



Trapping the lead ion in multi-components aqueous solution by natural clinoptilolite

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ABSTRACT

To study whether natural clinoptilolite could selectively capture Pb^{2+} ion in the aqueous solution containing salt and glycine as well as nitrosamines, the natural zeolite was utilized in the complex solution with pH value of 1.2 in comparison with other porous materials such as zeolite NaZSM-5 and activated carbon. Clinoptilolite exhibited the highest capability in adsorbing Pb^{2+} ion in the solution at 37 °C, achieving the capacity of 7 mg/g, two times more than that by other zeolites and six times over that by activated carbon, and the adsorption equilibrium could be achieved within 2 h. The impacts of solid–liquid ratio, initial concentration of Pb^{2+} and the competition of other metal ions or volatile nitrosamines on the adsorption were examined, and the change in Gibbs energy for the ion-exchanged of Pb^{2+} ion by clinoptilolite was discussed, through which the ion-exchange process was proven to be spontaneous. Moreover, both the selectivity of clinoptilolite toward Pb^{2+} ion in complex solution and the venial toxicity of clinoptilolite on the viability of RAW264.7 cells were investigated in this article.

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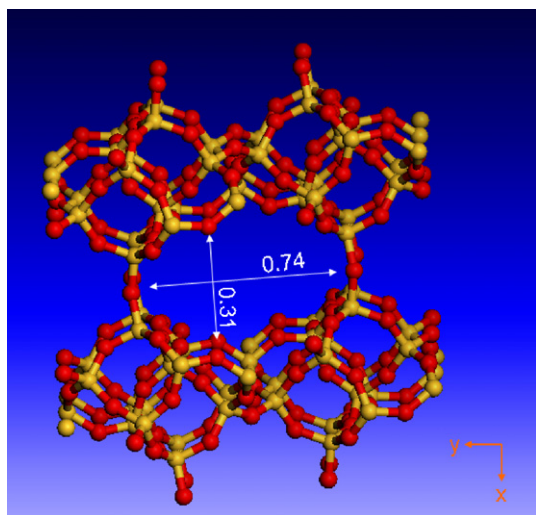
1. Introduction

The health hazard caused by lead ion in environment has been well established [1–6]. Once the concentration of Pb^{2+} ion exceeded 1.93 $\mu\text{mol/g}$ -bloods, lead poisoning occurred to damage the renal, gastrointestinal, skeletal, cardiovascular, muscular and other vital organs, leading to anemia [4,5]. In addition, partial to severe brain damage, mental retardation and some psychological abnormalities seem to be associated with lead poisoning [6]. Lead ion may enter human body through diet and drinking unexpectedly, and the lead uptake by humans is generally dominated by particle ingestion (oral-gastrointestinal pathway), especially the “absorption” of ingested Pb that is more in children [1–3]. Apart from the acute lead poisoning, which can be treated by washing the stomach with water followed by induced vomiting, accumulation of the trace amount of lead ion in human body also causes chronic lead poisoning. Accordingly, it will be necessary to prevent the harm of lead ions from metabolic activation by trapping them in stomach, for which zeolite is the valuable candidate due to its unique selective adsorption that has been widely applied in petrochemical and chemical industries [7,8]. There are a lot of literature on the potential application of zeolite in life science such as release drugs [9,10], enzyme mimetic drugs and anti-tumor drugs [11,12]; recently the

modified zeolite has been tried to trap nitrosamines in artificial gastric juice [13]. However, it is unclear how zeolite selectively captures the heavy metal ions such as Pb^{2+} ion in the complex solution with the composition close to that of artificial gastric juice.

The most widely used methods for removing heavy metals are chemical or electrochemical precipitation [14]. Some tree materials [14–16], agricultural wastes [17,18], fly ashes [19,20], clays or zeolites [21–22] have been reported to possess the capacity to adsorb and accumulate heavy metals. Concerning with the reducing heavy metals in solution by zeolite materials, clinoptilolite is the one to be often utilized [23–25], partially owing to its special ability of ion-exchange [26,27]. Clinoptilolite is the most common natural zeolite belonging to heulandite family with the molar Si/Al ratio above 4 [28], and its structure is characterized by large intersecting open channels of 10- and 8-member tetrahedral rings (Scheme 1). Low cost and special structure enable clinoptilolite to be utilized as the therapeutic adjuvant for mammary carcinoma and the neutralizer for excessive gastric acid [29,30]. Moreover, clinoptilolite was tried as the diet component of growing pigs to resist the poisoning of Pb in diet (500 or 1000 ppm) [31], and there were some commercial natural zeolites in purified form, which claimed heavy metal detoxification in human body [32]. However, many suspicions still remain on the potential application of the natural zeolite. How clinoptilolite captures the Pb^{2+} ion in the complex solution consisting of salt and amino acid as well as other metal ions? Does the impurity of the natural zeolite disturb the adsorption of lead ion? How serious is the inherent toxicity of clinoptilolite in the

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Scheme 1. The framework of the natural clinoptilolite viewed along [001].

organisms? Answering these questions is valuable not only for deep understanding the function of natural zeolite in the complex solution, but also for synthesizing new clinoptilolite-based functional materials to replace the natural zeolite for the potential application in life science.

Therefore, a series of adsorption experiments is performed in the complex aqueous solution containing amino acid, salt and volatile nitrosamines to investigate the uptake capacity of lead ion by natural clinoptilolite, and some other zeolites along with activated carbon are used for comparison. One of our aims is to check whether clinoptilolite possesses the selectivity toward Pb^{2+} ion in the complex solution, which is crucial for the potential application of clinoptilolite in protecting health.

2. Experimental

2.1. Materials and chemicals

The natural clinoptilolite sample was obtained from Jinyun (China) [27]. It contained 70–75% of clinoptilolite zeolite, and the main accompanied minerals were bentonite (10% or more), quartz and perlite impurities (7–10%). According to the results of physical-chemical property tests, it was the high grade zeolite mine with NH_4^+ exchange capacity of 21.68 mg/g [26], and the K^+ exchange capacity of 13–16 mg/g. The surface area and Si/Al ratio of the sample were similar to the data in literature [28,33], and the particle size was selected at 52–61 μm (250–280 meshes). To clean the clinoptilolite, the natural zeolite was washed with water to get rid of soil and the adhering particles at first, and then added into the 2 mol/L NaCl solution at the ratio of 10 mL/g, being shaken at 100°C for 2 h [26]. After then, the obtained solid was washed with deionized water and dried at 100°C for 24 h to give the sample of Na-clinoptilolite. Table 1 lists the chemical composition of Na-clinoptilolite.

Table 2

The ion-exchange quantity of different porous materials.

Sample	Pore size (nm)	Surface area (m^2/g)	Capacity of ion-exchange (mmol/g)	Pb^{2+} adsorbed at pH 1.2 (mmol/g)
NaZSM-5 (Si/Al = 12.5)	0.54 × 0.56	325	1.14	8.81×10^{-3}
NaZSM-5 (Si/Al = 26)	0.54 × 0.56	354	0.587	6.03×10^{-3}
Na-clinoptilolite	0.31 × 0.74	16	1.49	0.036
NaA	0.4	~800	5.48	–
NaY	0.74	766	8.79	–

Table 1

Chemical composition of Na-clinoptilolite sample.

Composition	Amount (%)	Composition	Amount (%)
Si ($SiO_2\%$)	63.40	Sulfide ($S^{2-}\%$)	<0.001
Al ($Al_2O_3\%$)	11.35	F, %	<0.02
Fe ($Fe_2O_3\%$)	0.88	Cr, $\mu g/g$	6.7
Mg ($MgO\%$)	0.60	Pb, $\mu g/g$	32.9
Ca ($CaO\%$)	2.27	As, $\mu g/g$	41.4
Na ($Na_2O\%$)	0.89	Cu, $\mu g/g$	6.1
K ($K_2O\%$)	1.97	Cd, $\mu g/g$	0.3
Ti ($TiO_2\%$)	0.14	Zn, $\mu g/g$	75.6
Mn ($MnO\%$)	0.07	Loss in ignition, %	14.80
Sulfate ($SO_3\%$)	3.54		

NaZSM-5 zeolites with different Si/Al ratio were commercially available powders (Table 2) [34]. MCM-22 with a surface of 481 m^2/g and the Si/Al ratio of 10 was provided by China University of Petroleum. The activated carbon, with 1.0 nm average pore size and the surface area of 1128 m^2/g , was the product of Chemviron Carbon (CAS number 7440-44-0, Belgium). One commercial available natural montmorillonite with the surface area of 10 m^2/g and the particle size of 63 μm was utilized. *N*-nitrosopyrrolidine (NPYR), one of volatile nitrosamines, was purchased from Sigma. The RAW264.7 cells were purchased from cell resource center of Shanghai (China).

Five hundred milliliters of complex solution with a pH value of 1.2 was prepared by adding 0.35 g sodium chloride, 0.5 g glycine and 31.6 mL hydrochloric solution of 1 M into distilled water [35]. A given amount of metal salt such as $Pb(NO_3)_2$, $Cu(NO_3)_2$ or $Cd(NO_3)_2$, was added into the solution prior to adsorption tests.

2.2. Experimental methods

The structure and BET specific surface area of clinoptilolite were determined by X-ray diffraction (XRD) analyses and nitrogen adsorption-desorption at $-196^\circ C$ as previously reported [13]. Scanning electron microscopy (SEM) images of samples were obtained with HITACHI S4800 microscopes, and the sample was coated with Au film to improve the conductivity prior to imaging.

Adsorption of Pb^{2+} , Cd^{2+} , Cu^{2+} ions by various zeolite samples in solution was studied using batch method. One hundred milligrams adsorbent was added into the 25 mL solution with an initial metal concentration of 50 mg/L in flasks, and the mixture was shaken at 37°C for 3 h and then centrifuged at 3000 rpm for 15 min to separate the solution and the solid [13]. The residual concentration (C_e) of Pb^{2+} or other metal ions in the solution was determined by atomic absorption spectrometry (VARIAN, AA240FS). To study the adsorption of NPYR and Pb^{2+} ions by clinoptilolite, 0.24 mmol/L NPYR and 0.24 mmol/L of Pb^{2+} ions were added in the solution. After the adsorption was finished, the residual Pb^{2+} ion in solution was determined by atomic absorption spectrometry, and the remained NPYR in the solution was detected by the improved spectrophotometric method [13,34], in which HBr in glacial acetic acid chemically denitrosated the nitrosamines to liberate gaseous product. The formed gaseous product was oxidized to NO_2 and then converted to NO_2^- that was detected by a Digital Visible Spectrophotometer at 540 nm [34].

To investigate the impact of Na-clinoptilolite mass on the adsorption of Pb^{2+} ion, 20, 40, 60, 80 and 100 mg of the zeolite were added into the 25 mL solution with an initial metal concentration of 50 mg/L in flasks, respectively, to carry out the experiment. In another tests to examine the influence of Pb^{2+} ion content on the adsorption, the Pb^{2+} -containing solution with different initial concentrations was used. 60 mg Na-clinoptilolite was added into the 25 mL Pb^{2+} solution with known concentration in flasks, and the test was performed in the same procedure as mentioned above.

RAW264.7 cells test was employed to assess the cellular toxicity of Na-clinoptilolite [36], and the assay of MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) was used to quantify the viability of the cell. Briefly, 2×10^5 RAW264.7 cells per well were seeded into a 96-well plate. After 1 h incubation, Na-clinoptilolite was added with the concentrations of 0, 0.05, 0.25, 1, 2.5, 5 mg/mL in PBS buffer (pH 7.4) that is the buffer solution of phosphate acid to maintain the growth environment of the RAW264.7 cells. After 24 h incubation with Na-clinoptilolite at 37 °C, MTT reagent in PBS solution was added to detect the metabolically active cells in each well. Then, the plates were read at 492 nm [36].

2.3. Calculation methods

The uptake of lead ion on adsorbent is obtained by simple mass balance:

$$q = \frac{V(C_0 - C_f)}{m} \quad (1)$$

The removal efficiency of lead ion is calculated from:

$$r (\%) = \frac{C_0 - C_f}{C_0} \times 100 \quad (2)$$

In these two equations, V is the volume of solution and m is the weight of adsorbent, and q represents the amount of lead ion adsorbed by zeolite (mg/g), C_0 and C_f mean the initial and final concentrations (mg/L), respectively. Langmuir and Freundlich equations are used to calculate adsorption capacity of zeolite. Freundlich equation is in the logarithmic form:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

where q_e is the equilibrium concentration on adsorbent (mg/g), C_e is the equilibrium concentration in solution (mg/L). K_F is taken as a relative indicator of adsorption capacity, $1/n$ is indicative of the energy or intensity of the reaction as well as the favorability and capacity of the adsorbent/adsorbate system [34].

The common form of Langmuir equation is

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \quad (4)$$

where q_e is the equilibrium concentration on adsorbent (mg/g), C_e is the equilibrium concentration in solution (mg/L), q_m (mg/g) and K_L (L/mg) are the Langmuir adsorption constants that relate to the capacity and the energy of ion-exchange, respectively.

Another isotherm, Dubinin–Radushkevich (D–R) isotherm that is calculated from the ion-exchange data, is expressed as follows:

$$\ln q_e = \ln X_m - K \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \quad (5)$$

where q_e and C_e are described under Eq. (3) (mg/g and mg/L, respectively), X_m is the maximum ion-exchange capacity of the clinoptilolite (mg/g), K is a constant related to the ion-exchange energy (mol^2/kJ^2), R is the gas constant ($\text{kJ}/\text{K mol}$), and T is the temperature (K).

Two sorption kinetic models were utilized to describe the sorption behavior of Na-clinoptilolite in the multi-component solution

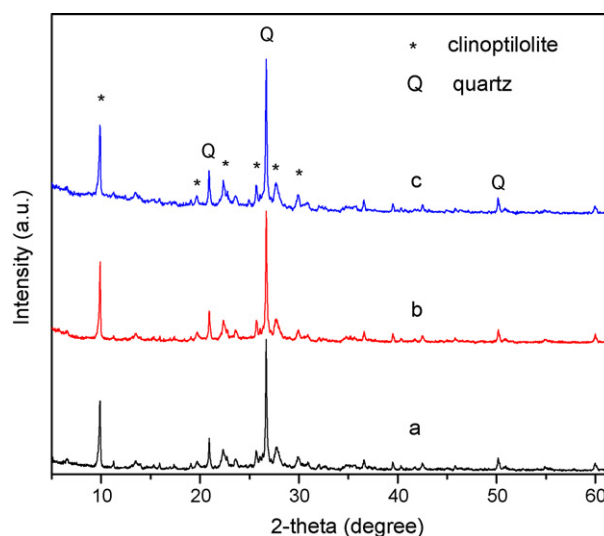


Fig. 1. XRD patterns of the natural clinoptilolite (a) before and (b and c) after used in the multi-component aqueous solution (b) without and (c) containing Pb^{2+} ion.

of Pb^{2+} , Cu^{2+} , and Cd^{2+} ions. The first model was the pseudo-first-order rate equation [38]:

$$\log(q_e - q) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

The second model was pseudo-second-order rate equation [21]:

$$\frac{t}{q} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \quad (7)$$

where t is the contact time (min), q is the sorption capacity of metal ion at time (mg/g), q_e is the sorption capacity at equilibrium (mg/g), k_1 is the first order rate constant (min^{-1}), k_2 is the second order rate constant ($\text{g}/\text{mg min}$).

The change in Gibbs free energy for the ion-exchange process is obtained using the following equation [21]:

$$\Delta G = -RT \ln q_m \quad (8)$$

3. Results and discussion

3.1. XRD and SEM measurements of natural Na-clinoptilolite

Fig. 1 illustrates the XRD patterns of Na-clinoptilolite samples before and after used in the multi-component aqueous solution, in which the characteristics of clinoptilolite appear with the 2θ value of 9.8° , 19.6° , 22.3° , 25.8° and 27.6° accompanied with the XRD peak of quartz around 21.0° and 26.7° . Quartz was the main impurity of this sample [27], but its content was less than 10% by weight. There was no serious difference on the morphology of Na-clinoptilolite agitated for 2 h in the acidic solution with low pH value, but some large particles of Na-clinoptilolite crystal were destroyed into small pieces for longer retention time (24 h), with the surface to be corroded more or less (Fig. 2). However, the special lattice structures of clinoptilolite still existed after aging for 24 h. In our laboratorial test capturing heavy metal cations, however, the zeolite usually stains in the solution no more than 2 h, usually only 1 h, so the structure variation of Na-clinoptilolite in the acidic solution for 24 h would have minor influence, if any, on the zeolite and its potential application. This result indicated the structural stability of clinoptilolite in the solution with pH value of 1.2, unlike zeolites NaY and NaA that collapsed soon in such strong acidic solution [37].

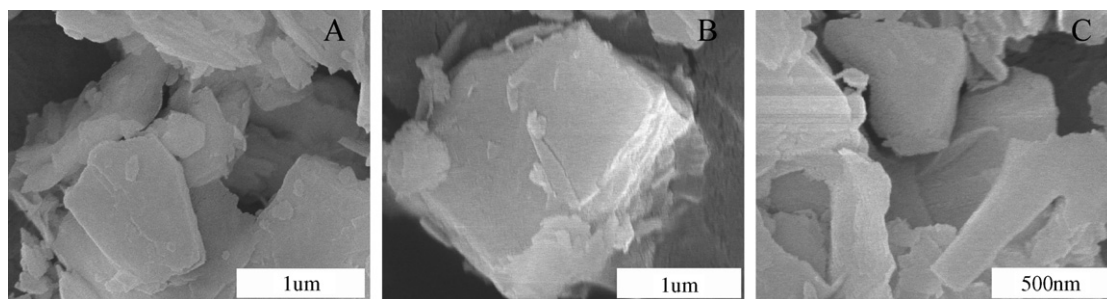


Fig. 2. The SEM of Na-clinoptilolite (A) before and after agitated in the solution with pH 1.2 for (B) 2 h and (C) 24 h.

3.2. Metal ions adsorption by different porous adsorbents

Fig. 3A demonstrates the adsorption of lead ion by various porous samples in the solution with pH value of 1.2, among them Na-clinoptilolite exhibited outstanding adsorption ability because it had the highest capacity of 6.95 mg/g at the initial Pb^{2+} concentration of 50 mg/L. Natural montmorillonite was assessed in the adsorption as a comparison, and it exhibited the adsorption capacity of 5.49 mg/g toward the lead ion. Based on the adsorption of Pb^{2+} ion by clinoptilolite and montmorillonite, it is hard to attribute the high ability of natural clinoptilolite in

adsorption of Pb^{2+} to the existence of montmorillonite impurity in the natural zeolite. Besides, montmorillonite was seldom used in life science. Therefore, the clinoptilolite with the low-toxicity, if any, and the high adsorption capacity toward Pb^{2+} ion in the strong acidic solution are chosen as the candidate for the potential application in life science. The surface area of adsorbent is not crucial for the uptake capacity of Pb^{2+} ion since the surface area of Na-clinoptilolite is quite small (Table 2); contrarily the activated carbon possessed the largest surface area (1128 m²/g), but its adsorption capacity of Pb^{2+} was only 1.2 mg/g. In general zeolite eliminates the harmful ions in solution through ion-exchange process [38,39]; thereby the lower Si/Al ratio should be beneficial for the adsorption of Pb^{2+} by zeolite. It was true that the zeolite NaZSM-5 with a Si/Al ratio of 12.5 could adsorb more Pb^{2+} ion than its analogue with the ratio of 26, whilst the clinoptilolite with a lower Si/Al ratio exhibited the higher uptake capacity of Pb^{2+} ion (Table 2). However, exception was found on zeolite MCM-22 whose Al content was larger than NaZSM-5 but it trapped less amount of Pb^{2+} ion (1.15 mg/g) under the same conditions. This irregularity reflects the complexity of the multi-component aqueous solution originating from competitive adsorption of other components [13]. This inference is justified by the experiments in the solution without glycine (Fig. 3A), in which both zeolite NaZSM-5 (12.5) and NaZSM-5 (26) exhibited an obviously increased capability.

The strong acidity of complex solution also affects the adsorption of zeolite, which is proven by the adsorption in the solution with pH value of 3.5 where another two zeolites, NaA (Si/Al = 1) and NaY (Si/Al = 2.86) could be survived. In the solution with relatively higher pH value (Fig. 3B) the uptake capacity of NaZSM-5 increased six to eight times, and four synthetic zeolites showed the performance similar to natural clinoptilolite in the solution with low initial Pb^{2+} concentration of 50 mg/L. However, different adsorption capacity of zeolites was revealed in the experiment with a high initial concentration of 180 and 365 mg/L. As demonstrated in Fig. 3B, the champion was NaA that had the lowest Si/Al ratio and the highest exchange capacity, and the last one was NaZSM-5(26) sample. Na-clinoptilolite had the capacity higher than NaZSM-5 (26) but lower than NaZSM-5 (12.5), which might result from the impurity of natural zeolite. In our opinion, the excellent adsorption performance of natural clinoptilolite toward Pb^{2+} ion in the solution with pH value of 1.2 may result from its specific structure plus its low Si/Al ratio: the narrow and elliptical pore opening may limit the entering of some bulky molecules such as glycine, but Pb^{2+} with the ion radius of 0.149 nm can freely shuttle in the channel to contact with the active sites.

For the deep understanding of these results, we calculate the ion-exchange capacity of zeolites and their actual ability of trapping lead ion in the complex solution with different pH values (Table 2). Theoretically, the ion-exchange capacity of Na-clinoptilolite, determined by the Si/Al ratio of the zeolite, should be higher than that of NaZSM-5, and in fact the former trapped more Pb^{2+} ions indeed than the latter in the solution with the pH value of 1.2 (Fig. 3A).

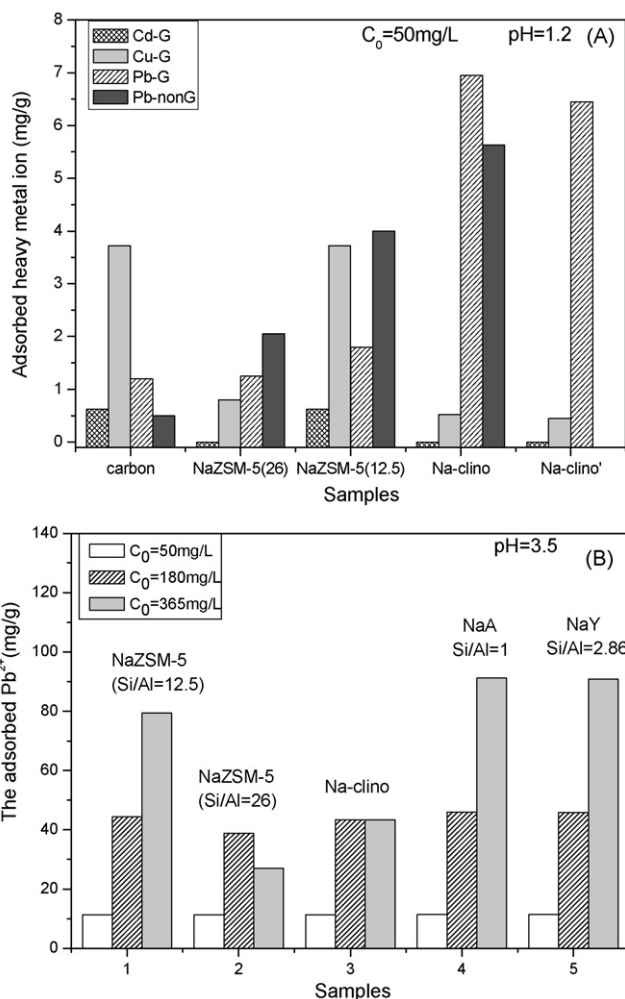


Fig. 3. Adsorption of heavy metal ion in complex solution with pH value of (A) 1.2 and (B) 3.5 by porous materials. Na-clino': used in the solution containing Pb^{2+} , Cu^{2+} and Cd^{2+} three cations, solid/liquid: 4 g/L.

Table 3

Adsorption of Pb^{2+} by Na-clinoptilolite in Pb^{2+} -NPYR mixed solution at 37 °C (Initial concentration of Pb^{2+} ion and NPYR: 0.2413 mmol/L, respectively; solid/liquid: 60 mg/25 mL).

Materials	Pb^{2+}		NPYR	
	Q_e (mg/g)	r (%)	Q_e (mg/g)	r (%)
NaZSM-5 (26)	0.42	2.03	4.36	58.75
Na-clinoptilolite	6.88	33.53	1.04	14.06

However, the difference between the amounts of Pb^{2+} ion adsorbed by two types of zeolite is larger than the difference between their theoretical ion-exchange capacities. That means, Na-clinoptilolite insists the selectivity toward Pb^{2+} ion in the strong acidic solution despite of the competition of other components, which is important to eliminate Pb^{2+} ion in solution.

As demonstrated in Fig. 3A, Na-clinoptilolite could trap the Pb^{2+} ion of 6.9 mg/g in the complex solution at pH 1.2, but adsorbed less Cu^{2+} ion (0.50 mg/g) or Cd^{2+} (0.005 mg/g) at the same conditions. In the complex solution containing three ions (the Na-clino' bar in Fig. 3A), Na-clinoptilolite also showed the selectivity toward Pb^{2+} ion, and the adsorptive capability of Pb^{2+} , Cu^{2+} and Cd^{2+} was 6.47, 0.45 and 0.005 mg/g, respectively. Existence of other metal ions in the complex solution reduced the amount of Pb^{2+} ion adsorbed by Na-clinoptilolite but did not change the selectivity, which is coincided with that reported in other solutions [33,34,40].

3.3. Competitive adsorption between Pb^{2+} ion and nitrosamines

Nitrosamines are well-known to be the carcinogen widely distributed in environment such as tobacco smoke and beer and even in stomach juice [5,13,37]. Na-clinoptilolite could keep the selectivity toward lead ion in the solution containing volatile nitrosamines (Table 3), and its adsorptive capability (6.88 mg/g) exceeded that for the nitrosamine (1.04 mg/g). Nonetheless, zeolite NaZSM-5 (Si/Al = 26) captured more nitrosamines (4.36 mg/g) than lead ion (0.42 mg/g) under the same conditions. Based on this result, it seems possible using the functional materials derived from natural clinoptilolite to remove the trace amount of Pb^{2+} ion in stomach juice.

3.4. Effects of adsorbent dose, Pb^{2+} initial concentration on clinoptilolite

Fig. 4A depicts the influence of adsorbent mass on the adsorption of Pb^{2+} ions, reflecting the dynamic equilibrium between lead ions distributed in solid and liquid. With the increased solid/liquid ratio, the amount of Pb^{2+} ion adsorbed by the zeolite rose firstly and then descended, achieving the maximum (7.45 mg/g) at the solid/liquid ratio of 2.4 g/L. The adsorption time-profiles of Pb^{2+} ions by Na-clinoptilolite in the complex solution are given in Fig. 4B. All of the sorption procedures reached equilibrium within 2 h although the systems with lower initial concentration of Pb^{2+} reached the equilibrium much faster than that with higher initial concentration. When the sorption achieved equilibrium, the proportion of Pb^{2+} adsorbed by zeolite, denoted as the value of r , was decreased as the initial concentration C_0 increased, but there was no simple linear relation between the r value and the C_0 . The amount of Pb^{2+} adsorbed by Na-clinoptilolite in the solution with high C_0 was much larger than that with low C_0 . For example, the zeolite could trap the Pb^{2+} species of 7.54 mg/g in the solution with C_0 of 50 mg/L but captured 1.13 mg/g in that with C_0 of 5 mg/L. One may attribute this difference to the shortage of active surface sites in sorbent when the concentrations of metal ion increased in the solution [41], because in the lower initial ion concentration, there are enough active sites on the clinoptilolite for adsorbing Pb^{2+} ions.

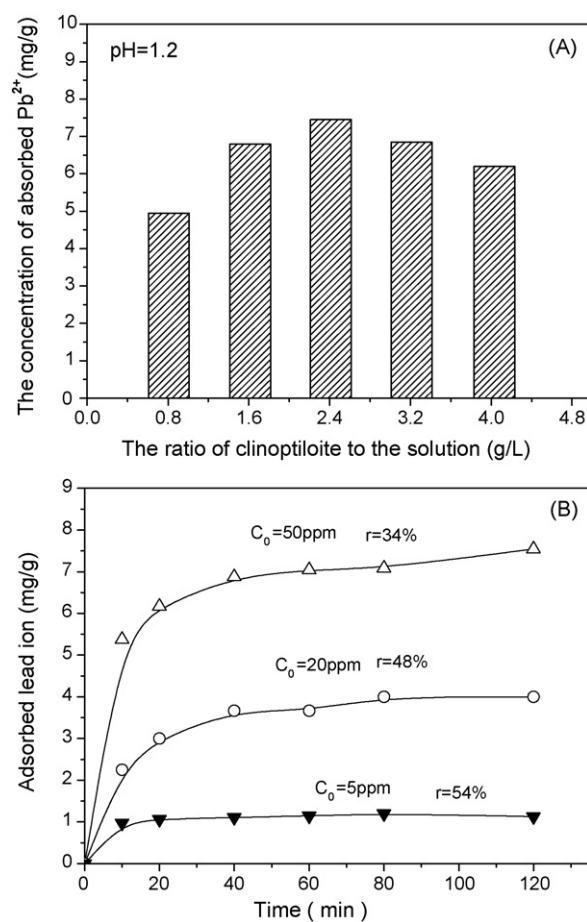


Fig. 4. Impact of (A) solid/liquid ratio and (B) initial concentration on the adsorption of lead ion by natural clinoptilolite at 37 °C in the complex solution.

In our opinion, however, this difference results from the competitive adsorption of other components in the solution. The low C_0 value means the fewer Pb^{2+} ions in the solution hence they have lower probability to contact with the adsorptive sites of zeolite due to competition of relatively large amount of other species.

3.5. Simulation on the adsorption isotherm of Pb^{2+} ion

For an overall analysis of adsorption isotherm, we try to correlate the experimental data with Freundlich and Langmuir equations (Table 4). The data obtained from the batch studies were applied well to both Langmuir and Freundlich models, but the former with

Table 4

Parameters for adsorption isotherm of Pb^{2+} in multi-component aqueous solution by the Na-clinoptilolite.

Adsorbate	Langmuir equation		
	q_m (mg/g)	K_L (L/mg)	R^2
Pb^{2+}	12.54	0.0436	0.9998
	Freundlich equation		
Pb^{2+}	K_F (L/g)	$1/n$	R^2
	0.683	0.693	0.9813
D-R equation			
Pb^{2+}	X_m (mg/g)	K	R^2
	5.8	1.62	0.916

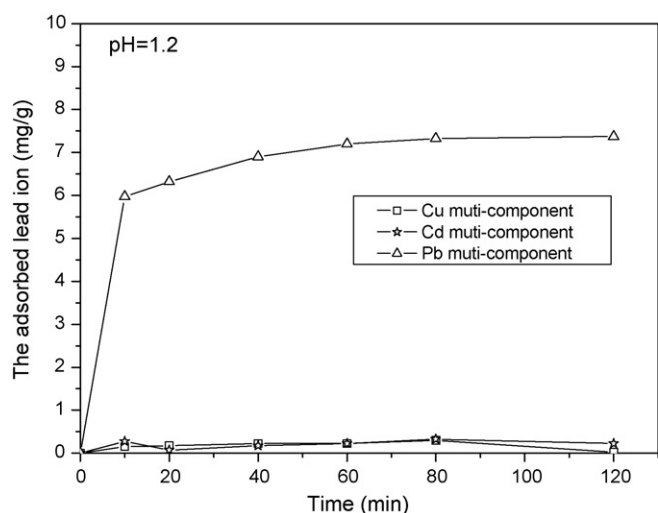


Fig. 5. The multi-component isotherms of Pb^{2+} , Cu^{2+} , and Cd^{2+} ion competing adsorption in the complex solution by Na-clinoptilolite pH 1.2 (solid-liquid ratio: 100 mg/25 mL; 37 °C; C_0 : 50 mg/L)

the coefficient R^2 value of 0.9998 was more satisfactory than the latter. Although Langmuir equation predicts the q_m value to indicate the amount of Pb^{2+} forming a monolayer over adsorbent, the calculated value is often unequal to the experimental data. For the natural clinoptilolite shaken in complex solution with pH value 1.2, the q_m value arrived to 12.54 mg/g, but the real uptake was 7 mg/g (Fig. 3A), probably due to the impact of impurity in the sample and the competitive adsorption of other components in the solution. On the other hand, simulation with D-R and Freundlich isotherms were also important for the adsorption procedure, because they did not assume a homogeneous surface, which was beneficial to describe the actual surface property of our samples. The Gibbs free energy of adsorbing Pb^{2+} by Na-clinoptilolite was calculated to be -6.5 kJ/mol, indicating that the adsorption process was spontaneous.

3.6. Kinetics study of competitive adsorption

Fig. 5 presents the multi-component isotherms of Pb^{2+} , Cu^{2+} and Cd^{2+} ions, in which all of the adsorption equilibrium can be achieved on the Na-clinoptilolite within 2 h. Presence of Cu^{2+} and Cd^{2+} ions in the solution did not hindered the adsorption of the natural zeolite toward Pb^{2+} ion, and its performance was still high, similar to that in the solution with single component of Pb^{2+} . This phenomenon implies that Pb^{2+} is the most easily cation to be bonded to the ion-exchange active sites of Na-clinoptilolite [42].

The slopes and intercepts of these isotherms were used to calculate the pseudo-first-order and pseudo-second-order constants k_1 and k_2 along with the equilibrium capacity q_e , in order to examine the competition adsorption among Pb^{2+} , Cu^{2+} and Cd^{2+} ions. The pseudo-second-order kinetics model (Table 5), with the better linearity (R^2 value), provided a good match between the theoretical and experimental q_e values. It appears that the ion-exchange pro-

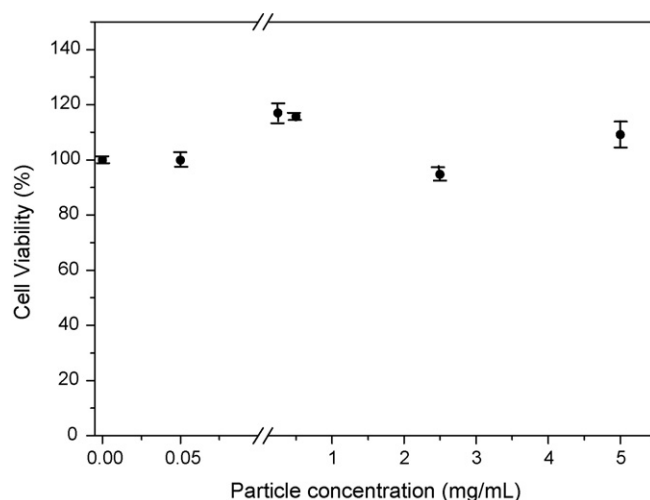


Fig. 6. MTT assay of RAW264.7 cells viability after the cells contact with Na-clinoptilolite for 24 h at different particle concentration.

cess follows the pseudo-second-order kinetics model. According to the theoretical q_e value from the pseudo-second-order kinetics model, the uptake capacity of three heavy metal ions decreased in the following order: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$, in accordance with the experimental q_e values.

3.7. Cytotoxicity test of natural Na-clinoptilolite

The impurity in clinoptilolite seriously affects the application of the natural zeolite because the sample contains lead, arsenic and cadmium. The major negative biological effect of clinoptilolite could be its toxicity in higher organisms (mammal) if the content of heavy metals such as Pb^{2+} and Cd^{2+} was high. The sample of raw clinoptilolite contains 30 ppm lead species. However, the Na-clinoptilolite sample still had the similar Pb-content (33 ppm, Table 1) even it had been soaked with NaCl solution whilst the content of Cd kept constant (0.3 ppm). This phenomenon implies the stability of lead species in the clinoptilolite because they cannot be ion-exchanged. The adsorption experiment in complex solution further confirms this inference, in which the amount of Pb^{2+} in the 25 mL solution is 0.002 mg but there is 0.003 mg of Pb^{2+} in the 100 mg solid to be used. The reduced concentration of Pb^{2+} in the solution (Fig. 3A) indicates that the Na-clinoptilolite indeed adsorbs the Pb^{2+} in solution and its original Pb^{2+} species have not entered the solution. Likewise, similar result is also observed in the natural zeolite capturing lead ion in the solution containing three metal ions as aforementioned. To examine the negative biological effect of clinoptilolite, Na-clinoptilolite was added into the solution to incubate with RAW264.7 cells, and Fig. 6 illustrates the in vitro cytotoxicity of Na-clinoptilolite. Surprisingly the toxicity of Na-clinoptilolite seems to be venial on the cells. Among five concentrations of the zeolite used in the test, only the addition with the ratio of 2.5 mg/mL lowered the viability of cell down to 94.7% whilst the addition of 0.05, 0.25 or 0.5 mg/mL increased the cell via-

Table 5

Sorption kinetic parameters of the multi-component of Pb^{2+} , Cu^{2+} , and Cd^{2+} ion in complex solution by Na-clinoptilolite (pH was 1.2; solid-liquid ratio was 100 mg/25 mL; 37 °C; C_0 was 50 mg/L).

Ions	$(q_e)_{\text{exp}}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		$(q_e)_{\text{cal}}$ (mg/g)	k_1 (min^{-1})	R^2	$(q_e)_{\text{cal}}$ (mg/g)	k_2 (g/mg min)	R^2
Pb^{2+}	7.3	2.54	0.0516	0.977	7.58	0.039	0.999
Cu^{2+}	0.25	0.123	0.0352	0.864	0.264	0.479	0.995
Cd^{2+}	0.23	0.12	0.11	0.864	0.24	1.5	0.998

bility exceeding 100%, and no negative effect was observed in the addition of 5 mg/mL. On the basis of these results, together with the report using clinoptilolite in the diet of pig and as the therapeutic adjuvant [29–31], it is safe to infer that the functional materials derived from clinoptilolite will have the potential application in capturing the trace amount of lead ions in stomach juice to prevent the accumulation of Pb²⁺ ion in human body.

4. Conclusion

- (1) Natural clinoptilolite is the excellent lead-trapper in the complex solution containing amino acid with pH value of 1.2, achieving the capacity of 7 mg/g, several times higher than that by NaZSM-5 zeolite and activated carbon.
- (2) The adsorption of lead ion by the natural clinoptilolite in the complex solution with the pH value of 1.2 achieves equilibrium within 2 h, and the adsorption isotherms preferably obey the Langmuir equation.
- (3) Na-clinoptilolite has a venial toxicity on the viability of RAW264.7 cells.

This study is our first preliminary approach to demonstrate the performance characteristics of natural clinoptilolite for capturing Pb²⁺ ion in the solution with the composition similar to artificial gastric juice. Further comprehensive investigations are required to clearly identify detail characteristics of the process.

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