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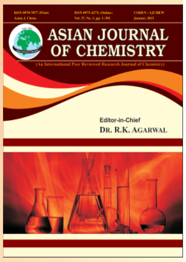

Releasing and Transforming Characteristics of Heavy Metals in Sediments of Huludao Estuary, China

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Releasing and transforming characteristics of heavy metals in the sediments collected from Huludao estuary, China were investigated under varying pH conditions. Equilibrium state of releasing and reabsorbing was reached after 12 h and addition of hydroxyapatite reduced releasing of heavy metals with higher effect on Cu and Pb and to a lesser degree, on Zn and Cd. The hydroxyapatite spiking enhanced transforming of Cu, Zn, Pb and Cd from exchangeable and carbonatic phases to relatively stable phases, especially at pH 4 and 5. These pH values reduced the structural destroy of hydroxyapatite as compared to pH 3 and enhanced the dissolution of metals as compared to pH 7 and 9. The XRD, FTIR and SEM analysis results furthermore corroborated the conclusion that better hydroxyapatite effect could be obtained at pH 4 or 5.

Keywords: Sediments, Heavy metals, pH, Releasing, Transformation, Hydroxyapatite.

INTRODUCTION

With the rapid industrialization and economic development in coastal region, heavy metals are continuing to be introduced to estuarine and coastal environment through rivers discharge, oceanic dumping and aeolian processes[1-3]. Sediments are effectively sink for trace metals in marine and estuarine ecosystems, but also act as a source of metals for aquatic organisms[4-6]. The former studies found that almost more than 90 % of heavy metals existed in aquatic systems are bound to suspended particles and sediments[7]. However, these do not mean that these heavy metals are permanently removed from the aquatic system. If the environmental conditions (such as redox, salinity, pH, DOC, *etc.*) were changed, the accumulated metals could be remobilized[8].

Many techniques including excavation, extraction and disposal procedures as well as stabilization have been used to improve aquatic safety and insure human health. The immobilization techniques for soils and sediments are typically less expensive and disruptive to functioning ecosystems. Such techniques are based on a fundamental understanding of the natural geochemical processes affecting the speciation and fate of heavy metals and enhance the natural attenuation mechanisms controlling metals migration, bioavailability and toxicity. Previous studies have generally focused on reducing the mobility of heavy metals in contaminated soils[9-11], as well as sediments by using hydroxyapatite[12,13], which was proved as an effective reagent for immobilization. In order to investigate mechanism of hydroxyapatite effect on immobilization of heavy metals, some studies about the effect of pH on heavy metal sorption on mineral apatite were carried out[14,15]. But these experiments were all performed in a relatively uncomplicated system which was composed of metallic ions and solid hydroxyapatite as well as some other ions and did not include soil or sediment particulates. On the other hand, the system consisting of not only heavy metals and solid hydroxyapatite but also soil or sediment particulates was also existed and used to investigate efficiency as well as mechanism of hydroxyapatite on metal immobilization, but pH values of these systems were not adjusted and controlled and the effect of pH on hydroxyapatite effect was not determined[11-13]. The objective of the present study was to evaluate the effectiveness of hydroxyapatite at Cu, Zn, Pb and Cd releasing and transforming in a complicated system which was composed of metallic ions, solid hydroxyapatite as well as sediment particulates under varying pH conditions.

EXPERIMENTAL

Huludao City (40°56'N, 120°28'E) lies along the coast of western Liaoning Province, Northwest of Liaodong Gulf, with obviously continental climate and distinctly seasonal difference. The primary industries of Huludao City are petrochemical industry, nonferrous metallurgy, mechanical shipbuilding and energy power. Jinxi Chemical Factory and Huludao Zinc Plant (the largest zinc smelting plant in Asia) are main industrial enterprises in Huludao City. Wuli river, Cishan river and

Liangshan river are three freshwater rivers flowing through Huludao City strongly affected by industrialization. The sampling site was chosen alongshore the Longwan District of Huludao City, where is the estuary of Wuli river, Cishan river and Liangshan river.

Surficial sediments, approximately 5 cm in depth from the surface, were collected with a plastic scoop and stored in polyethylene bags. During sampling, 4 sub-samples approximately 20 cm from each other in distance were obtained and mixed into one homogeneous sample. Then the particulate samples were transported to the laboratory, getting rid of most of water by filtering and air-drying. The agglomerates in the sample were broken and grounded through a mortar. Particulates with diameter of larger than 0.85 mm were discharged by sieving. All further analyses were performed on the particulates with diameter of already less than 0.85 mm.

Hydroxyapatite was spiked to the sediments at a molar rate of 6:5 (phosphorus:metal). Then deionized water was added to particulate samples at a weight rate of 1:5. The pH values of suspensions were adjusted to 3, 4, 5, 7 and 9 by using 0.01 mol/L HNO_3 and 0.01 mol/L NaOH. Suspensions was continuously mixed with magnetic stirring apparatus at the constant water content and equilibrated over a period of 7 days at room temperature. Slurry samples of 15 mL were collected at 20, 60, 120, 150 and 180 min, 6, 9, 12, 24, 36, 48 and 60 h, 72, 96, 5, 6 and 7d and then passed through a membrane filter with a pore size of 0.45 μm. Metals and phosphorus in the supernatant solution were determined separately *via* FAAS (AAnalyst400, Perkin Elmer, USA) or GFAAS (AAnalyst600, Perkin Elmer, USA) and ultraviolet spectrophotometer (UV-2102 PCS, UNICO (Shanghai) Instruments Co., Ltd, China).

Supplement of deionized water was terminated after 7 days and the slurry was stirred continuously for another 7 days in order to volatilize and eliminate water from particle samples. Then the wetted particulate samples were air-dried for 16 days for further determination of species distribution of heavy metals.

Fractionation of heavy metals was carried out using the sequential extraction procedure[16]. All the five operationally defined binding fractions (exchangeable, bound to carbonates, bound to Fe/Mn oxides, bound to organic materials and residues) could then be determined.

Detection method: Digestion of $HCl-HNO_3-HClO_4$ followed by a flame atomic adsorption spectrometer (AAnalyst400, Perkin Elmer, USA) analysis was applied to measure Cu, Zn, Pb and Cd in the solid particles. An environmental scanning electron microscopy (PHILIPS XL-30, Philips-FEI, the Netherlands) was used to investigate the surface and structural characteristics of the solids. An X-ray diffractometer (XRD-6000, Shimadzu, Japan) with CuK_α radiation at 40 kV and 30 mA was used. Solids used for XRD analysis were freeze-dried, crushed and mounted on a glass sample holder. XRD patterns were collected using a step-scanning rate of 0.06° 2θ/s.

RESULTS AND DISCUSSION

Heavy metals in sediments: The concentrations of Cu, Zn, Pb and Cd in the sediments collected from Huludao city were 1605, 4209, 641 and 124 mg/kg, exceeding background sediment values in Liaoning Province of 55, 60, 22 and 1058 times, respectively[17].

Percent distribution patterns of heavy metals were illustrated in Fig. 1. It could be found that distribution patterns of Cu, Zn, Pb and Cd were different from each other except that the percentages of heavy metals present as residual phase were all low with the highest percentage of 6.2 % for Zn. Copper in the sediments was mainly existed in organic phase and the remaining Cu was mostly present in exchangeable fraction and carbonatic fraction. Zinc in the sediments was mostly existed in carbonatic fraction and the percentage of this phase was up to 56.8 %. The other four phases only reached less than 43.2 % and followed a decreasing order of Fe/Mn-oxides phase > residual phase > exchangeable phase > organic phase. The percentage of Pb in the carbonatic phase was also higher and nearly up to 50 %. The other relative important phase for Pb was Fe/Mn-oxides-bound phase. Cadmium in the sediments was almost present as exchangeable phase and the percentage of this fraction was up to 79 %. In general, the percentage of heavy metals which were more easily available for hydrobiont (exchangeable phase + carbonatic phase) was relatively higher, especially for Cd. This implies that heavy metals discharged to the water tend to be much more bioavailable, although they could be easily sequestrated by sediments.

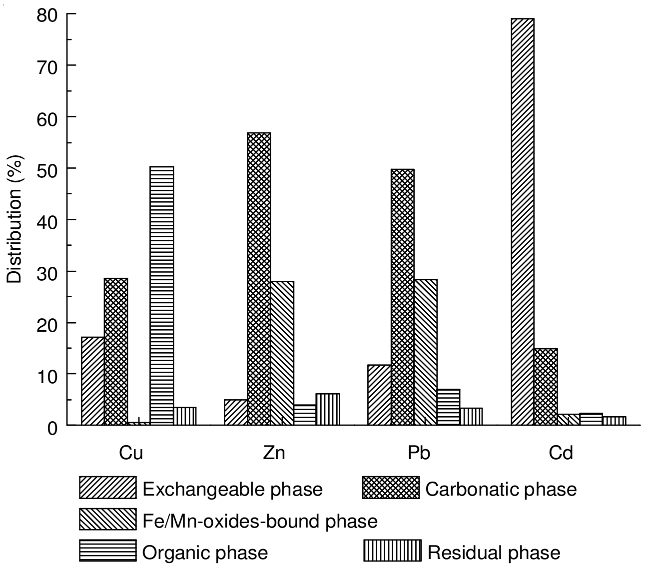

Fig. 1. Per cent distribution of heavy metals in the sediments

Releasing behaviour of heavy metals: Releasing characteristics of heavy metals from sediment particulates at varying pH values were shown in Fig. 2. It could be found that more Cu and Pb released to the solution along with the increasing of reaction time at pH values of 3 or 4 and the upward trend in releasing was ended 12 h later. However, the amounts of Cu and Pb separated from the sediments at pH values of 5, 7 and 9 were significantly lower and there was almost no change as time goes by. Hence, the calculation of releasing amounts of heavy metals was made according to concentrations of heavy metals released and then existed in solution. Compared to releasing amount of heavy metals from the sediments without hydroxyapatite spiking, addition of hydroxyapatite reduced releasing of Cu and Pb when pH values of suspensions were

3 or 4. In other word, hydroxyapatite enhanced the stability of Cu and Pb in the sediments. When pH value was 3, the contents of Cu and Pb released to solution reduced by 59 and 67 %, respectively with hydroxyapatite addition. Releasing of Cu and Pb lessened by 47 and 79 % as hydroxyapatite spiking when pH was 4. But hydroxyapatite had less effect on releasing behaviour of Cu and Pb when pH values were 5, 7 and 9 with slightly ascending for Cu and descending for Pb. This was partly due to the lower decreasing of Cu and Pb at these pH values in despite of hydroxyapatite addition or not. It should be noted that the concentration of Pb in solution was lower than GFAAS detection limit when pH was 9. So the broken line of Pb was not intact and the data points for pH 9 as well as those for pH 7 after 120 h later were not found in Fig. 2.

Equilibrium state of releasing and reabsorbing was reached after 12 h for Zn and Cd, which was the same as Cu and Pb. But hydroxyapatite effect on reducing the releasing of Zn and Cd was obviously lower than that of Cu and Pb, especially at pH values of 3 or 9. When pH was 4, about 15 % of Cd and 10 % of Zn were reduced to release to solution and nearly 30 % of Cd and 12 % of Zn for pH of 5. Releasing of Cd and Zn reduced by 30 and 20 % as hydroxyapatite spiking when pH was 7. Releasing behaviours of Zn and Cd varied by pH values were similar to those of Cu and Pb, namely, the lower pH, the more Zn and Cd released despite of hydroxyapatite spiking or not. Significant difference between Zn/Cd and Cu/Pb was that when pH was 5, the amount of Zn and Cd released to solution was still higher and obviously higher than that at pH of 7 and 9. But for Cu and Pb, the concentrations in solution were much lower than those at pH of 3 and 4 and closed to those at pH 7 and 9.

Releasing behaviour of phosphorus: Releasing characteristics of phosphate anion resulted from hydroxyapatite decomposition at varying pH values were illustrated in Fig. 3. As a whole the concentration of phosphate anion in the solution almost remained unaltered after 12 h. The point of equilibrium state of phosphate releasing and reabsorbing was reached 6 h later for pH of 4 and 5 and that for pH of 7 and 9 was 2 h. The amounts of phosphate anion released to solution were all lower after 12 h except for pH of 3. Equilibrium concentration of phosphorus was approximate 3.1 mg/L when pH was 3. However, Equilibrium concentrations of phosphorus in the solution of the other pH values were all lower than 1 mg/L and average concentrations were about 0.2 mg/L. Nevertheless the concentration of 0.2 mg/L was still higher than threshold value of eutrophication for phosphorus and the threshold value of phosphorus was 0.035 mg/L if total phosphorus was the main eutrophication-related factor (OECD, organisation for economic Co-operation and development).

Species distribution of heavy metals: Distribution patterns of Cu, Zn, Pb and Cd in the sediments after releasing experiment were summarized in Fig. 4. On the whole, the transformation behaviours of Cu among the five species patterns were different and complicated with the varied pH values and hydroxyapatite effect on species transformation was relatively inapparent as compared to the other three metals. When pH

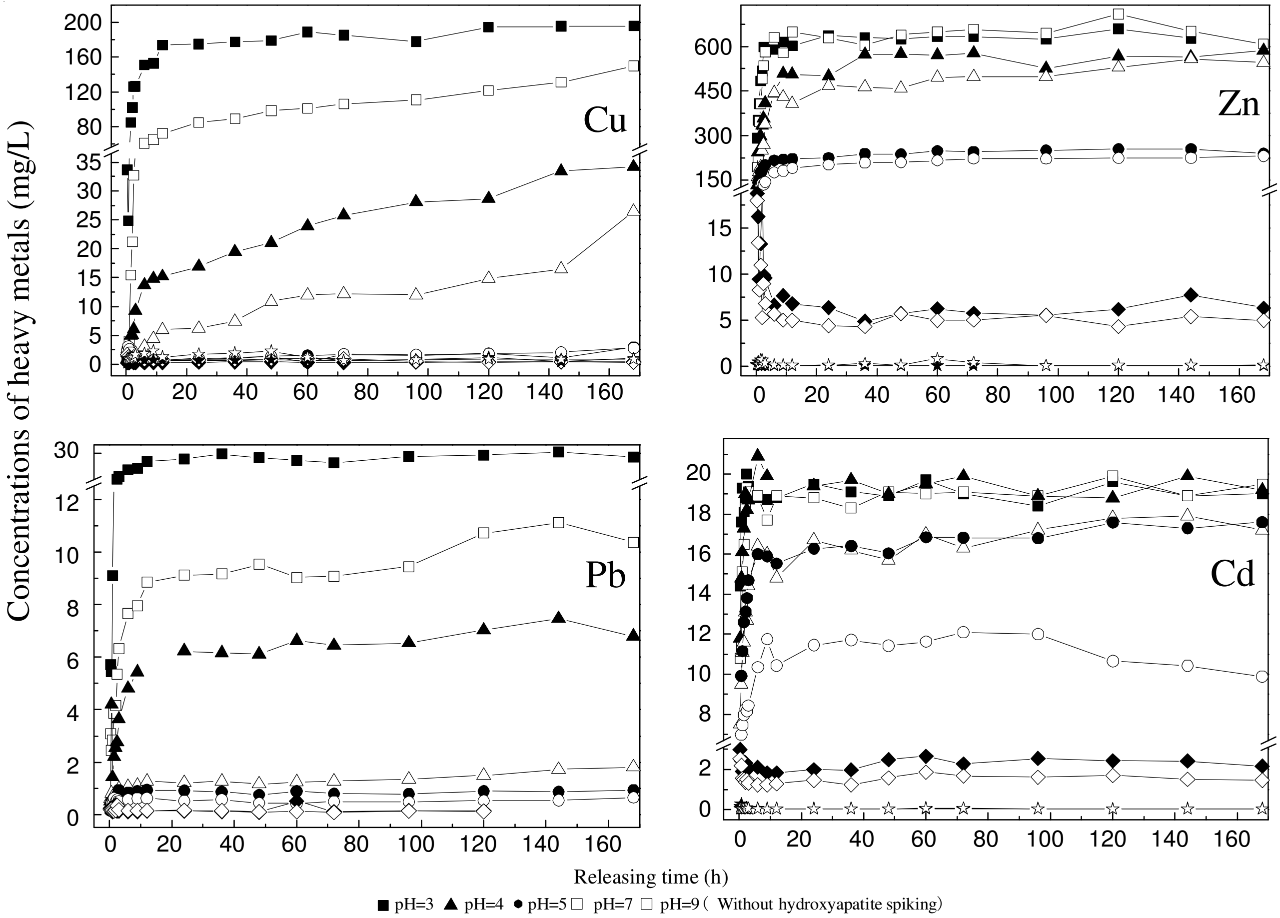

Fig. 2. Effect of pH values on releasing characteristics of Cu, Zn, Pb and Cd

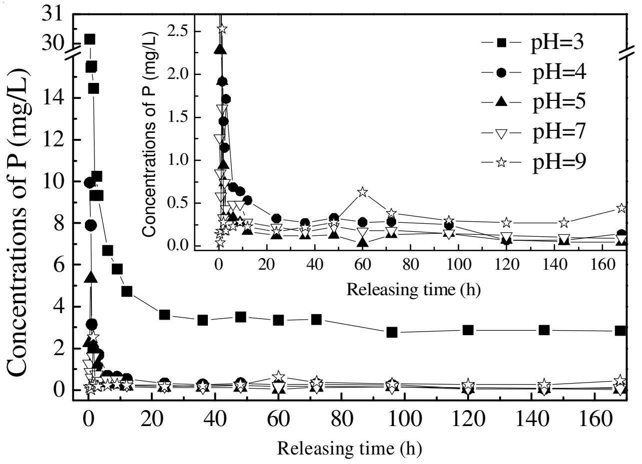

Fig. 3. Effect of pH values on releasing characteristics of phosphorus

values were 3 or 9, addition of hydroxyapatite only led to approximate 2 % of Cu shift from exchangeable phase (pH 3) or organic phase (pH 9) to the other phases. Effect of hydroxyapatite on species transformation was somewhat increased when pH was 7 and about 8.8 % of Cu existed as carbonatic fraction changed to organic fraction. When pH values changed to 4 or 5, almost 15.7 % of exchangeable Cu transformed to organic and residual phases (pH 4) and 9.8 % of organic Cu changed to carbonatic and residual phases (pH 5). Comparative analysis of Fig. 4 and Fig. 1 indicated that the releasing experiment at varied pH values changed the species distribution patterns of Cu in spite of hydroxyapatite effect and pH of 3 and 4 enhanced increasing of exchangeable Cu and pH of 7 and 9 led to carbonatic Cu increasing. Only pH value of 5 led to the decreasing of exchangeable and carbonatic Cu and these Cu almost transformed to organic fraction and less to residues.

Addition of hydroxyapatite had more effect on Zn species transformation as compared to Cu. The similarity between Zn and Cu was that hydroxyapatite effect was relatively lower when pH values were 3 and 9 and higher for pH 4 and 5. When pH was 3, about 7.4 % of carbonatic Zn transformed to the other phases such as organic phase (3.3 %) and residual phase (2.2). Approximate 11.3 % of exchangeable Zn and 0.9 % of carbonatic Zn shifted to organic, Fe/Mn-oxides-bound and residual phases by 5, 3.3 and 3.9 %, respectively according to pH 4. The pH value of 5 also caused a decreasing of exchangeable and carbonatic Zn as well as Fe/Mn-oxides-bound Zn and these Zn transformed to organic and residual phases. The differences between Zn and Cu could be found by comparative analysis of Fig. 4 and Fig. 1 and pH values of 7 and 9 led to the decreasing of carbonatic Zn, although pH of 3 and 4 enhanced increasing of exchangeable Zn which was similar to Cu.

Effect of hydroxyapatite on transformation of Pb was the most remarkable among the four metals and addition of hydroxyapatite enhanced shift of Pb from exchangeable and carbonatic phases to the other phases in despite of pH values.

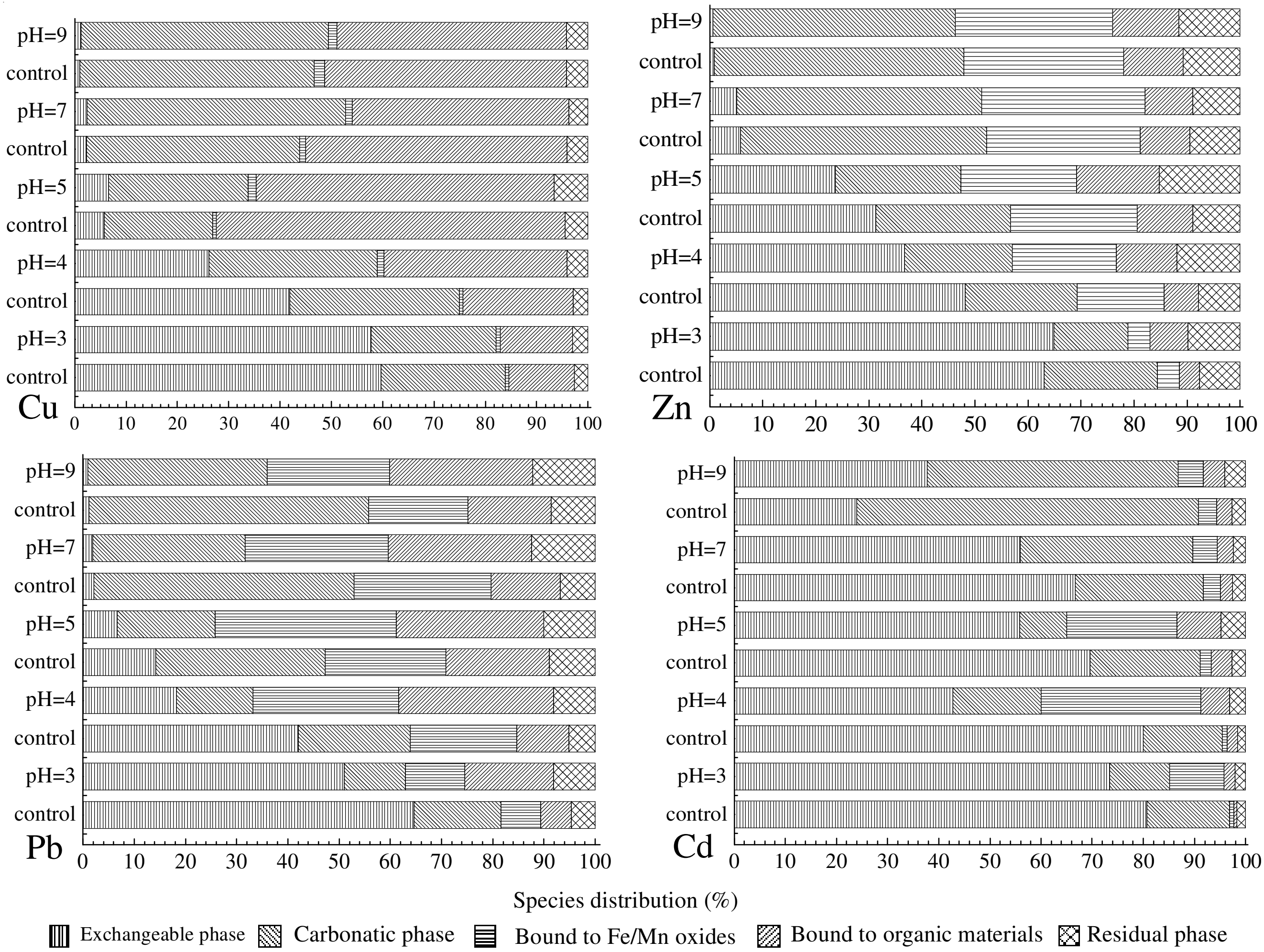

Fig. 4. Per cent distribution of heavy metals in the sediments after releasing experiment

When pH values were 7 and 9, the changes were mainly took place from carbonatic fraction to Fe/Mn-oxides-bound, organic and residual fractions with the carbonatic decreasing of 21.1 and 19.5 %, respectively. But when pH changed to 3, 4, or 5, not only carbonatic phase but also exchangeable phase were transformed to Fe/Mn-oxides-bound, organic and residual phase, with the highest decreasing of 23.8 for exchangeable Pb and increasing of 20.2 % for organic Pb at pH 4. Compared Fig. 4 with Fig. 1, it could be also found that pH of 3 and 4 enhanced increasing of exchangeable Pb.

After spiking with hydroxyapatite, Cd was primarily changed from exchangeable phase to the other phases except for pH 9. When pH was 9, about 17.8 % of carbonatic Cd transformed to the other phases with the more increasing of exchangeable phase (13.7 %). Although the shifts were all from exchangeable phase at pH 4 and 7 , the intensity in transformation was different between them. Up to 37.2 % of exchangeable Cd transformed to the other phases and mainly changed to Fe/Mn-oxides-bound phase at pH 4, but only 10.7 % of exchangeable Cd shifted to the other phases and almost changed to carbonatic phase. The variational tendencies for pH 3 and 5 were similar to each other and Cd was transformed from both exchangeable and carbonatic phases to Fe/Mn-oxides-bound phase as well as less to organic and residual phases.

In summary, the addition of hydroxyapatite enhanced transforming of Cu, Zn, Pb and Cd from exchangeable and carbonatic phases to relatively stable phases including Fe/Mn-oxides-bound, organic and residual phases, especially at pH 4. The changed percentages were 15.9 % for Cu, 12.2 for Zn, 30.8 % for Pb and 37.2 % for Cd and respectively transformed to organic phase, organic and residual phases, Fe/Mn-oxides-bound and organic phases and Fe/Mn-oxides-bound phase.

Mechanisms of hydroxyapatite effect on heavy metals: The possible mechanisms for metal retention by hydroxyapatite included ion exchange processes at the surface of hydroxyapatite and substitution of Ca in hydroxyapatite by other metals[14,18] and dissolution of hydroxyapatite and then precipitation of metal with phosphate anion[19,20]. Formation of $M_{10}(PO_4)_6(OH)_2$ by ion exchange and substitution need to last a long period of time, but the crystallinity of $M_{10}(PO_4)_6(OH)_2$ enhanced. Dissolution and precipitation process is relatively fast, which lasted a short time, but the crystallinity of resulting $M_{10}(PO_4)_6(OH)_2$ mineral is poor, mingled with more carbonated structure-containing hydroxyapatite mineral. In the present study, metals and phosphate anion released to solution were lower at pH 7 and 9 (Figs. 2 and 3). So, the reactions between metals and hydroxyapatite primarily related to ion exchange and substitution of Ca and the hydroxyapatite effect on metal immobilization was somewhat inapparent at pH 7 and 9 as there were only 30 days for incubation. Under very acidic condition of pH 3, the crystal structure of hydroxyapatite was destroyed via dissolution of hydroxyapatite (Fig. 3) and precipitation of metal with phosphate anion took place to form crystal of carbonated structure. These structural compounds tended to dissolve at very acidic condition and the hydroxyapatite effect on metal immobilization was also in apparent at pH 3. The dissolution of hydroxyapatite and metals were moderate to form crystal at pH 4 and 5. These pH values reduced the structural destroy of hydroxyapatite as compared to pH 3 and also enhanced the dissolution of metals as compared to pH 7 and 9.

XRD and FTIR patterns of sediments spiked with or without hydroxyapatite were analyzed in the present study. Fig. 5 showed selected XRD patterns of sediments before and after addition of hydroxyapatite at pH 4. The peaks of hydroxyapatite at 31.12° and 32.08° and of reaction product of hydroxyapatite with metals at 54.94° and 55.12° were all enhanced by addition of hydroxyapatite. These changes were much more apparent at pH 4 than at the other pH values which were not showed in the present work. Like XRD, the FTIR were illustrated in Fig. 6 only including pH 4 as the stronger variation of absorption peaks obtained at pH 4. Also increasing of hydroxyapatite and reaction product of hydroxyapatite with metals was proved by two major absorbance peaks at 1384.64 and 684.61 cm^{-1}.

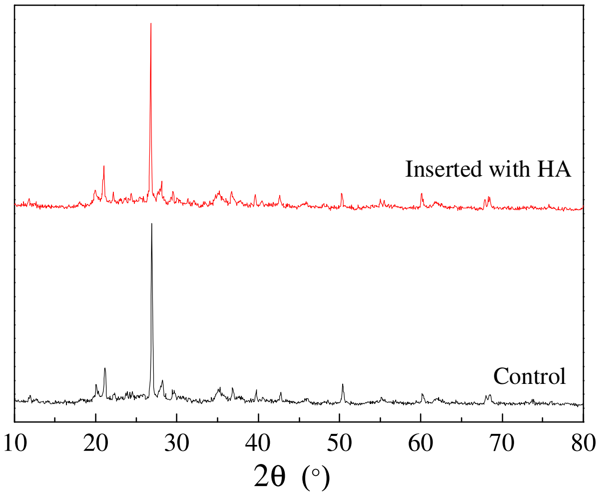

Fig. 5. XRD patterns of sediments before and after interaction with hydroxyapatite at pH 4

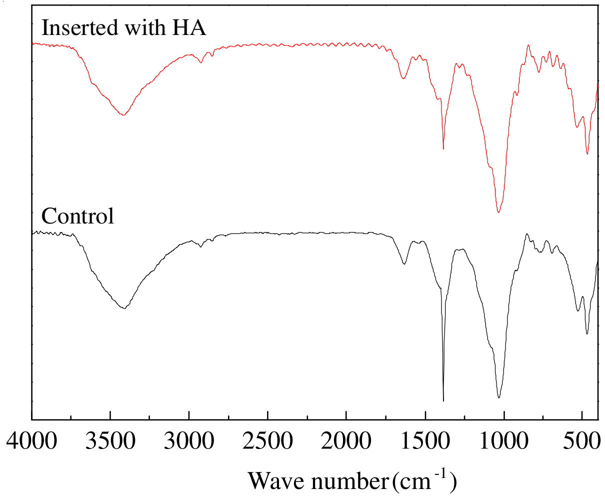

Fig. 6. FTIR patterns of sediments before and after interaction with hydroxyapatite at pH 4

The SEM results indicated that there were less surface and structure changes between sediments with and without hydroxyapatite addition as the lower content of hydroxyapatite and metals as compared to the inherent components of sediments. But energy spectra based on SEM results (not showed in the present work) showed that much more crystal zinc was formed with hydroxyapatite at pH 4 and 5. Weight proportions of Zn in the elements distribution patterns of sediments after hydroxyapatite spiking were 1.86, 2.87, 2.63, 2.15 and 1.55 %, respectively for pH 3, 4, 5, 7 and 9. But no peak of zinc was observed in the energy spectrum of sediments without hydroxyapatite spiking. However, the crystal copper, lead or cadmium were not observed in energy spectra in despite of hydroxyapatite addition or not at varied pH values. This was mainly due to the relatively fewer contents of Cu, Pb and Cd in the sediments and detection limit of element energy spectra analysis was 1 %.

Conclusions

In conclusion, the following may be drawn based on the results of this study:

- More heavy metals released to the solution along with the increasing of reaction time and the upward trend in releasing was ended after 12 h. The lower pH value, the more heavy metals released, but hydroxyapatite spiking reduced the releasing of heavy metals with higher effect on Cu and Pb and to a lesser degree, on Zn and Cd.
- Hydroxyapatite spiking enhanced transforming of heavy metals from exchangeable and carbonatic phases to relatively stable phases, especially at pH 4 and 5. Cu, Zn, Pb and Cd were respectively transformed to organic phase (15.9 %), organic and residual phases (12.2 %), Fe/Mn-oxides-bound and organic phases (30.8 %) and Fe/Mn-oxides-bound phase (37.2 %) at pH 4.
- The releasing experiment and species distribution analysis indicated the better hydroxyapatite effect was reached under pH 4 or 5 conditions. This was partly due to the moderate dissolution of hydroxyapatite and releasing of metals to form crystal at pH 4 and 5. The XRD, FTIR and SEM analysis results furthermore corroborated these conclusions.

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