Inactivation of lead and zinc in sediment using lanthanum modified zeolite

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Abstract. Access accumulation of zinc and lead in sediment would be harmful to human beings. In the present study, Lanthanum Modified Zeolite (LMZ) was developed with fly ash and its binding capabilities toward zinc and lead were investigated. The Langmuir adsorption maximum of LMZ for Zn\textsuperscript{2+} and Pb\textsuperscript{2+} were 22.78 and 105.26 mg/g, higher or at least comparable to adsorbents developed in recent studies. Dosing LMZ to polluted sediment could transfer zinc and lead from environmental available forms to refractory form, and higher dosage would enhance the immobilization performance.

1. Introduction
As the wide application in modern agriculture and industry, a huge amount of lead and zinc were mined every year. With large scale exploitation, considerable amount of lead and zinc enter the environment. Li et al surveyed the lead concentration of a small creek near Fenghuang pit, Hunan, China. It was observed that the average lead concentration in surface water was 0.145mg/L\textsuperscript{[1]}. According to a survey in New South Wales, Australia, zinc concentration in the Malonggo river was higher than 8mg/L which originates from an abandoned pit nearby\textsuperscript{[2]}.

It was well known that lead is a toxic metal which would harm children’s brain and nervous system. A human health based water quality criteria of lead revealed that Pb concentration in river higher than 13.45μg/L would lead to an adverse effect. Although zinc is an essential element for living organisms, access accumulation would cause toxic effect, especially for aquatic organisms like grass carp, etc. USEPA demonstrated that zinc concentration in aquaculture water should not surpass 0.12mg/L, which is a little higher compared to the water quality standard for fisheries in China (0.1mg/L).

Using inactivation agents for the remediation of heavy metal polluted soil and sediments has been recognized as an ideal method, for its satisfied performance and low cost. In fact, large quantities of novel materials have been developed, such as steel slags, red mud, iron oxide modified zeolites\textsuperscript{[3]}. In our previous study, we have developed a novel adsorbent, lanthanum modified zeolite (LMZ) using coal fly ash. LMZ could adsorbed both anion and cationic pollutants in water, and its ability to immobilize phosphorus in sediments have also been clarified\textsuperscript{[4]}. In this study, we are trying to investigate the heavy metal immobilization performance of LMZ toward Pb and Zn, which would broaden the application of LMZ in the real application.
2. Materials and Method

2.1 Synthesis of LMZ
ZLC was prepared via a sequential two-step method. Briefly, 15 g coal fly ash was mixed with a 2 M NaOH solution at a solid/liquid ratio of 1:6. The solution was subjected to a 24 h hydro-thermal reaction at 95°C with constantly agitation, which resulted in the formation of zeolite, along with a waste alkaline solution. Subsequently, the slurry was neutralized using 90 ml of 2 N LaCl₃ solution. Obtained solid product was then washed with water and ethanol, dried under 45°C in an oven, and grounded to powder, allowing it to pass an 80 mesh sieve. The crystal phase and surface morphology in ZLC was characterized by Scanning Electronic Microscope (HATACHI TM3000, Japan), respectively.

2.2. Adsorption experiments
Adsorption experiments were conducted in 50ml centrifuge vessels. A 0.1g of LMZ was mixed with 40 ml of lead or zinc solution in each vessel, and the suspensions were rotated in a shaker for 24 h. In our preliminary experiment, 24 h was shown to be adequate for the reaction to reach equilibrium. Suspensions were then centrifuged at 180 rpm for 15 min, and Pb²⁺ and Zn²⁺ concentrations in the supernatant were analyzed via Atomic Adsorption Spectrum (Analytik Jena Zeenit 700, Germany), respectively. All the experiments were undertaken in triplicate, and the mean data as well as the standard deviations were reported.

Adsorption amount of lead and zinc were calculated via the following equation:

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Q_e = \frac{(C_0 - C_e) \times V}{m}
\]

where V is the solution volume in L, C₀ and Ce is the initial and final concentrations in mmol/L, and m is the dry weight of the adsorbent in g.

2.3. Immobilization of heavy metals in sediments
Sediment was obtained from Xingqing Lake, Xi’an, China (N 34°15’18.50″, E 108°58’44.53″) at April, 2018. The sediment was air dried for several weeks and passed though a 30 mesh sieve to eliminate the gravels and aquatic organisms. The zinc and lead concentration in sediment were spiked to 703.70 and 297.35 mg/kg using ZnCl₂ and PbCl₂ regent, respectively. Six hundred grams of sediment was packed into three glass cylinders (with a 15 cm internal diameter and a length of 60 cm) to simulate the remediation scenario. An amount of 5.05 and 10.10 g LMZ was mixed with sediment in two of the cylinders, and the other one was set as a control. The immobilization experiment was conducted for 60 days, after that sediment samples in each cylinder was collected for the analysis of heavy metal fraction with a BCR method.

3. Results and discussion

3.1 Characterization of LMZ
In our previous studies, LMZ has been characterized by X-ray Diffraction patterns, where LMZ was proven to be the mixture of NaP1 zeolite and amorphous lanthanum oxide. In the present study, SEM-EDS was employed to further examine the surface morphology and element composition. As were shown in Fig.1, lots of aggregates could be seen on LMZ surface, which was identified to be lanthanum oxide according to previous studies[^4]. The EDS spectra indicated that Si, Al, Na, Cl and La were the main element detected on the LMZ surface. The element Si and Al could be attributed to the zeolite fraction, where La was originated from lanthanum oxide. Additionally, since Si and Al could still be detected on LMZ surface, it was concluded that zeolite particles were not fully wrapped by lanthanum oxide, revealing that LMZ has a composite surface.
3.2 Adsorption isotherms

To obtain the binding capacity of LMZ towards Zn$^{2+}$ and Pb$^{2+}$, adsorption isotherms were conducted and were shown in Fig. 2. The isotherms were fitted with Langmuir and Freundlich model and the fitting parameters were listed in Tab.1. The equation of the Langmuir model could be given as follows:

$$\frac{C_e}{Q_e} = \frac{C^*}{Q_{max}} + \frac{1}{K_L \times Q_{max}}$$

(2)

whereas the Freundlich model could be given as:

$$\log Q_e = \frac{1}{n} \log C_e + \log K_F$$

(3)

where $K_L$ is a constant related to adsorption strength (L/mg), $Q_{max}$ is the maximum adsorption capacity (mg/g), $K_F$ is Freundlich constant (mg/g), and $1/n$ is the adsorption density.

As were shown in Fig. 2 and Tab.1, adsorption isotherms were better fitted by Langmuir model, indicating that both zinc and lead adsorption followed the monolayer adsorption assumption. The Zn$^{2+}$ and Pb$^{2+}$ binding capacity of LMZ were 22.78 and 105.26 mg/g, respectively. Compared with adsorbents developed in recent studies, the adsorption capacities of LMZ toward Zn$^{2+}$ and Pb$^{2+}$ were higher or at least comparable, indicating that LMZ has a high potential to bind heavy metals.

Binding mechanism for cationic pollutant adsorption by LMZ might be cation exchange[5], electrostatic attraction and ligand exchange[6]. It’s well known that zeolite surface is permanently negatively charged, and exchangeable ions (in this case is sodium ion) were adsorbed on its surface to make it electrically neutral. Zn$^{2+}$ and Pb$^{2+}$ ions could be removed irreversibly by zeolite through exchanging with the sodium ions, or simply adsorbed by the negatively charged zeolite surface. On the other hand, lanthanum oxides, which was same with γ-Al$_2$O$_3$ and goethite, could chemically adsorb Zn$^{2+}$ and Pb$^{2+}$ by forming inner-sphere complex.
3.3 Immobilization of lead and zinc in sediment

Since LMZ could adsorb lead and zinc effectively from water, it could be expected that the material could also be employed as an inactive agent for the remediation of heavy metal polluted soil and sediment. Thus, a 60 day inactivation experiment was undertaken in lab-scale, and BCR extraction of zinc and lead fraction in different treatments were shown in Fig. 3.

For zinc, dosing LMZ to polluted sediment resulted in a significant transmission of zinc fractions. In the control treatment (A), 35% of zinc existed as acid soluble fraction, whereas 27% existed as reducible fraction. By dosing 5.05 g of LMZ (B), the percentage of acid soluble fraction decreased to 31%, and reducible fraction decreased to 21%. At the same time, the percentage of residual fraction increased from 26% to 36%. Therefore, it could be concluded that dosing LMZ would transform zinc from environmental available fractions to refractory fraction. Increasing LMZ dosage to 10.10g (B) would lead to a more severe transmission.

As for the case of lead, 58% of lead in control treatment was in oxidizable fraction. When different dosage of LMZ were added to the sediment, the percentage of oxidizable fraction decreased to 45% and 39%, respectively. At the same time, residua fraction increased from 28% to 40% and 48%. Therefore, LMZ could transfer zinc and lead from environmental available forms to more refractory form.

According to the results of BCR extraction, LMZ was proven to be an ideal inactivation agent for the simultaneous immobilization of zinc and lead in polluted sediment.

Fig. 2 Adsorption isotherms of Zn\textsuperscript{2+} and Pb\textsuperscript{2+}

| Absorbate | Langmuir model | Friendlich model |
|-----------|----------------|-----------------|
|           | $Q_{max}$  | $K_L$  | $r^2$  | $K_F$  | $1/n$  | $r^2$  |
| Zn\textsuperscript{2+} | 27.78     | 0.404   | 0.992   | 7.13    | 0.85     | 0.798 |
| Pb\textsuperscript{2+} | 105.26    | 1.080   | 0.995   | 75.61   | 1.88     | 0.948 |
4. Conclusions
In this study, LMZ was developed with coal fly ash and its immobilization capability of zinc and lead was examined. The Langmuir adsorption maximum of LMZ for Zn\(^{2+}\) and Pb\(^{2+}\) were 22.78 and 105.26 mg/g, respectively. By dosing LMZ, zinc and lead in sediment could transfer from environmental available forms to refractory form, and higher dosage would enhance this effect. In a word, LMZ could simultaneously immobilize zinc and lead in sediment.

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