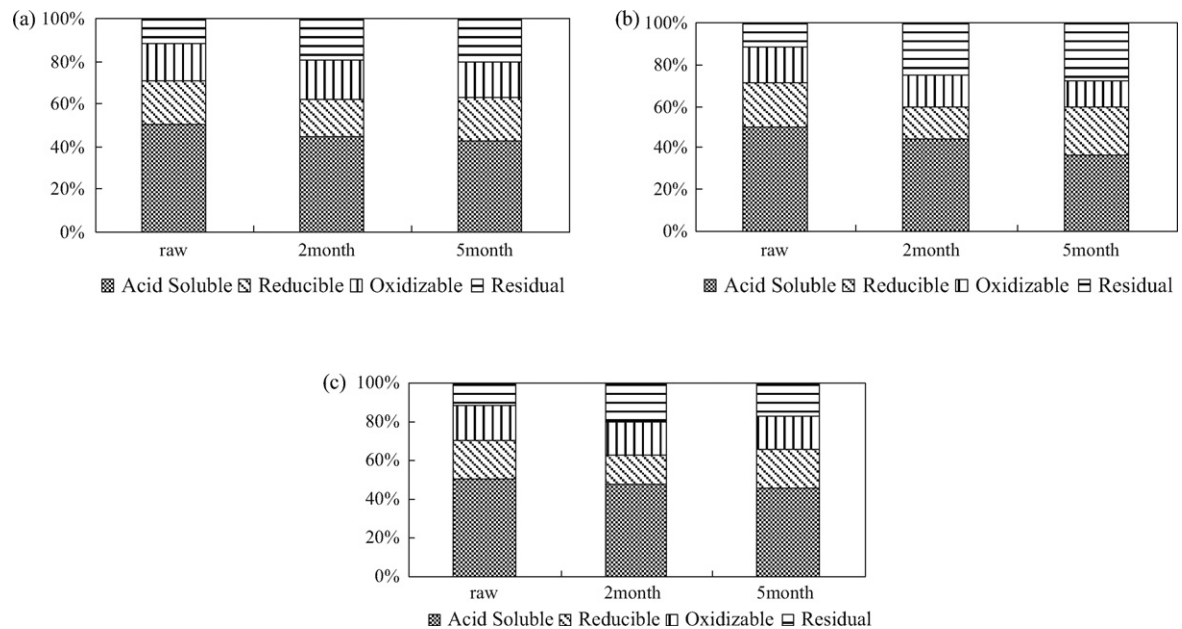

Fig. 2. Zn^{2+} speciation after the treatment of different additives (a) apatite; (b) ferrihydrite; (c) apatite + ferrihydrite.
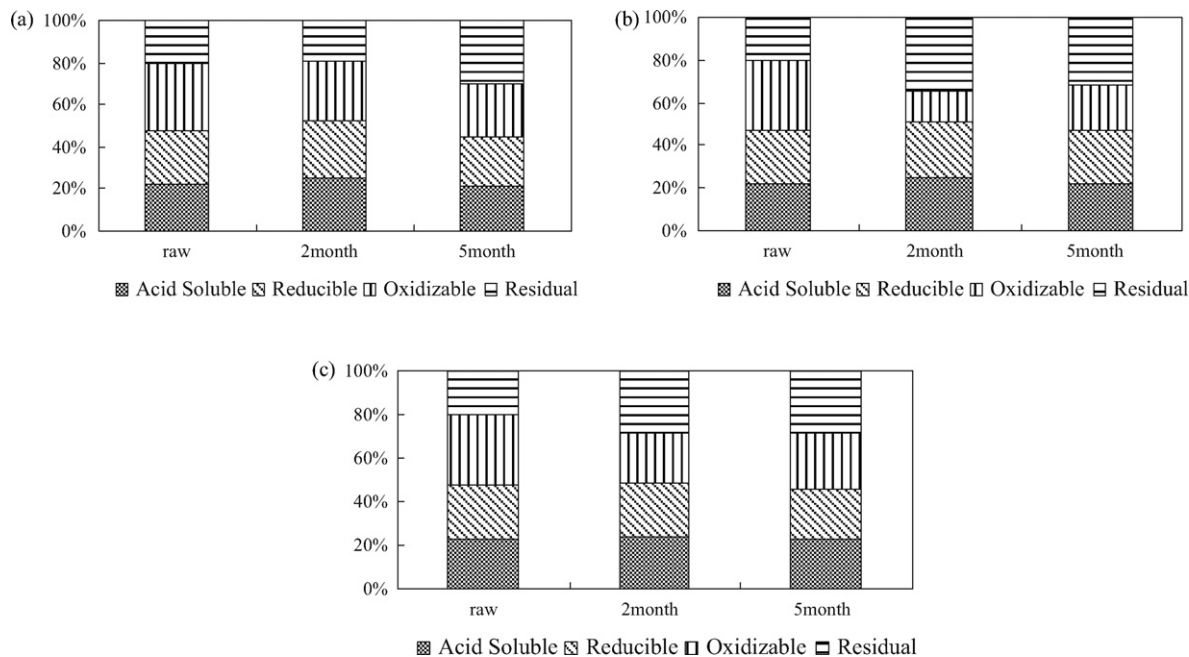
Fig. 3. Cd^{2+} speciation after the treatment of different additives (a) apatite; (b) ferrihydrite; (c) apatite + ferrihydrite.

When ferrihydrite was added, oxidizable fraction increased about 20% after 2 months. Residual fraction changed little and it can easily be found that ferrihydrite had not pushed the increase of residual fraction proportion from the observation of 5 months.

When the composite additives were added, a satisfactory effectiveness appeared after 2 months. Acid soluble and reducible fraction decreased by 8% and 10.5%, respectively. Oxidizable fraction barely changed. Relatively, residual fraction increased by 20% and this effect maintained after 5 months. It can be drawn that ferrihydrite enhanced the effectiveness of apatite on stabilization of Pb in the sediments. It also should be observed that because the additives changed the sediment-aquatic environment in a short-term, metal speciation varied a lot in the initial 2 months.

3.1.2. Zinc

From Fig. 2(a), it can be observed that Zn^{2+} in residual fraction increased by 9% after 5 months when apatite was added. The effect of ferrihydrite was shown in Fig. 2(b), the most obvious change was caused by the residual fraction. Zn^{2+} in the residual fraction increased by 16% after 5 months. When composite additive was added, Zn^{2+} in the residual fraction increased by 10% after 5 months and Zn^{2+} in the oxidizable phase dropped slightly in whole process and no obvious change was found from Fig. 2(c). Apparently, it can be found that no synergic effect of apatite and ferrihydrite was found in immobilizing Zn^{2+} comparing to that of Pb^{2+}. In the whole process, the reducible and oxidizable fractions were quite stable and no great changes were found in these two phases.
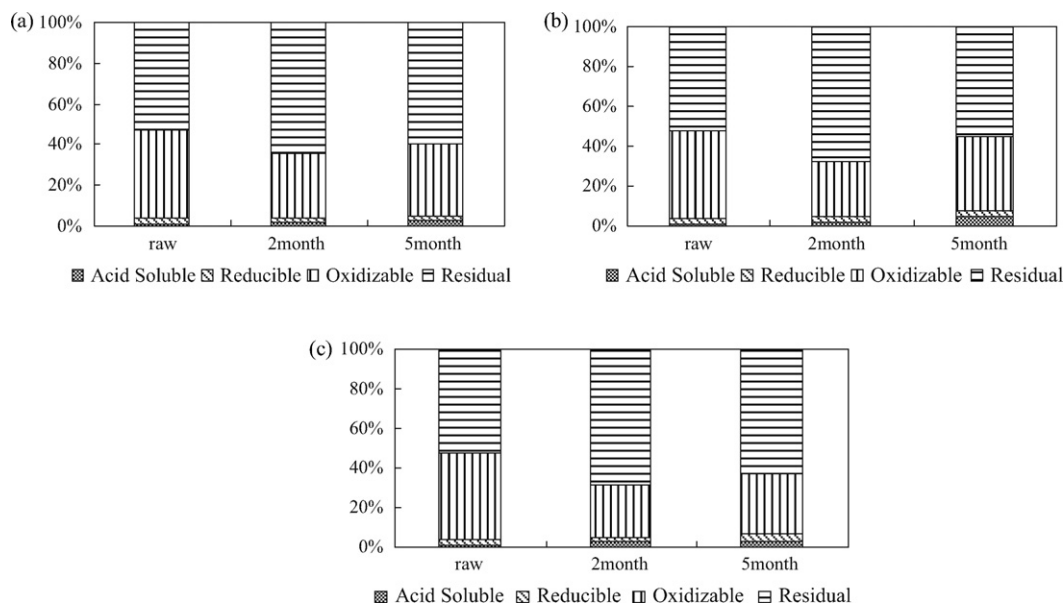

Fig. 4. Cu^{2+} speciation after the treatment of different additives (a) apatite; (b) ferrihydrite; (c) apatite + ferrihydrite.
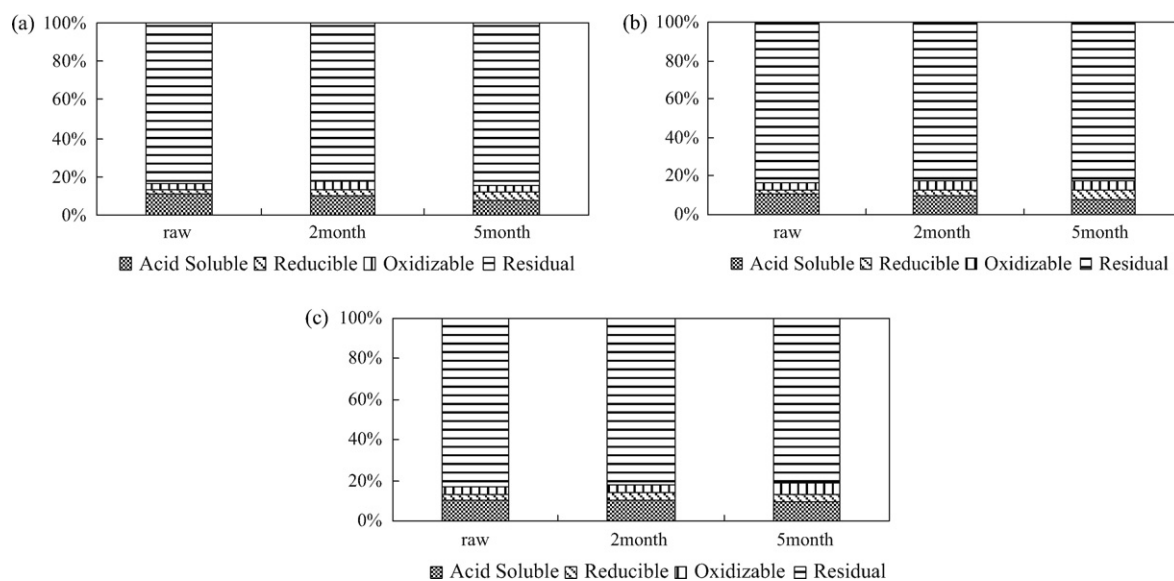
Fig. 5. Ni^{2+} speciation after the treatment of different additives (a) apatite; (b) ferrihydrite; (c) apatite + ferrihydrite.

3.1.3. Cadmium

From Fig. 3(a) it can be found that when apatite was added, Cd^{2+} in the residual fraction had an increase trend by about 10% and the oxidizable fraction decreased by about 8% after 5 months. The reducible fraction had little change. As for the acid soluble fraction, it kept stable during the whole process. From Fig. 3(b), it can be found that when ferrihydrite was added, there was no obvious change regarding metal speciation which meant ferrihydrite had little effect on immobilizing Cd^{2+}.

From Fig. 3(c), it shows a relatively better effect of the composite additives. The acid soluble fraction varied within the range of 2% and reducible fraction had barely changed. The oxidizable fraction continued to decrease, and reached the minimum in the 2nd month. Relatively, the residual fraction increased more than 10% after 5 months.

3.1.4. Copper and nickel

From Fig. 4, it can be seen that the speciation of Cu^{2+} was mainly stabilized in the oxidizable and residual fraction. It meant that all the additives would not affect the speciation proportion of Cu^{2+}. Carbonates, phosphates and clays can keep Cu^{2+} low mobility in the sediment by the chemisorption. Actually, Cu^{2+} would distribute between these two fractions and maintain stable. The mobility and toxicity of Cu^{2+} was greatly reduced, meanwhile, the exchange with upper water was limited. Thus, it would not be harmful to the sediment.

The speciation of Ni^{2+} was stabilized in the residual fraction (Fig. 5). The carbonate fraction proportion increased partly at first. But the acid soluble and reducible fraction did not disappear after 2 weeks, and residual fraction increased to nearly 80% when each additive was added.

3.2. Support of SEM/AVS results

SEM/AVS had been endorsed as the best technology for assessing the bioavailability of five important toxic metals (Pb, Zn, Cu, Cd and Ni) [31].

SEM/AVS results showed that composite additives had a satisfactory result in controlling the bioavailability and toxicity of heavy metals comparing to apatite, ferrihydrite alone, respectively. Its SEM/AVS ratio declined from 12.6 to 9.3 (see Table 2) while ferrihy-

drite adding also decreased the SEM/AVS ratio, which was far from the composite results. On the contrary, when apatite was added, metal bioavailability in sediment became more active (see Table 2).

From Table 2, it can be seen that when apatite was singly added, it caused a great decrease of AVS from 3.4 to 1.6. Although the concentration of heavy metals (ΣSEM) declined, the results of ΣSEM/AVS still inclined from 12.6 to 18.8.

From Table 2, it can be found that when ferrihydrite was added, ΣSEM decreased from 42.1 to 28.7, but AVS of the sediment did not decrease obviously (from 3.4 to 2.6). Ferrihydrite had effectively prevented the reduction of volatile sulfur compounds, therefore the results of ΣSEM/AVS did not increase rapidly. If not, it would lead to a dramatic increase of the bioavailability and toxicity. Pb^{2+} and Zn^{2+} were affected the most after ferrihydrite was added. Their concentrations decreased from 10.7 μmol g^{-1} and 28.9 μmol g^{-1} to 6.7 μmol g^{-1} and 20.4 μmol g^{-1}, respectively. The other metals changed little, such as Ni decreasing merely from 1.1 μmol g^{-1} to 0.3 μmol g^{-1}, and Cd (0.084 μmol g^{-1}), Cu (1.2 μmol g^{-1}) maintaining at the original level.

From Table 2, we can see that a satisfactory result has been achieved. When ferrihydrite and apatite were added together, the concentrations of heavy metals decreased much more, such as the concentration of Pb decreasing from 10.7 μmol g^{-1} to 5.4 μmol g^{-1}. ΣSEM decreasing from 42.1 to 25.5, AVS of the sediment did not decrease noticeably (from 3.4 to 2.7), and the result of ΣSEM/AVS was changed from 12.6 to 9.3, which suggests that using ferrihydrite or apatite alone cannot reduce the bioavailability and toxicity of metals.

Thus, the composite additives of ferrihydrite and apatite did not only have a good effectiveness on the stabilization of heavy metals in the sediments, but decreased the bioavailability and toxicity as well. Meanwhile, the concentrations of heavy metals simultaneously declined, such as the concentration of Zn decreasing from 28.9 μmol g^{-1} to 19.0 μmol g^{-1}, Ni from 1.1 μmol g^{-1} to 0.2 μmol g^{-1}.

3.3. Comparison of SEM/AVS with BCR results

When 5% apatite was added, it increased the redox potential in sediment, which made the AVS declined sharply. This change made Pb and Zn, formerly binding with sulfide phase, release into
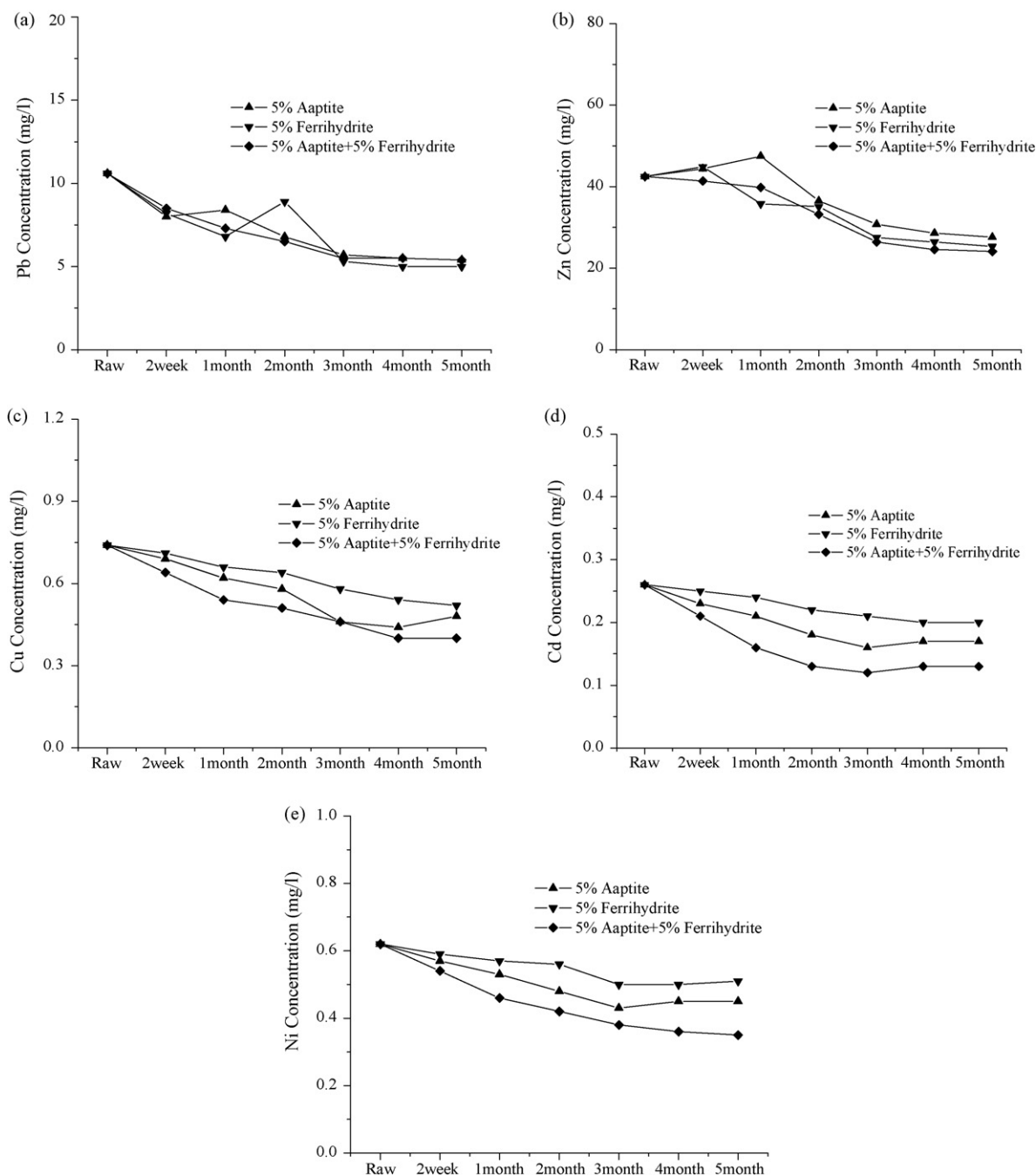
Table 2
SEM/AVS results after 5 months treatment by three additives.

	Concentration (μmol g^{-1} dry)[*]						ΣSEM	ΣSEM − AVS	ΣSEM/AVS
	Cd	Cu	Ni	Pb	Zn	AVS			
Raw	9.5×10^{-3}	1.3	1.1	10.7	28.9	3.4	42.1	38.7	12.6
5% Apatite	8.2×10^{-3}	0.9	0.3	6.7	21.4	1.6	29.5	27.9	18.8
5% Ferrihydrite	8.4×10^{-3}	1.2	0.3	6.7	20.4	2.6	28.7	26.1	11.1
5% Ferrihydrite +5% apatite	8.2×10^{-3}	0.8	0.2	5.4	19.0	2.7	25.5	22.8	9.3

[*] Average ± standard deviation ($n = 3$).

aquatic system again. BCR results indicated that 5% apatite adding increased the percentage of Pb, Zn in the acid soluble phase in two weeks, which was mainly from the AVS drop. However, as part of the oxidizable phase, the decreasing of AVS did not change the pro-

portion of heavy metals in the oxidizable fraction. Pb and Zn in the oxidizable phase maintained in a quite stable state in the whole process. Loss of AVS did not influence the Pb and Zn binding with oxidizable phase. This result demonstrated that although apatite

Fig. 6. TCLP concentrations after the treatment of different additives (a) Pb; (b) Zn; (c)Cu; (d) Cd; (e) Ni.

enhanced the bioavailability and toxicity of Pb and Zn in the sediment in a short time, Pb and Zn still stay in a relatively stable state. Especially, apatite did had a good stabilization on Pb, whose the oxidizable and residual fraction percentage was more than 60% after 5th month.

Compared with apatite in removal of Pb and Zn., ferrihydrite behaved quite different. When ferrihydrite was added, it did not greatly influence the transformation of AVS. The results showed that AVS only drop 0.77, which was far less than that of apatite. This may contribute to ferrihydrite itself, which effectively retard the oxidation of AVS in sediment. Fe(II) was oxidized to Fe(III). Here, ferrihydrite not only adsorbed the heavy metals but also afforded the electron in sediment. SEM-Pb/AVS and SEM-Zn/AVS declined from 3.2, 8.6 to 2.6 and 7.9, respectively. This result showed that ferrihydrite had a good impact in reducing the bioavailability and toxicity of heavy metals in sediment. BCR results showed that no obvious effect was found on ferrihydrite in immobilizing of Pb. However, residual fraction of Zn increased to 16% after 5 months, which mainly came from the decreasing of acid soluble and oxidizable phases.

From Table 2, Figs. 1(c) and 2(c), we can see that SEM-Pb/AVS and SEM-Zn/AVS declined from 3.2, 8.6 to 1.9, 6.9, respectively. The residual fraction of Pb, Zn reached 24%, 20%, respectively, after 5 months stabilization action. It can be concluded that apatite and ferrihydrite did not prevent each other on stabilizing heavy metals in their role. On the contrary, apatite + ferrihydrite composite addition had a synergic effect both on controlling and stabilizing of the bioavailability and toxicity of heavy metals.

3.4. The leaching of heavy metals by TCLP evaluation

The United States Environmental Protection Agency Land Disposal Restrictions (LDR) Program sets treatment standards for the wastes banned from land disposal. The treatment standards are often based on the constituent concentrations in the Toxicity Characteristic Leaching Procedure (TCLP) extract from the wastes. Thus, TCLP is commonly used either to determine whether a waste is hazardous or to determine whether a treated waste meets the treatment standards for land disposal. The procedure is designed to study the mobility of both organic and inorganic substances present in liquid, solid and multi-phase wastes and thus, must be considered in the development of treatment technologies.

The aim of stabilization is to form new, less soluble mineral phases that are more geochemically stable in the leaching environment. The TCLP test can provide information on the potential leachability of metals in the sediments under strongly (pH 2.9) acid conditions, thus to further evaluate the long-term effect of stabilized sediment after 5 months treatment.

The result as shown in Fig. 6(a) and (b) that before treatments, TCLP-extractable Pb concentrations in the raw sediment far exceeded $5\,mg\,L^{-1}$ critical level of hazardous waste while TCLP-extractable Cd concentration was below the level ($1\,mg\,L^{-1}$).

The concentration of Pb was $10.6\,mg\,L^{-1}$ in the raw sediment. After 5 months treatment, initial concentration of Pb was reduced to below $5\,mg\,L^{-1}$ by composite additive. The results meant that more than 50% weakly-bounded Pb converted from non-stable phase to relatively stable phase, which was in accordance with the BCR results. The transformation of speciation was mainly from the acid soluble to the oxidizable fraction. Apatite and composite additive additives were effective in reducing the TCLP Pb to below the critical level in the sediment samples (Fig. 6a).

As for Zn, the concentration was $42.5\,mg\,L^{-1}$ in the raw sediment, which was quite unstable comparing to Pb. The leaching results showed that the sequence of stabilization effect was composite > ferridhydrite > apatite. 44% weakly-bounded Zn was

reduced from leaching solutions after composite additives treatment.

Mean concentrations of Cu, Cd and Ni were relatively low in all untreated sediment leachates(<1 mg L^{-1}). Above 80% Cu and Ni stay in the oxidizable and residual phases so that their initial leaching concentration was quite low ($0.74\,mg\,L^{-1}$ and $0.62\,mg\,L^{-1}$). Therefore, there was only about 20% Cu and 10% Ni reduction in leachates.

Total concentration of Cd in untreated sediment was $0.26\,mg\,L^{-1}$, which was below TCLP critical level (<1 mg L^{-1}). However, about 25% Cd was mobile and unstable in the sediment. TCLP results showed that 50% reduction was found in composite attenuation leachates after 5 months treatment.

In brief, composite additives with apatite and ferrihydrite showed its good stabilization effect on immobilizing Pb, Zn, Cu, Cd, Ni multi-contaminated sediment. Around 50% Pb, Zn, Cd were decreased in their leaching solutions and the concentration of Pb, Cd was below the TCLP level. Meanwhile, concentration of Cu and Ni in leaching solutions was also decreased to a relatively low level and more than 20% reduction in their leachates was found. TCLP demonstrated that a proportion of heavy metals converted from unstable form to stable phases after a long-term (5 months) attenuation. These results are of great significance with respect to the immobilization of the sediment, because they showed that apatite and composite additive additives can amend the sediment to a material that would be considered non-hazardous.

4. Conclusions

The effect of composite additives on immobilization of heavy metals in the sediments of Suzhou creek was investigated and the following results were achieved:

1) Composite additive had a good effect on in-situ stabilizing Pb, Zn, Cu, Cd, Ni in multi-contaminated sediment. Compared to untreated sediment, Pb^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} in residual fraction increased by 20%, 10%, 10% and 10% with composite treatment after 5 months, respectively.
2) $\Sigma SEM/AVS$ results showed that its ratio declined from 12.6 to 9.3 with composite adding. Apatite additive made the ratio increased, thus increasing the mobility and bioavailability of heavy metals in the sediment. Meanwhile, ferrihydrite had a positive effect on controlling the $\Sigma SEM/AVS$ ratio because it effectively retarded the oxidation of AVS in sediment.
3) Composite additives not only had a good effectiveness on the stabilization of heavy metals in the sediments but lowered the bioavailability and toxicity of sediments as well after 5 months additive treatment.
4) TCLP results demonstrated that apatite, ferrihydrite and their composite treatments had a relatively long-term stabilization effect on multi-contaminated sediment. Around 50% Pb, Zn and Cd were decreased in their leaching solutions and the concentration of Pb and Cd was below the TCLP level. Meanwhile, concentration of Cu and Ni in leaching solutions was also decreased to a relatively low level and more than 20% reduction in their leachates was found.

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