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Removal of Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} from aqueous solution by synthetic clinoptilolite

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ABSTRACT

Removal of heavy metal ions from wastewater by natural clinoptilolite has been well investigated. However, the removal efficiency of heavy metals with natural clinoptilolite is not consistent due to its uncertain quality. Furthermore, the impurities in natural clinoptilolite significantly affect the investigation on the sorption behavior and mechanism of clinoptilolite. In this study, we investigated the adsorption (ion-exchange) and regeneration behavior of modified synthetic clinoptilolite including the influence of pH, solid/liquid ratio, and ion-exchange temperature on the adsorption process, adsorption kinetics and isotherms, and competitive adsorption behavior of Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+}. The maximum adsorption capacity of NaCl-modified synthetic clinoptilolite for Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} is as high as 31.47, 181.8, 44.64, and 33.76 mg/g, respectively, which is much higher than the reported values in the studies on modified and unmodified natural clinoptilolite. The present study shows that the amount of adsorption of NaCl-modified synthetic clinoptilolite for Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} is less affected by the operation temperature. Kinetics study shows that the pseudo-second-order kinetic equation has a better description for the adsorption behavior of NaCl-modified synthetic clinoptilolite. Isotherms study suggests that the adsorption process of NaCl-modified synthetic clinoptilolite follows the Langmuir model. Competitive adsorption investigation suggests that some cation sites in the open-framework of clinoptilolite can only be exchanged by selective alien cations and this phenomenon reveals the origin of the selectivity of zeolites in ion-exchange.

1. Introduction

With the development of economy, the heavy metal contaminants produced by human activities are having severe influence on the quality of natural water in the world wide. Because heavy metal contaminants are not biodegradable and tend to accumulate in living organisms causing several diseases that affect the kidney, nervous, hematopoietic, and gastrointestinal systems of humans, the World Health Organization (WHO) recommended extremely low maximum acceptable concentration for heavy metal cations in drinking water [1], which have been adopted by most of governments in the world. To meet such strict standards, several heavy metal cations removal methods from wastewater such as electrochemical treatment, reverse osmosis, chemical treatment, adsorption, and ion exchange have been developed [2–5]. For the heavy metal cations contaminated water with high concentration, electrochemical treatment, reverse osmosis, or chemical treatment can be effectively used to decrease the concentration. However, application of these methods becomes costly at lower concentrations. At low concentration, adsorption and ion-exchange processes by zeolites have advantages on removal ability and efficiency and cost.

Zeolites either occurred in nature or synthesized are highly porous crystalline aluminosilicates with different channel and cavity structures that make them attractive adsorbents. Their structures consist of a three-dimensional framework and have a negatively charged lattice [6]. The negative charge is balanced by cations which would be eventually exchangeable with certain type of cations present in solution. Natural zeolite of clinoptilolite has been extensively investigated in ion exchange processes as sorbent material for heavy metal removal, owing to its high reserve, advantageous ion exchange capacities, and low cost [7–12]. However, results of the previous investigations on cation exchange capacity or adsorption capacity, selectivity, removal efficiency, and terminal concentrations of metal ion in solution are discrepant. One possible reason is that the ion-exchange process is influenced by several factors such as concentration and nature of cations and anions, operation temperature, and pH. However, another highly possible reason is that the crystallinity and purity of natural clinoptilolite was different

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from sample to sample.

Even though the reserve of clinoptilolite in nature is large, synthesis of clinoptilolite is not easy and the studies on its synthesis were very limited [13–19]. Our efforts on reproducing the synthesis process reported so far were all failed. After a systematic investigation on the synthesis, we finally obtained a reproducible recipe for the synthesis of highly crystalline clinoptilolite and successfully scaled up the production in tons.

In this context, we investigated the removal of Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} from solution by ion-exchange of synthetic clinoptilolite. To the best of our knowledge, this is the first investigation on the removal of heavy metal cations from solution by synthetic clinoptilolite.

2. Experimental section

2.1. Synthesis and modification of clinoptilolite

The reactants used in synthesis were potassium hydroxide (Quimis, 99%), sodium hydroxide (Quimis, 99%), fumed silica (Aerosil 380, Evonik/Degussa), sodium aluminate (Riedel de Haën, 54% Al_2O_3:41% Na_2O:5% H_2O), and deionized water. The synthetic clinoptilolite was initially prepared according to the traditional composition, similar to the previous reports [14,15,17]. Appropriate amounts of potassium hydroxide and sodium hydroxide and deionized water were mixed under stirring until the solution became clear. The sodium aluminate was added to the aqueous solution and stirred for 30 min. The fumed silica was added under manual stirring until a homogeneous gel was obtained. The final molar composition of aluminosilicate gel obtained was $1.5Na_2O:0.5K_2O:10SiO_2:Al_2O_3:200H_2O$. After stirring for 4 h, the seed crystal, which was natural clinoptilolite received from Specialty Minerals Inc.(USA), was added to the solution. The amount of added seed crystal, was 6 wt% of raw material. The mixture thus prepared was stirred 6 h and then transferred into a 100 L stainless steel autoclaves and maintained at 160 °C for 36 h. The solid product was separated by centrifugation, washed several times with distilled water and dried at 80 °C.

Modification was made by mixing the synthetic clinoptilolite with the pretreatment solutions of 1.0 mol/L HCl, NaOH, NaCl, KCl, $CaCl_2$, and $MgCl_2$. The solid/liquid ratio for zeolite and solution was 20 g/L. After stirring at ambient temperature for 24 h, the solids were thoroughly rinsed with deionized water and dried at 100 °C for 24 h.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of natural (received from Specialty Minerals Inc., USA and Xiangming Inc., Shenyang, China, respectively), as-synthesized, and modified clinoptilolites were recorded in 2θ range of 4–40° on a Rigaku D/max-2550 diffractometer equipped with a graphite monochromator using Cu Kα radiation ($\lambda = 1.5418$ Å) operated at 50 kV and 200 mA. The step size was 0.02 and the scan rate was 12°/min. Chemical compositions of clinoptilolite were determined with an X-ray fluorescence (XRF) spectrometer (PANalytical, AXIOS) and Thermo Scientific iCAP 7600 DUO ICP-OES. The concentrations of heavy metals in solutions were measured by flame atomic absorption spectrophotometer (AAS-700, PerkinElmer). Scanning electron microscope (SEM) images were recorded with the electron microscope JEOL JSM-6700F. Thermogravimetric (TG) analysis was carried out on a TA TGA Q500 unit with a heating rate of 10 °C/min in air. Thermal stability of modified and as-synthesized clinoptilolite was analyzed with XRD patterns after calcination at different temperatures (500–900 °C).

2.3. Batch adsorptions

Modified clinoptilolite was added to Zn, Pb, Cd, or Cu nitrate solutions with a clinoptilolite/solution ratio of 10 g/L. The concentrations of Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} were 400 mg/L. According to the solubility product principle, the precipitation will not happen until the reaction quotient (*Q*) of a solid in solution reaches its solubility product constant (K_{sp}). On the basis of their solubility product constants, Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} will precipitate in hydroxide form at approximate pH of 6.6, 7.9, 8.4, and 5.3 respectively [20–22]. Therefore, the pH in the experiments was set less than 5.0 unless specially claimed. The pH of solutions was adjusted by either 1.0 mol/L NaOH or HNO_3 solution. The mixtures were continuously stirred at a speed of 200 rpm at 25 °C (water bath) for 240 min. Subsequently, the suspension was filtered by using 0.45-μm filter paper, and the final concentration of heavy metals in the filtrate was determined by flame atomic absorption spectrophotometer (AAS-700, PerkinElmer) to determine the amount of adsorption of clinoptilolite for heavy metals. The heavy metal-loaded clinoptilolite was regenerated, and the regenerative reagent and the process were the same as that in modification treatment. After regeneration, the adsorption experiments were carried out as described above and the amount of adsorption of the regenerated clinoptilolite was determined.

NaCl-modified clinoptilolite was used in studying the influence of operation conditions such as initial pH, solid/liquid ratio, and ion-exchange temperature on the adsorption behavior. The initial pH values were adjusted to 2, 3, 4, and 5. The solid/liquid ratios were 2, 5, 10, and 20 g/L. The ion-exchange temperatures were 25, 45, and 65 °C.

All experiments were performed for 4 parallel control groups and the average results were presented.

2.4. Adsorption kinetics and isotherm

In adsorption kinetics studies, the sorbents were added to the heavy metal nitrate solution with the concentration of 400 mg/L for Zn^{2+}, Cd^{2+}, and Cu^{2+} and 2000 mg/L for Pb^{2+}. The solid/liquid ratio was 10 g/L. The pH was adjusted to 5, and the adsorption was performed with time intervals of 10, 30, 60, 90, 120, 240, and 480 min at 25 °C. In adsorption isotherm investigations, the initial concentrations of Zn^{2+}, Cd^{2+}, and Cu^{2+} nitrate solutions were 10, 50, 100, 200, 400, and 600 mg/L, and the initial concentrations of Pb^{2+} nitrate solution were 50, 100, 400, 1000, 2000, and 2500 mg/L. The adsorption time was 240 min. Other experimental conditions and methods were the same as those used in the kinetics studies.

2.5. Competitive adsorptions

The solid/liquid ratio in competitive sorption experiments was 10 g/L. The concentration of the solution simultaneously containing four heavy metal ions was 400 mg/L, and the pH was adjusted to 5. The adsorption time was 240 min at 25 °C with stirring at 200 rpm. The amount of adsorption for each heavy metal in multi-component adsorption was compared with that in single heavy metal batch adsorption experiment.

2.6. Kinetics and isotherm model

For the experimental results in adsorption kinetics investigation, the pseudo-first-order and pseudo-second-order kinetic equations were used for fitting. The pseudo-first-order kinetic equation is [23]:

$$Q_t = Q_e(1\text{-}e_1^{-Kt}) \tag{1}$$

where Q_e is the equilibrium adsorption capacity (mg/g) of the sorbent in the fitting equation, Q_t is the adsorption amount (mg/g) at the adsorption time *t* (min), and K_1 is the pseudo-first-order kinetic equation rate constant (min^{-1}).

The pseudo-second-order kinetic equation is [24,25]:

$$Q_t = K_2Q_e^2t/(1 + K_2Q_et) \tag{2}$$