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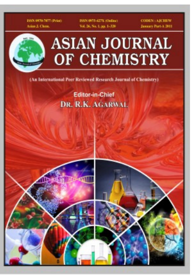

Enhanced Adsorption and Transformation of Cu and Zn in Sediments by Hydroxyapatite

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The adsorption and transformation characteristics of Cu and Zn in sediments with or without hydroxyapatite spiked were investigated in the present study. The isothermal adsorption results show that the hydroxyapatite enhanced the adsorption capacity of sediments and the maximum adsorption capacity of Cu and Zn increased by 70 and 150 % as compared to the sediments without hydroxyapatite spiking. The equilibrium adsorption/desorption experiment results indicate that the adsorption rates of Cu and Zn were both much more than 93 % with or without hydroxyapatite spiking. However, the hydroxyapatite obviously reduced the desorption rates of Cu and Zn from the sediments. Hydroxyapatite facilitated the transformation of Cu and Zn from less stable phases to more stable phases, especially advanced the translation of Cu and Zn from exchangeable fraction to the other fractions. These results imply that the addition of hydroxyapatite to the sediments facilitated the stability of heavy metals in the sediments and restrained the environmental risk of heavy metals to the aquatic environment to some extent.

Keywords: Sediment, Hydroxyapatite, Adsorption, Desorption, Transformation, Cu/Zn.

INTRODUCTION

Because of toxicity and bioaccumulation potential, the behaviour, transport and ultimate fate of heavy metals in aquatic environments have drawn great interest. It has been found that sediments play crucial roles in the cycling and bioavailability of heavy metals and represent the largest pool of metals in aquatic environments[1-6]. The previous 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].

The toxic potential of heavy metals in sediments depends on sediment composition, particularly the amount and type of clay minerals, organic materials and Fe/Mn oxides[9-10]. Most studies on heavy metal adsorption and related mechanism have been focused on individual synthetic and commercial mineral sorbents[11-13]. However, these studies have not considered the adsorption and transformation behaviors of heavy metals in the sediments when the above minerals, including hydroxyapatite, were inserted into the sediments, although these processes would be important for risk adjustment of heavy metals in the river. Hydroxyapatite could strongly interact with and sequestrate heavy metals and has been widely used in contaminated water and soil treatment.

The main objective of this study was to examine the adsorption of Cu and Zn onto the sediments after inserting with hydroxyapatite and to investigate the species transformation of Cu and Zn in the sediments by application of hydroxyapatite. These results would be helpful when evaluating the heavy metal immobilization potential of hydroxyapatite in contaminated sediments and present a technical possibility for the disposal and cycle-use of heavy metals widely existed in the environment and for the treatment and management of heavy metal-contaminated municipal sludge.

EXPERIMENTAL

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 (Guilin Red Star Biotechnology Co., Ltd., Guangxi, China) was added to the homogenized sediments at rates of 0.5, 1 and 5 % w/w. The hydroxyapatite-spiked sediments were kept in a cool and dry place with a moisture content of 60 % for 60 days. Then the hydroxyapatite-spiked sediments were air-dried.

Meanwhile, the Cu and Zn-spiked sediment samples were obtained by addition of Cu-acetate and Zn-acetate to the sediments at level of 0.02 mol Cu/kg and 0.02 mol Zn/kg. The necessary amount of Cu-acetate and Zn-acetate was brought in solution and added to the sediment which was mixed during Cu and Zn addition to make sure the metals were evenly distributed in the sediments. The hydroxyapatite was added 60 days later after Cu and Zn equilibration in sediment at a rate of 5 % w/w. Then the spiked sediment were wetted with a moisture content of 60 % and re-equilibrated over a period of 60 days at room temperature before measurements were performed.

General procedure: Adsorption of Cu and Zn onto the unaltered sediments and the sediments spiked with hydroxy apatite were measured in duplicate in chemically defined solutions under eight different Cu and Zn concentrations (1, 2, 4, 6, 8, 10, 15 and 20 mg/L). The solutions were prepared by diluting 1 g/L $Cu(NO_3)_2$ and $Zn(NO_3)_2$ reference solutions through a minimal mineral salt (MMS) solution[9] and adjusting pH at 6.0 ± 0.1 using 0.01 mol/L HNO_3 and NaOH (25 ± 1 °C). Sediment samples of 0.1 g were weighted into a 100 mL polyethylene tubes and then 50 mL solutions with eight different Cu and Zn concentrations were added into the tubes. The sediment suspensions were stirred continuously for 24 h and filtered through 0.45 μm Millipore filters. Before filtering, the pH was re-adjusted to the initial level and the changes in pH after 24 h were found to be minor (all these adjustments were only within ± 0.5 pH). The amounts of adsorbed Cu and Zn were calculated as the difference between the amount added initially and that remaining in the equilibrium solutions. Copper and zinc adsorptions to the sediments were analyzed by Langmuir adsorption isotherm.

In order to evaluate the adsorption/desorption characteristics of Cu and Zn in the sediments with hydroxyapatite spiking, 1 mmol/L $Cu(NO_3)_2$ and $Zn(NO_3)_2$ solutions of 20 mL were used to be absorbed by sediments of 1 g for 24 h and then the equilibrium adsorption amounts of Cu and Zn were calculated as the difference between the amount added initially and that remaining in the equilibrium solutions. The sediments were washed with double distilled water for 0.5 h and then desorbed by two extracting solutions of varying pH values. Two acidic solutions were prepared from acetic acid at pH 2.93 ± 0.05 (#1) and 4.93 ± 0.05 (#2) following the technique for preparation of extraction fluids as discussed in the USEPA toxicity characteristic leaching procedure[14].

Fractionation of Cu and Zn was carried out using the sequential extraction procedure[15]. 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: Cu and Zn in the initial, equilibrium and extracted solutions were measured by flame atomic absorption spectrometer (WYX-9004, Shenyang, China).

RESULTS AND DISCUSSION

Isothermal adsorption characteristics of the hydroxyapatite-spiked sediments: The adsorption isotherm curves of hydroxyapatite-spiked sediments for Cu and Zn are shown in Fig. 1, as well as those of sediments without spiking with hydroxyapatite which considered as control. With increasing concentration of Cu and Zn, the absorbed amount of Cu and Zn increased. In general, Cu adsorption was greatly higher than that of Zn. The maximum adsorption of heavy metals onto the sediments ranged from 13.32 to 21.19 mg/g for Cu and ranged from 4.68 to 9.58 mg/g for Zn. This implies that Cu was more strongly retained by the sediments than Zn. The preferential retention of Cu than Zn by the sediments was in agreement with the results reported in the literatures on Cu and Zn adsorbed to different adsorbents, such as goethite and hematite[16], aluminum hydroxides[17], humic substances[18], oxisols, ultisols and alfisols[19]. The differences of physicochemical property of Cu and Zn, such as ionic radius, electronegativity, softness parameter and first hydrolysis constant result in the differences of Cu and Zn adsorption affinity[20].

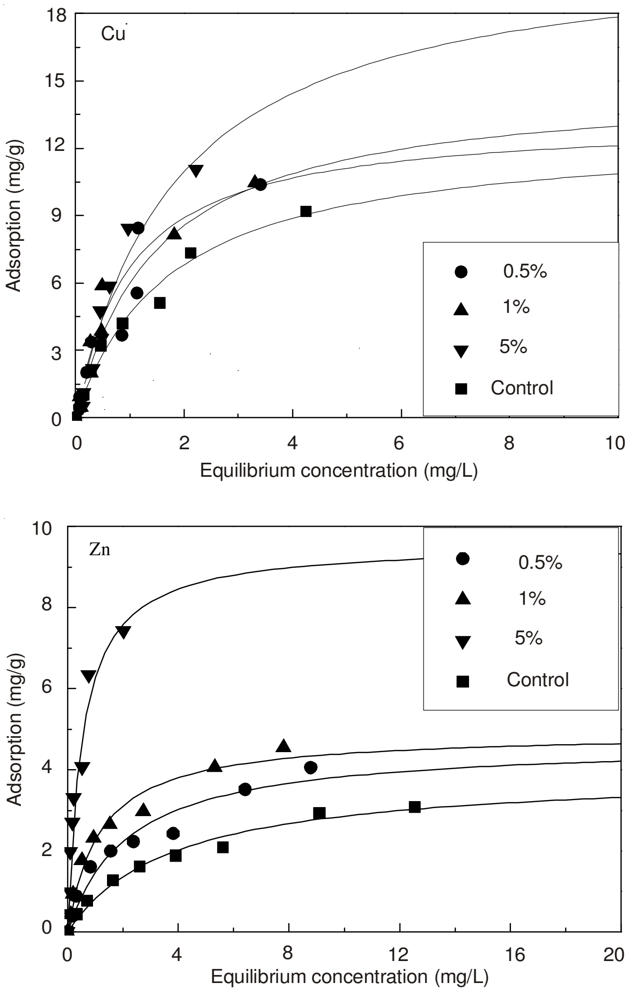

Fig. 1 Langmuir isotherms of Cu and Zn adsorbed onto the sediments before and after hydroxyapatite spiking

With the proportion increasing of hydroxyapatite spiked in the sediments, the amount of Cu adsorption to the sorbent increased, especially for the ratio of 5 %. The Cu adsorption isotherms for sediments spiked with different ratio of hydroxy-

TABLE-1
ADSORPTION/DESORPTION RATE OF Cu AND Zn IN THE SEDIMENTS AFTER EXTRACTING WITH TCLP (%)

	Cu				Zn			
	Control	0.5 %	1 %	5 %	Control	0.5 %	1 %	5 %
Adsorption rate	99.39	98.48	98.05	99.63	93.55	98.13	96.03	98.88
Desorption rate #1	19.78	10.95	4.96	0.47	54.09	0.65	0.74	0.58
Desorption rate #2	46.37	30.69	18.41	1.65	81.01	0.91	0.85	0.94
Retention rate #1	79.73	87.70	93.19	99.16	42.95	97.49	95.32	98.31
Retention rate #2	53.30	68.26	80.00	97.99	17.77	97.24	95.21	97.95

apatite exhibited different magnitudes of associated sorption. The sediments spiked with 0.5 % of hydroxyapatite adsorbed or retained slightly more Cu as compared to the unaltered sediments. Adsorption onto the sediments spiked with 1 % of hydroxyapatite showed a pattern very similar to adsorption onto the sediments spiked with 0.5 % of hydroxyapatite, although the maximum adsorption was slightly decreased from 14.92 to 13.32 mg/g. By contrast, sediments spiked with 5 % of hydroxyapatite adsorbed and retained up to 21.19 mg/g of Cu and significantly exceeded that of unaltered sediments. Effect of hydroxyapatite spiked in the sediments on adsorption characteristics of Zn was similar to that of Cu. Hydroxyapatite also improved the affinity of sediments for Zn, but the influence degree was more intensive. With increasing of hydroxyapatite spiked in the sediments, the adsorption affinity of 5 % hydroxyapatite-spiked sediments for Zn was approximately 1.5 times than that of unaltered sediments, but the adsorption capacity of 5 % hydroxyapatite-spiked sediments for Cu was about 70 % more than that of unaltered sediments.

Adsorption/desorption characteristics of the hydroxyapatite-spiked sediments: Adsorption/desorption characteristics of Cu and Zn determined by equilibrium adsorption/desorption experiment were listed in Table-1. The preliminary experiment results indicated that more Cu and Zn adsorbed onto the sediments with or without hydroxyapatite along with the increasing of reaction time and the upward trend in adsorption amount was ended after 14 h. Also the desorption equilibrium time was about 14 h. So the adsorption and desorption experiments were both carried out for 24 h in order to facilitate the experiment operating. As a result, in the experiments, the best adsorption rates of Cu and Zn were obtained both for the sediments with or without hydroxyapatite spiked and the adsorption rates were more than 93 %.

The adsorption of Zn onto the unaltered sediments was more leachable than Cu. Less than 20 % of Cu was leached when extraction fluid was at pH of 4.93 and less than 47 % was removed when extraction fluid was at pH of 2.93. But for the similar adsorbed content of Zn, up to 54 % by extraction fluid of pH 4.93 and 81 % by extraction fluid of pH 2.93 were leached. This may be due to the difference in binding ability of Cu and Zn. The leachability of Cu and Zn were both reduced after hydroxyapatite being spiked to the sediment, especially for Zn. Desorption percentage of Cu by extraction fluid of pH 4.93 from the hydroxyapatite-spiked sediments was decreased to 11 % when the spiked hydroxyapatite ratio was 0.5 % and when the spiked hydroxyapatite ratio was up to 5 % only 0.5 % of adsorbed Cu leached. When the pH of extraction fluid decreased to 2.93, the same decreasing trend was investigated, *i.e.* the desorption rates of Cu decreased along with the hydroxyapatite-spiking ratio increasing. Desorption ability of Zn was also restrained by hydroxyapatite and the effect of hydroxyapatite spiking was much more obvious. No matter what pH values of the extraction fluid used and no matter what rates of hydroxyapatite spiked to the sediments, the desorption rates of Zn from the sediments spiked with hydroxyapatite were all decreased to less 1 %. In the present study, the retention rates shown in Table-1 in a sense represent the stability of Cu and Zn in the sediments. The higher retention rate values, the more heavy metals remained in the sediments after the TCLP extracting and thus the more stability of heavy metals in the sediments. So the hydroxyapatite spiking to the sediments enhanced the stability of Cu and Zn in the sediments.

Species transforming characteristics of Cu and Zn in sediments spiked with hydroxyapatite: Per cent distributions of Cu and Zn in the sediments are summarized in Fig. 2. Distribution patterns of Cu and Zn were different from each other after they added to the sediments for a period of 120 days except that the percentage of Cu and Zn present as residual phase was both lower. Copper in the sediments was mainly existed in carbonatic phase and Fe/Mn-oxides phase and the remaining Cu was mostly present in exchangeable fraction and organic fraction. Zinc in the sediments was almost existed in exchangeable fraction and the percentage of this phase was nearly up to 60 %. The other four phases only reached less than 40 % and followed a decreasing order of Fe/Mn-oxides phase > carbonatic phase > residual phase > organic phase. In general, the percentage of more easily available for hydrobiont of both Cu and Zn (exchangeable phase + carbonatic phase) was obviously higher as compared to that of heavy metals existed in sediments for a long period. This implies that heavy metals recently discharged to the water tend to be bioavailable although they could be easily absorbed and sequestrated by sediments.

After hydroxyapatite added to the sediment for a period of 60 days, the distribution patterns of Cu and Zn spiked in the sediments were significantly changed, especially for Cu and Zn existed in exchangeable phase and organic phase, as well as carbonatic phase for Zn. The percentage of Cu and Zn present in exchangeable fraction was declined by 10 % for Cu and 50 % for Zn and this phase was nearly transformed to Fe/Mn-oxides phase and organic phase for Cu and carbonatic phase and Fe/Mn-oxides phase for Zn. Meanwhile, Cu in the sediments was partly transformed from carbonatic fraction to more stable fractions. As a whole the spiked-hydroxyapatite facilitated the transformation of Cu and Zn from relatively more mobile phase to more stable phase, but due to the short period of treatment, the transformation of Cu and Zn to the residual fraction did not take place.

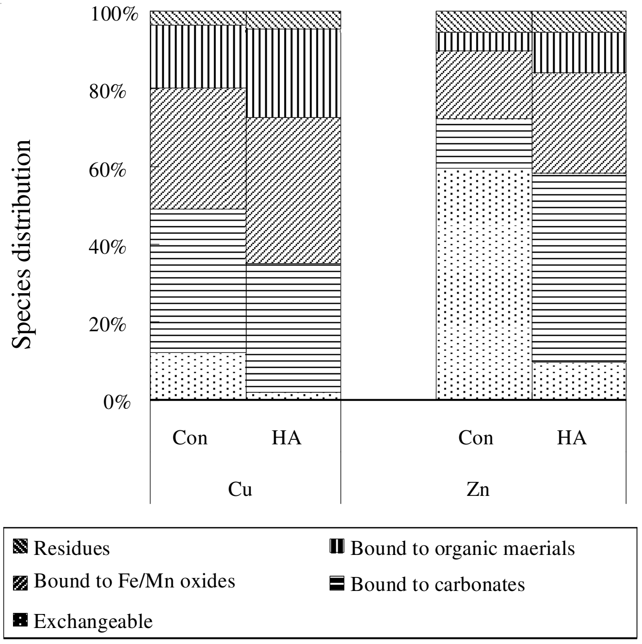

Fig. 2 Species distribution patterns of Cu and Zn in the sediments before and after hydroxyapatite spiking

Species distribution analysis of heavy metals in soils or sediments was usually applied to investigate the environmental effect and bioavailability of metals[21,22]. The non-residual fraction of metal in the sediments, namely, metals existed as exchangeable, carbonatic, Fe/Mn-oxides and organic phases except for residual phase could be used to examine the bioavailability of metals[23]. But exchangeable fraction, namely, metals present as exchangeable and carbonatic phases in the present study sometimes was the more suitable criterion for bioavailability estimation[21]. According to the criterion of non-residual fraction, it could be found that addition of hydroxyapatite did not alter the bioavailability of Cu and Zn in the sediments of short-term contamination. But based on the criterion of exchangeable fraction, the stability of Cu and Zn enhanced.

XRD and FTIR patterns of hydroxyapatite interacted with Cu and Zn analyzed in the present study. Fig. 3 showed XRD patterns of hydroxyapatite before and after interacting with heavy metals. The peaks of hydroxyapatite at 3.88 Å were obviously reduced and almost disappeared, meanwhile reaction products of hydroxyapatite with metals at 8.23, 2.00 and 1.50 Å were all enhanced. Like the XRD results, the FTIR results illustrated in Fig. 4 also indicated that there were new products appeared. The reaction between hydroxyapatite and metals caused broadening of absorption band at 1100-1000 cm^{-1}.The absorption peaks at 1577 and 1259 cm^{-1} weakened, but the absorption peaks at 868 and 455 cm^{-1} strengthened. Surface complexation and coprecipitation are the most important mechanisms with ion exchange and solid diffusion also contributing to the overall interaction process[24-27]. These two interaction mechanism were both existed in the present study and the XRD and FTIR results indicated that complexation and coprecipitation contributed more for Cu interacted with hydroxyapatite and ion exchange and solid diffusion contributed more for Zn interacted with hydroxyapatite.

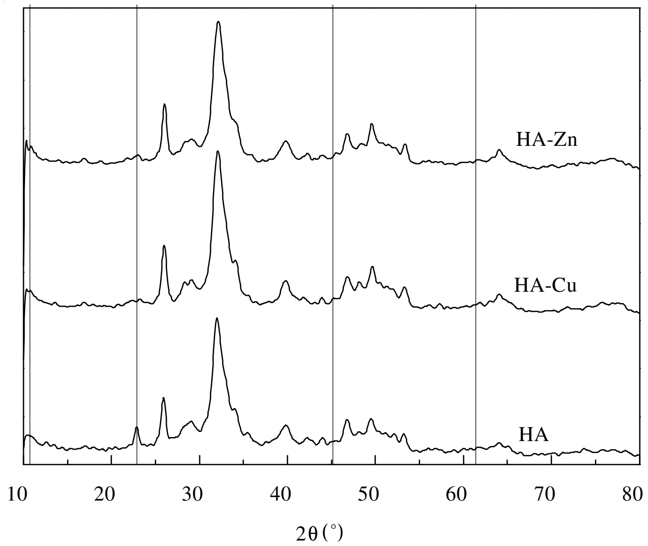

Fig. 3 X-ray powder diffraction patterns of the hydroxyapatite before and after heavy metals adsorbing

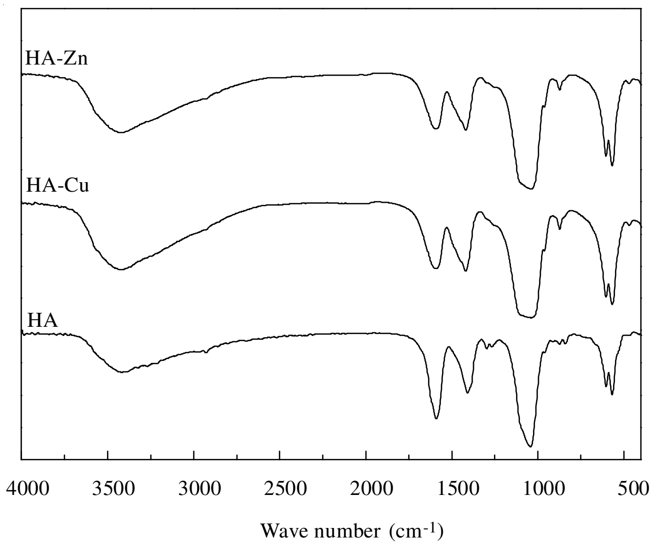

Fig. 4 Infrared spectra of the hydroxyapatite before and after heavy metals adsorbing

Conclusion

Hydroxyapatite spiked in the sediments enhanced the adsorption capacity of sediments and the maximum adsorption capacity of Cu and Zn increased by 70 and 150 % as compared to the sediments without hydroxyapatite spiking. The adsorption rates of Cu and Zn were less changed in equilibrium adsorption/desorption experiments after the hydroxyapatite spiking. However, the hydroxyapatite obviously reduced the desorption rates of Cu and Zn from the sediments. Meanwhile, hydroxyapatite spiked in the sediments facilitated the transformation of Cu and Zn from less stable phases to more stable phases, especially enhanced the shift of Cu and Zn from exchangeable fraction to the other fractions. These results imply that the addition of hydroxyapatite to the sediments facilitated the stability of heavy metals in the sediments and restrained the environmental risk of heavy metals to the aquatic environment to some extent.

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