Research article

Effects of modified zeolite on the removal and stabilization of heavy metals in contaminated lake sediment using BCR sequential extraction

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ARTICLE INFO

ABSTRACT

Sediment can be applied on land as a soil conditioner. However, toxic substances such as heavy metals within the sediment often lead to soil contamination if no proper management is conducted prior to land application. In order to reduce the bioavailable portion of heavy metals such as Pb, Cu, Zn and Cd, zeolite as a kind of stabilizer was investigated on the effect of metal stabilization in sediment. Zeolite was firstly modified and screened to get the best condition for removal of heavy metals. Results showed that the granulated zeolite with NaCl conditioning had the highest CEC and metal sorption. Using BCR sequential extraction, the selected modified zeolite effectively stabilized Pb, Cu, Zn and Cd in sediment to different extents. It was most suitable for Cd stabilization by reducing its acid exchangeable fraction while increasing the contents of the reducible and residual fractions. Modified zeolite also immobilized Cu, Zn and Pb in sediment by enhancing one stable fraction while decreasing the acid exchangeable fraction.

1. Introduction

Lake sediment is a crucial composition in lake ecosystem for its role as the storage bank for organic and inorganic nutrients, and for toxics and hazards simultaneously. Heavy metals, as a kind of persistent toxic substances, enter into lakes through various pathways and accumulate in sediment by adsorption, complexation or sedimentation with suspensions or sediments in waters (Ji et al., 2004). Heavy metals in sediment are usually in a certain dynamic equilibrium with the above water body, and could enter the water when the surrounding environment changes, thus resulting in heavy metal contamination in waters (Müller and Pluquet, 1998).

For its characteristic of being nutrient-rich, a conventional way of utilizing the lake sediment is to apply it on land to increase soil fertility, use it in wetlands for biological habitation, or use it to remedy seriously disrupted soils for development of surface plants. However, most land application is by simply mixing the sediment with soil or applying it onto the soil surface (Bedell et al., 2006; Chen et al., 2002; Perin et al., 1985). Due to the fact that heavy metals accumulate in sediments in various forms, part of them are likely to be mobilized to become environmentally toxic in the course of utilization. Within the exchangeable or carbonates-bond fractions of heavy metals released by sediment, only less than 1% is considered safe to the environment, and over 50% of the total amount possesses high risk and possibly enters the food chain (Perin et al., 1985).

Traditionally, using stabilizer such as fly ash (Rijkenberg and Depree, 2010; Tomasevic et al., 2013), ground granulated blast-furnace slag (Wang et al., 2015), iron/manganese oxides (Wang et al., 2015), phosphates (Rijkenberg and Depree, 2010), compost (Rijkenberg and Depree, 2010), limestone (Wildt et al., 2004) or Ca-rich clay minerals (Yin and Zhu, 2016) can minimize the mobile metals in the environment, hence controlling the spread of pollution. Some stabilizers are found to be potentially toxic to environment. For example, red mud is usually abundant with chromium and Al^{3+}, and sludge from waste water treatment plant has arsenic of high quantity (Müller and Pluquet, 1998). Therefore, efficiency, source, cost and potential toxicity should be taken together to suggest a suitable stabilizer for a specific heavy metal remediation project. In recent years, zeolite has received much attention in scientific community due to its special physico-chemical property, accessible source and low cost, and is being widely used in industry, agriculture and pollution control. Zeolite has a crystal structure that is made by silicon (aluminium) oxygen tetrahedron arranged into three dimensional lattice (Breck, 1974). Various large or small holes and channels in the structure give rise

to the great openness of zeolite, making the material selectively absorb molecules of appropriate size. In addition, substitution of some of the silicon (Si) with aluminium (Al) (or other metals) leads to a negative charge on the framework, with cations (principally sodium (Na$^+$), potassium (K$^+$), and calcium (Ca^{2+}), less frequently lithium (Li$^+$), magnesium (Mg^{2+}), strontium (Sr^{2+}) and barium (Ba^{2+})) distributed within the pore structure (Pabalan and Bertetti, 2001) and have weak connection with the framework (Breck, 1974). These structure properties make zeolite possess great ion exchange ability, subsequently resulting in its strong and selective adsorption of some particular metal ions. Examined by X-ray Powder Diffraction, it was assumed that the fraction of clinoptilolite was the main reason for ion exchange and adsorption in all kinds of zeolite components (Mondale et al., 1995) and deemed to be the most effective ion exchange and selection material (Humidpour et al., 2010). The metal removal efficiency of clinoptilolite for different metals follows the order: Pb^{2+} > Cd^{2+} > Cs$^+$ > Cu^{2+} > Co^{2+} > Cr^{3+} > Zn^{2+} > Ni^{2+} > Hg^{2+} (Tomasevic et al., 2013). It was reported that zeolite could stabilize heavy metals in contaminated soils and reduce metal transfer to upper part of plants (Humidpour et al., 2010; Sun et al., 2014). Recent work utilizing zeolite for metal removal and remediation mainly focused on sewage (Ashmawy et al., 2012; Zorpas et al., 2000), soil (Li et al., 2009; Mahabadi et al., 2007; Shi et al., 2009), and water (Egashira et al., 2012; Wingenfelder et al., 2005). Research of utilizing zeolite to stabilize heavy metals in sediment is yet limited. Using the sediment generally accepted as 'waste' for land application while keeping the accompanied risks to minimal is an optimal and effective solution for sediment reuse, conforming to the demands of resource utilization.

Most of natural zeolites occur in forms of zeolitic-rich tuffs with zeolitic composition accompanied with other impurities (Delkash et al., 2015). Pretreatment of zeolite to cleanse the impurities or alter the properties would affect the adsorption process of zeolite (Song et al., 2015). Zeolite with modifications using mineral acid or base treatment has been proposed to improve zeolite surface areas and porosity (Christidis et al., 2003). Therefore, the objectives of the study were (a) to investigate the impact of modification on the performance of metal removal by zeolite in aqueous environment and (b) to assess the stabilization effect of zeolite on heavy metals in sediment. Samples of sediment from Dongting Lake known for heavy metal contamination (Li et al., 2013) were collected for experiments. For a better metal stabilization effect, zeolite was modified and screened for particle size and modification condition. Following that, BCR sequential extraction was conducted to study the influence of modified zeolite on the speciation of Pb, Cu, Zn and Cd in the sediment.

2. Materials and methods

2.1. Sediment description

Sediment samples were collected from Dongting Lake, Hunan. A map of the sampling site was provided as Fig. 1. Dongting Lake is one of the biggest natural water resources in South China, and due to developed economy in the adjacent area, it suffers from high loads of untreated wastewater (Li et al., 2013). The upper 0–10 cm depths of sediments were randomly collected and then homogenized, after which subsamples were kept at 4 °C prior to laboratory analysis.

Pseudo-total trace metal contents were assessed on sample triplicate after nitric acid digestion employing US EPA standard method (EPA3050B, 1996). Metal content was determined by Atomic Absorption Spectroscopy (AAS) (AAnalyst700, Perkin Elmer). Potential ecological risk index (PER) developed based on

sedimentary theory was introduced to assess the ecological risk degree of heavy metals in the present sediment. Risk index (RI) can be calculated by the following formulas proposed by Hankanson (Hakanson, 1980):

$$C_f^i = C_D^i \Big/ C_B^i \tag{1}$$

$$E_r^i = T_r^i \times C_f^i \tag{2}$$

$$RI = \sum_{i=1}^{m} E_r^i \tag{3}$$

Where RI is the sum of the potential risk of individual heavy metal, E_r^i is the potential risk of individual heavy metal, T_r^i is the toxic-response factor for a given metal, C_f^i is the contamination factor, C_D^i is the present concentration of heavy metals in sediments, and C_B^i is the pre-industrial record of heavy metal concentration in sediments. Based on the Hakanson's approach, the toxic-response factors for Pb, Cu, Zn and Cd are 5, 5, 1, and 40, respectively. In this study area, the pre-industrial concentration records for Pb, Cu, Zn and Cd were replaced by their corresponding background values, namely 23.3, 20.2, 83.3 and 0.33 mg/kg (Li et al., 1986).

2.2. Zeolite modification and screening

The natural zeolite used in the experiments came from Gongyi, Zhengzhou (Henan Province, China). Three grain size fractions were used as received from the supplier: bulk particle of 2–2.5 mm (named as fraction I), granulated particle of 0.5–1 mm (named as fraction II), and powdered zeolite of <0.5 mm (named as fraction III). Samples were washed with distilled water to remove soluble salts possibly present prior to conditioning and capacity measurements. The pH of the zeolite in three forms was tested using pH meter (soil/water = 1:5).

Natural zeolite different in three forms were activated using HCl, NaOH and NaCl solutions to prepare for the modified zeolite. The experimental protocol was modified from a study done by Lin et al. (1998). Five grams of zeolite of each form were immersed in 100 ml solutions in conical flasks containing 2 mol/L HCl, NaOH or NaCl. The conical flasks were then shaken in a water bath at 75 °C for 3 h, followed by centrifugation at 3000 rpm for 15 min. The liquid supernatant was decanted and all treated zeolites were washed with de-ionised water for several times and then dried in muffle at 105 °C for 2 h. Following that, the modification was repeated once and the zeolites were settled for 24 h before centrifugation, washing and drying. Identification of mineral species in the natural and modified zeolite was carried out by X-ray diffraction (XRD) of the random-oriented powder samples using Japan Rigaku 2555 X-ray diffractometer (Cu 40 kV, 250 mA). Selected natural and modified zeolites samples were also submit for BET analysis to examine the surface area (SA) and pore volume (PV).

Cation exchange capacity (CEC) of the natural and modified zeolites was determined by extracting NH$_4^+$ with 1 mol/L NaCl (pH 7) from NH$_4^+$-saturated sample prepared by equilibrating with 1 mol/L ammonium acetate (pH 7) at room temperature. The exact concentrations of ammonium ions in the solutions were determined using US EPA standard method (EPA5220, 1999).

The metal removal efficiency of the natural and modified clinoptilolite was evaluated by polluting the sorbent with 0.1 M KNO$_3$ solutions containing Pb(II), Cu(II), Zn(II) and Cd(II) at the concentration of 400 mg/L each with a solid/solution ratio of 1:100 in conical flasks. Then the conical flasks were put in a steady rate
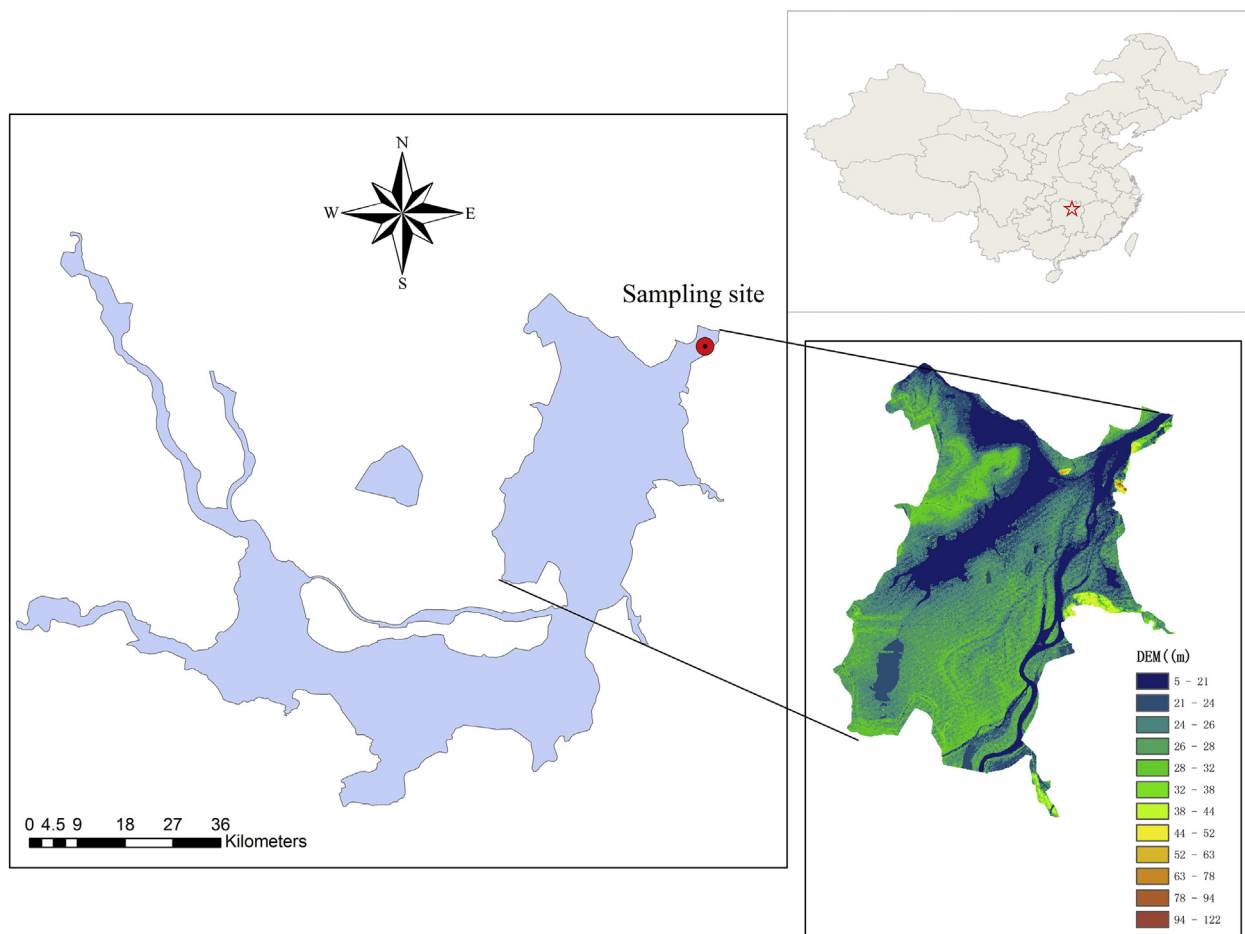
Fig. 1. Sampling site in East Dongting Lake.

shaker for 6 h. After centrifugation, supernatants from the samples were collected and filtered through 0.45 μm PTFE filter (FILTER-BIO®). Samples were acidified with 1 drop of HCl (GR) prior to analysis on AAS (AAnalyst700, Perkin Elmer). Desorption of metals from zeolite was examined by shaking the DI water rinsed (to wash off the remaining adsorption solutions) and drained zeolite fractions in 30 ml 0.1 M KNO$_3$ solution for 6 h. The upper solutions were treated as in the adsorption procedure and sent for metal analysis.

Following that, the modified zeolite showing the highest metal removal efficiency was characterized by scanning electron microscopy (SEM) to investigate the surface change.

2.3. Metal speciation in zeolite treated sediment

BCR sequential extraction procedure was applied to all zeolite-sediment mixture to analyze the chemical fractionation of metals bound to sediment as affected by zeolite. Prior to the extraction, the modified zeolite showing the highest metal removal efficiency was mixed with the sediment at the ratio of 1:10 (zeolite:sediment). The mixture was added with 25% distilled water and kept in cool and dark place for incubation of 1wk. Following that, the zeolite-sediment mixture was dried at 60 °C for 48 h. All samples including controls without added zeolite were subjected to BCR sequential extraction by adopting methods in Fathollahzadeh et al. (2013). Concentrations of metals in solutions were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) (PE5300D, Pelkin Elmer). The accuracy of the experiment was

evaluated through the recovery rates by dividing the sum of the four individual fractions by the total metal content.

2.4. Statistical analysis

One or two-way ANOVA was performed on all data to determine if significant difference existed between treatments. Least significant difference (LSD) was used to separate means where ANOVA showed significance at P < 0.05. Similar letters in tables and on top of the histogram indicate statistically equal values at P < 0.05.

3. Results and discussion

3.1. Sediment risk assessment

The sediment has an organic matter content of 10.9% and a moisture of 22.4%. The sediment pH was 7.7 and the electric conductivity was 9.4×10^{-3} S/m. The concentrations of the four metals at the status quo were Pb(69.8 mg/kg), Cu(46.0 mg/kg), Zn(174 mg/kg) and Cd(4.7 mg/kg), all above the background values (Li et al., 1986), indicating the current pollution status of the sediment in the region. According to the PEI index, the potential risk of the four metals was 15(Pb), 11(Cu), 2(Zn) and 570(Cd), showing the individual risk of being low, low, low and very high. The excess Cd results in an overall considerable risk of the sediment (Table 1). It shows that though Pb, Zn and Cu are the normal contaminants found in waters and sediments in East Dongting Lake, Cd

Table 1
Sediment's potential ecological index.

	Pb	Cu	Zn	Cd
C_D^i [a]	69.8	46.0	174.0	4.7
C_B^i	23.3	20.2	83.3	0.33
C_F^i	2.99	2.28	2.08	15.8
T_R^i	5	5	1	40
E_R^i	15	11	2	570
Risk level	Low	Low	Low	Very high
RI	598 (considerable risk)			

[a] C_D^i = present concentration, C_B^i = concentration of background, C_F^i = contamination factor, T_R^i = toxic-response factor, E_R^i = Potential risk of individual heavy metal, RI = sum of the potential risk of individual heavy metal.

contributes the most to the potential environmental risk at the study region.

3.2. Zeolite characterization

The pH of zeolite of three forms were 8.65 (I), 8.76 (II) and 8.53 (III). The average pH of zeolite after modification were found to be 3.65 (HCl), 11.33 (NaOH) and 8.17 (NaCl). The information of mineral species can be found in the XRD analysis for zeolite pre- and post-modification (Fig. 2). The natural zeolite used was mainly clinoptilolite, with minor quantities of other composites in the order of montmorillonite > quartz > ferrosilite > leucite. Acid modification slightly changed the mineral composition of zeolite as shown by the presence of split peaks at 2θ of 20−25°. The spectra of NaOH and NaCl modified zeolite show nearly similar patterns to that of the natural sample, illustrating absence of structural degradation during modification. The three modification protocols also diminished the intensity of the diffraction peak of leucite.

BET analysis showed the acid modification greatly improved the specific surface area and pore volume of zeolite (Supporting Information A). Likewise, NaCl modification increased the SA and PV to a less extent. Whereas, NaOH remarkably reduced the SA to 8.7 m^2/g and PV to 0.049 cm^2/g.

Cation exchange capacity (CEC) of the natural and modified zeolite was shown in Fig. 3. Fraction II zeolite showed the highest CEC values that varied between 216 and 260 mmol/100 g (P < 0.05), whereas fraction III zeolite only had CEC of 2.6−8 mmol/100 g. In fraction I and II, neither HCl nor NaOH conditioning improved
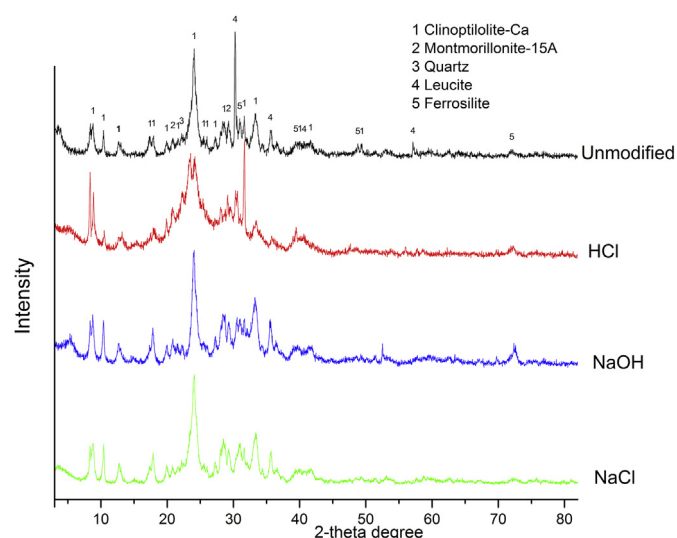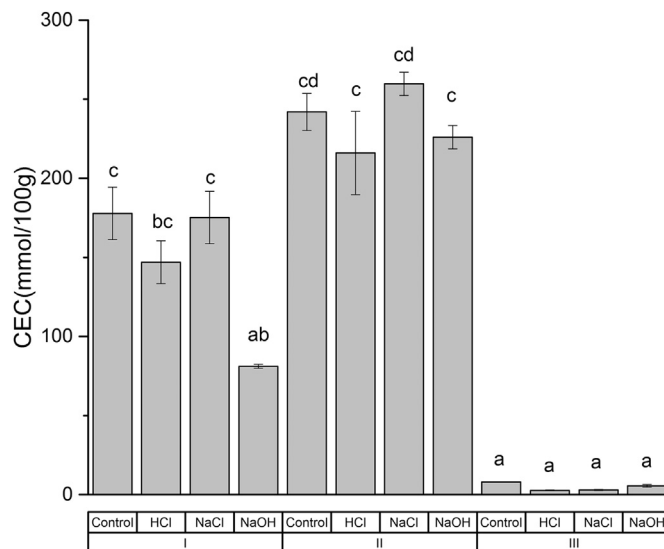
Fig. 3. CEC of the zeolite in different size and modification condition (I. bulk particle, II. granulated particle, III. powder).

zeolite performance on CEC. The greatest improvement in CEC was seen in NaCl modified fraction II zeolite, with the CEC value reaching up to 260 mmol/100 g.

3.3. Metal removal efficiency of zeolite in solution

Among the three fractions of zeolite, it is found that the powdered zeolite (fraction III) had the least metal removal of all four metals when compared with the other two fractions (Fig. 4). This is in correspondence with the CEC result where fraction III zeolite had the lowest CEC, indicating the overriding significance of CEC in determining metal adsorption capacity. In most scenarios, the fraction II zeolite showed higher metal removals than that of the fraction I zeolite, due to the higher specific surface area the granulated zeolite could have, consequently more adsorption sites could have been provided. Whereas for the fraction III zeolite, porosity that accounts for metal adsorption and exchange could have been disrupted, hence the CEC and metal adsorption quantity did not increase as the specific area increases.

When considering the effect of different conditioning, it is found that NaOH and NaCl greatly improved the metal removal efficiency of zeolite while HCl reduced the ability. There are two reasons of increased metal adsorption for the salt modified zeolite: firstly the salt could possibly clean water and impurities in zeolite inner pores as evidenced by the smoother XRD spectrum (Fig. 2). This further increases the pore size and specific surface area (Supporting Information A) and further improves the metal adsorption ability (Zhang et al., 2016); secondly, there are exchangeable Na$^+$ and Ca^{2+} in natural zeolite, with the abundance of Ca^{2+} > Na$^+$. When zeolite is conditioned with excess Na$^+$ provided by the salt, Ca^{2+} in zeolite can be replaced, which in turn results in an increased Na$^+$ and a decreased Ca^{2+} in zeolite. This change is likely to cause a reduction of Si:Al ratio in the zeolite's framework, hence more negative charges are presented in zeolite to attract cations (Curkovic et al., 1996). The increase of metal removal from solution by NaOH modified zeolite could be more likely as a result of metal precipitation when introducing OH$^-$ into the solution rather than metal adsorption. After NaOH treatments, a decrease in SA and PV is observed, which is likely caused by mesopore formation with desilication and dealumination (Kubù
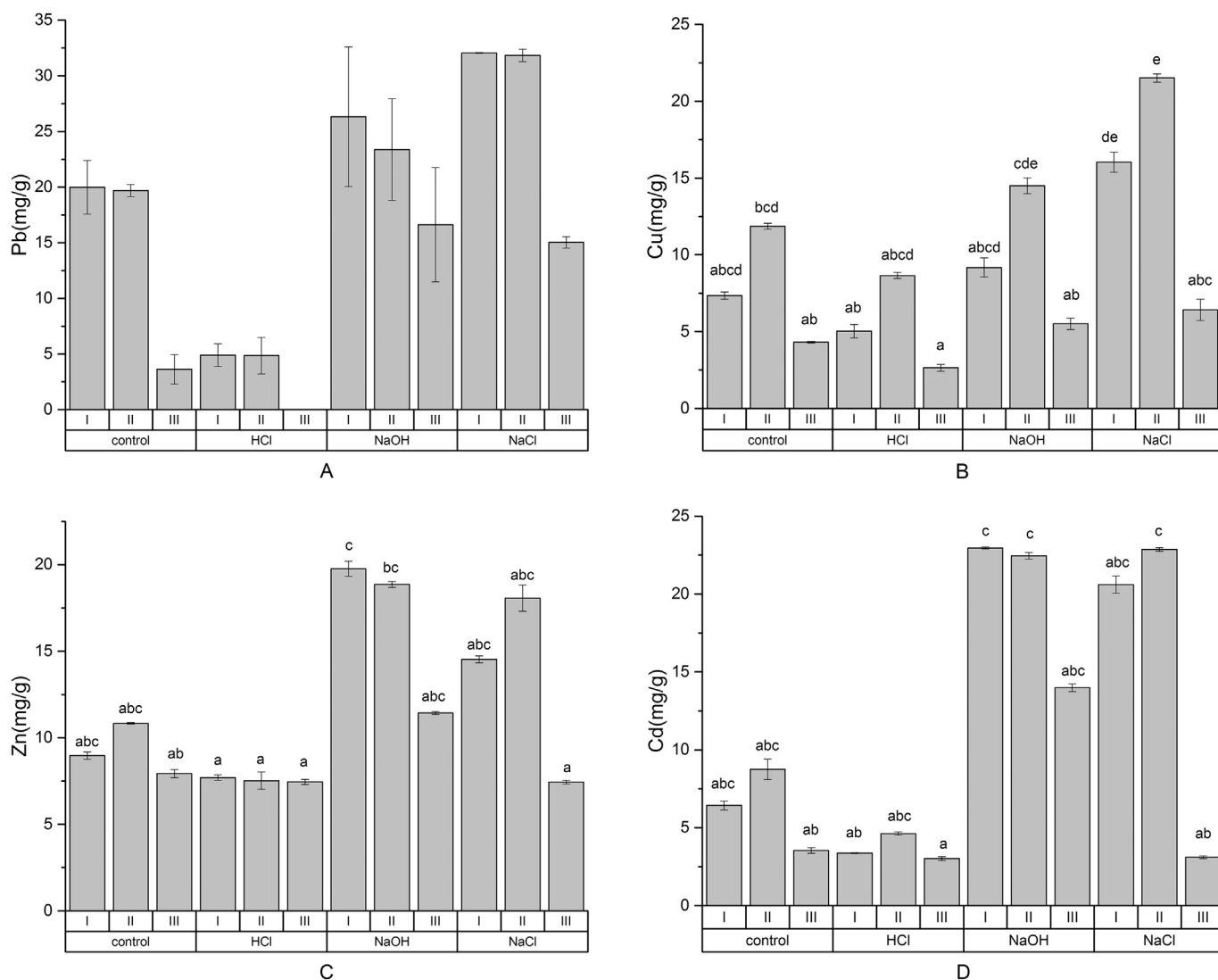
Fig. 2. XRD image of the natural and modified zeolite.

Legend in figure:
1 Clinoptilolite-Ca
2 Montmorillonite-15A
3 Quartz
4 Leucite
5 Ferrosilite

Fig. 4. Removal of Pb(A), Cu(B), Zn(C) and Cd(D) by natural and modified zeolite (mg/g) (Significance was not shown in Fig. 4A as no interaction between particle size and modification condition).

et al., 2015; Ates and Akgül, 2016). Whereas for HCl conditioning, no increased metal removals occurred possibly due to a competition of the sufficient H$^+$ with metal ions for zeolite's adsorption sites (zeolite pH 3.65). It was also acknowledged by other researchers that acid treatment could cause partial dissolution of both Si-tetrahedron and free linkages, which further destroys specific exchange sites of the zeolite (Christidis et al., 2003). This was evidenced by the slight change of spectrum in the XRD analysis. Some scientists deduced that acid treatment reduces the CEC due to dealumination of the structure, but such treatment can improve capacity and Si/Al ratio, favoring the adsorption/separation of non-polar molecules from water or gas flows (Fatollahzadeh et al., 2013). Metal desorption results show that minor quantities of metals desorbed from the fraction I and II zeolite, nevertheless almost all sorbed metals were lost in the fraction III zeolite (Supporting Information B).

Therefore, NaCl modified zeolite was chosen for subsequent BCR sequential extraction. The improved performance on metal removal of NaCl modified fraction II zeolite was supported by the SEM image where a cleaner surface and unblocked porous structure was shown as compared to the unmodified zeolite (Fig. 5).

3.4. Metal fractionation in zeolite treated sediment

The bioavailability and ecotoxicity of heavy metals relies on their speciation in sediment. Among the four fractions extracted in BCR sequential extraction, the first step extracts the soluble and exchangeable fractions of heavy metals that contain the metals of the most unstable form. Metals extracted in this step have high mobility and can be readily available to biota, thus having the highest toxicity and being referred to as direct toxicity. The step 2 extracted the reducible part of heavy metals which is the portion bond to hydrous oxides and amorphous ion/manganese oxides. Step 3 extracted the metals in the oxidizable form, which is the portion combined with organics and sulfide. When the redox potential is changed, heavy metals of the above two fractions could be transformed to more readily available form, resulting in hazardous effects on biota. Thus the reducible and the oxidizable forms of metal are grouped as potential toxicity. The residual part of heavy metals remained to be extracted in the fourth step is usually considered as the inert portion because it normally does not participate in chemical reaction and is quite stable in spite of environmental changes (Peng et al., 2009).
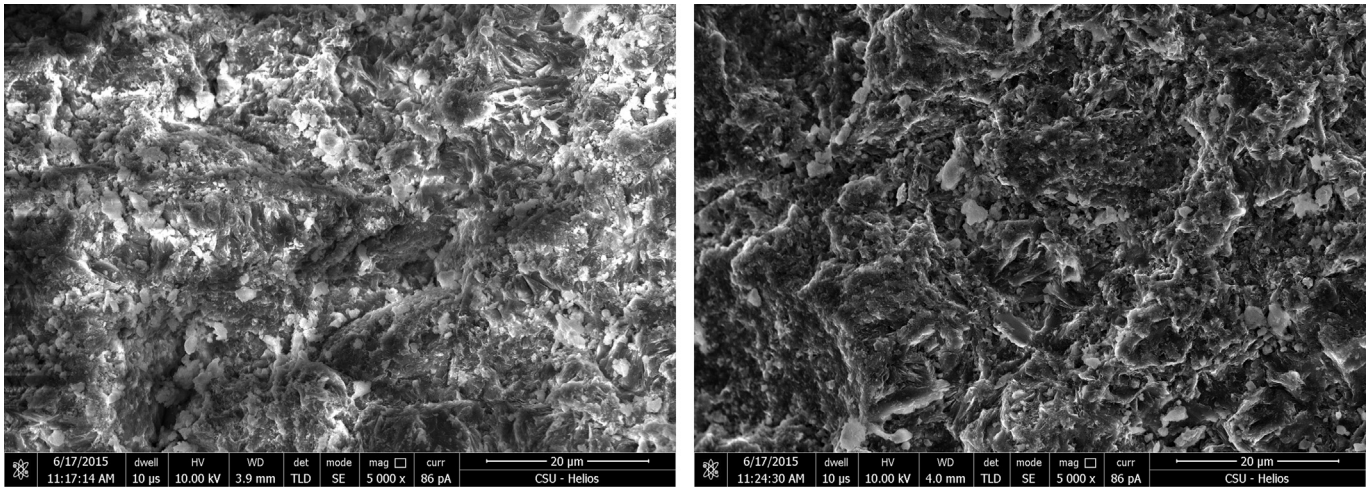
Fig. 5. SEM image of the natural (left) and NaCl modified (right) granulated zeolite. The white area in the natural zeolite (left) indicates the impurities on the surface and in the pores.

Table 2
BCR fractionation of zeolite treated sediment (STD in bracket, same footnotes indicate statistically equal values at P < 0.05.).

Metal fractionation	Zn(mg/kg)		Cu(mg/kg)		Pb(mg/kg)		Cd(mg/kg)	
	Control	Zeolite	Control	Zeolite	Control	Zeolite	Control	Zeolite
Exchangeable	17.09[b] (0.08)	13.76[a] (0.11)	2.43[b] (0.17)	1.76[a] (0.02)	2.80[b] (0.38)	1.01[a] (0.27)	1.65[b] (0.05)	1.21[a] (0.01)
Reducible	21.49[a] (0.68)	24.57[b] (0.27)	1.83[a] (0.28)	1.67[a] (0.05)	11.02[a] (0.63)	14.91[b] (0.82)	0.93[a] (0.03)	1.27[b] (0.05)
Oxidizable	13.18[a] (0.30)	12.82[a] (0.43)	11.57[a] (0.54)	12.82[b] (0.43)	6.54[a] (1.12)	7.10[a] (0.22)	0.26[a] (0.05)	0.28[a] (0.05)
Residual	121.9[a] (1.01)	122.5[a] (0.74)	30.40[a] (0.27)	29.79[a] (0.44)	48.89[a] (1.04)	47.23[a] (0.97)	1.20[a] (0.03)	1.30[b] (0.04)
Recovery (%)	99.8%	99.8%	101%	100%	99%	101%	86.0%	86.4%

The total concentrations of all four metals and the sums of the four sequential extraction steps were in good agreement (Table 2). Higher recovery values were shown for Zn, Cu and Pb, indicating a full extraction of metals from each step in the BCR procedure. A lower recovery rate was found for Cd (86.0%), slightly lower than that found in Kartal et al. (2006) (Cd 91.9%). It is found that Cu in the polluted sediment mainly existed in the oxidizable and residual forms, taking up to 90% of the total concentration (Fig. 6). Over 70% of Zn and Pb existed in the residual fraction. Whereas most cadmium in the sediment was found in the exchangeable fraction
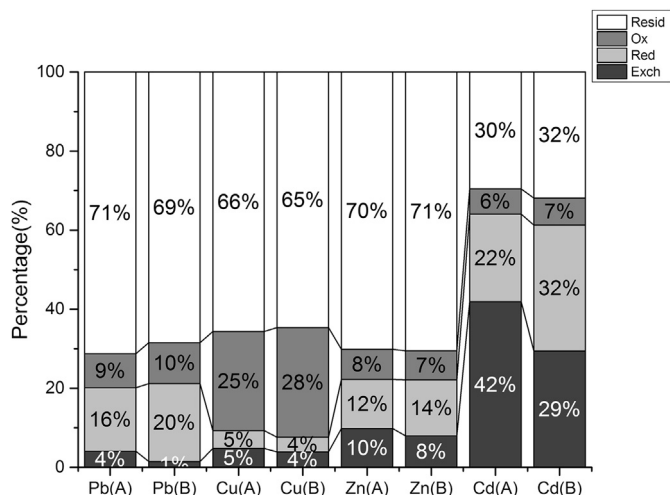
(42%) (Fig. 6), indicating its higher mobility and bioavailability compared to the other three metals. Therefore, the mobility of the four metals followed the sequence of Cd > Zn ≈ Pb > Cu. In a study done by Kartal et al. (2006), they assessed the mobility of a series of metals in street sediment and reported a mobility sequence of Cd ≈ Zn > Pb > Cu > Mn > Co > Ni > Cr > Fe.

When the modified zeolite was added to the sediment, the metal speciation was accordingly altered to different extents. With no exception, the exchangeable fraction of Pb, Cu, Zn and Cd were all significantly reduced following zeolite addition (P < 0.05), suggesting that the direct metal toxicity may be alleviated. This is in accordance with some findings that metal bioavailability was inhibited upon the addition of zeolite (Castaldi et al., 2005; Li et al., 2009). The addition of zeolite reduced 19.5% of the exchangeable Zn (Table 2), meanwhile it increased 14.3% of the reducible Zn, indicating a transformation of the unstable Zn to stable forms. The exchangeable fraction of Cu was decreased by 21.1%, meanwhile the oxidizable Cu was increased by 10.8%. This alteration of metal speciation suggests that the addition of zeolite resulted in an alleviated direct toxicity and an increased potential toxicity. A small portion of Cu freed from the exchangeable part was sequestered by organics/sulfide in the oxidizable fraction following the addition of zeolite. The highest reduction of exchangeable fraction of metal was seen in Pb (64.5%), and the reducible Pb was increased by 26.2%. The best stabilization effect of zeolite was seen in Cd, for which the exchangeable fraction was decreased by 26.7%, and both the reducible and residual fractions were significantly increased by 36.6% and 8.3%, individually. Therefore the addition of zeolite can most effectively reduce the bioavailability and ecotoxicity of Cd. In fact it is imperative to take actions against Cd pollution of the sediment as it is posing a very high risk to the ecosystem in Dongting Lake region (Table 1).

Fig. 6. Metal fractionation in contaminated sediment. A: control, B: NaCl modified zeolite.

There are two reasons that can be accounted for metal stabilization in sediment using modified zeolite: firstly, the addition of modified zeolite resulted in an increase in sediment pH (from 6.8 to 7.7), which subsequently caused a weakened competition of H^+ with heavy metal ions for ligands (such as OH^-, CO_3^{2-}, SO_4^{2-}, Cl^-, S^{2-}, and phosphate, etc.), making it easier for metal ions and ligands combined into a relatively more stable form (Peng et al., 2009). Meanwhile, the increase in the environmental pH could promote zeolite surface adsorption of heavy metal ions. Secondly, the modified zeolite has a higher CEC than the natural one, leading to a higher metal exchange that could have occurred in the zeolite structure.

4. Conclusions

Natural zeolite of three different sizes were conditioned with acid, alkali or salt and screened to investigate the metal removal efficiency. Granulated zeolite (fraction II) with NaCl conditioning had the highest CEC and adsorption capacity, whereas the powdered zeolite, irrespective of modification conditions, had the lowest metal exchange and adsorption. Acid or alkaline treatment degraded zeolite quality in metal exchange and adsorption.

Metal speciation and redistribution before and after the addition of zeolite to sediment was investigated using BCR sequential extraction. It was found that the oxidizable and residual fractions of Cu accounted for 90% of total Cu in the sediment. Cadmium is shown to be the most mobile metal, whereas Pb and Zn mainly existed in the residual form. The metal mobility of Zn, Cu, Pb and Cd were all drastically reduced, and the effect of stabilization was shown by the transformation of metal from the direct toxic fraction to the more stable forms. Amongst the four metals, the best metal stabilization was seen in Cd, where the exchangeable fraction was greatly reduced and the reducible and residual fractions were all increased correspondingly. For Dongting Lake which is currently found to be Cd rich, using the modified zeolite is a possible solution to alleviate the hazards likely posed to the lake and the surrounding environment, especially in consideration of land application of sediment as resource utilization.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2016.04.046.

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