Journal of Hazardous Materials 229–230 (2012) 292–297

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Ammonia-nitrogen and phosphates sorption from simulated reclaimed waters by modified clinoptilolite

Hanxin Huo[a,b], Hai Lin[a,b,*], Yingbo Dong[a,b], Huang Cheng[a,b], Han Wang[a,b], Lixia Cao[a,b]

[a] *School of Civil and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China*
[b] *Key Laboratory of the Ministry of Education of China for High-Efficient Mining and Safety of Metal Mines, Beijing 100083, China*

HIGHLIGHTS

- The salt and thermally modified clinoptilolite can effectively sorb NH_3-N and phosphates.
- The phosphorus and nitrogen removal was consistent with Langmuir isotherm model.
- The modified clinoptilolite possesses rapid adsorption and slow balance characteristics.
- The adsorption is more in line with the Elovich adsorption dynamics equation.
- The entropy effect plays the role of the main driving force in the adsorption.

ARTICLE INFO

Article history:
Received 4 January 2012
Received in revised form 31 May 2012
Accepted 1 June 2012
Available online 7 June 2012

Keywords:
Modified clinoptilolite
Sorption mechanism
Ammonia-nitrogen
Phosphates

ABSTRACT

This paper presents the investigation of the ammonia-nitrogen and phosphates sorption from simulated reclaimed wastewater by modified clinoptilolite. The results showed that the modified clinoptilolite has a high sorption efficiency and removal performance. The ammonia-nitrogen and phosphates removal rate of the modified clinoptilolite reached to 98.46% and 99.80%, respectively. The surface of modified clinoptilolite became loose and some pores appeared, which enlarged the specific surface area; the contents of Na and Fe increased, and the contents of Ca and Mg decreased. The modified clinoptilolite possesses rapid sorption and slow balance characteristics and ammonia-nitrogen and phosphates sorption is more consistent with the Langmuir isotherm model. The adsorption kinetics of ammonia-nitrogen and phosphates follows the Elovich adsorption dynamics equation, which describes the sorption of ammonia-nitrogen and phosphates in aqueous solution as mainly a chemical sorption. Results from the thermodynamics experiment involving ammonia-nitrogen and phosphates sorption reveal that the process is a spontaneous and endothermic process, and is mainly driven by entropy effect.

1. Introduction

In many countries, eutrophication is the main water pollution problem of lakes, water reservoirs, oceans, and the like [1]. In order to solve the eutrophication problems induced by the traditional secondary biological effluent and realize reuse of wastewater, which reduces sewage discharge and improves water shortage conditions, studies of sewage treatments in many countries have been done, especially those involving the removal of nitrogen and phosphorus [2,3].

The main methods of removing nitrogen and phosphorus include precipitation, crystallization, biological removal, and adsorption and ion exchange [4–7]. The adsorption and ion exchange technology is a more effective way to remove nitrogen and phosphorus, due to its advantages, namely small floor area, simple process, and high efficiency, among others. In effect, finding new efficient materials that may be used for adsorption and ion exchange became a research highlight [8]. The natural zeolite, which are aluminosilicates containing a number of channels in their structure, have large adsorption ratio surface area comparing to other mineral materials. In recent years, researchers focused on sorbents based on zeolites. Natural zeolites are an abundant cation exchange material that is economically feasible for water and wastewater treatment. For example, the cation exchange capacity of Dogantepe zeolite was found to be 164.62 mequiv./100 g [9]. However, natural zeolites have deficiencies in the processing of some wastewaters, such as recycled water. In order to get more efficient treatment effects, natural zeolites are usually modified. The modification methods of natural zeolites include the acid- and alkali-treatment as well as, the salt-, thermal-, surfactant- and microwave modification [10,11]. However, only a few studies

* Corresponding author at: School of Civil and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China.
E-mail address: linhai@ces.ustb.edu.cn (H. Lin).

0304-3894/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2012.06.001

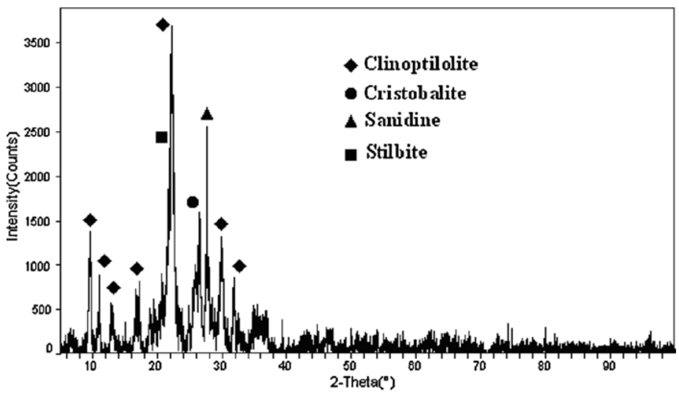

Fig. 1. XRD pattern of the natural zeolite.

on sorption mechanism have been conducted [12]. In the current study, the salt (NaCl and $FeCl_3$) and thermal modification of zeolite was used to treat the simulated reclaimed waters and the adsorption mechanism of NH_3–N and P were studied.

2. Materials and methods

2.1. Materials

The zeolitic material, which had particle size range from 50 μm to 74 μm, was supplied by Jiekun Zeolite New Technology Processing Co., Ltd. in Xuanhua, Hebei province. The mineralogical composition of zeolite was determined as 80% clinoptilolite, 15% feldspar [(Na, K, Ca)$AlSi_3O_8$], and 5% quartz [SiO_2]. The XRD pattern of the material is given in Fig. 1. The main component of the natural zeolite was clinoptilolite associated with cristobalite, sanidine and stilbite.

2.2. Water sample

According to the condition of the reclaimed water, the simulated wastewater sample was prepared containing ammonia-nitrogen and phosphates of 20 mg/L and 5 mg/L respectively. The reagents used in this experimental work were ammonium chloride and dipotassium hydrogen phosphate. The pH value of water sample was adjusted to 6.0.

2.3. Modification of the natural zeolite

Modification experiments were carried out in 300 mL flasks containing 2 g of natural zeolite and 100 mL 2% NaCl solution, flasks were maintained at 25 °C and shaken at 200 rpm for 2 h. Secondly, the zeolite modified by NaCl was dried at 105 °C and then treated for 1 h by 0.4% $FeCl_3$ solution. Finally, the modified zeolite was calcinated at 200 °C in muffle furnace for 1 h and cooled in closed container. Then clinoptilolite was kept, a after the end of the modification procedure, in dry place.

2.4. Sorption experiment

Water samples containing 20 mg/L of ammonia-nitrogen and 5 mg/L of phosphates were prepared at 25 °C. The 400 mL flasks containing the water samples and 0.5 g of modified clinoptilolite were rotated for some time in a thermo stated rotator (30 °C, 200 rpm) in order to achieve sorption equilibrium.

2.5. Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) experiments

SEM and EDS experiments were conducted to provide information about the morphology and elemental composition of the natural and modified clinoptilolite, respectively.

2.6. Sorption isotherm experiment

Water samples containing 5, 10, 20, 40, 50, 70, 100, and 150 mg/L of ammonia-nitrogen and phosphates were prepared. First, the water samples and 0.5 g of modified clinoptilolite were placed in several 400 mL flasks. The flasks were then placed in a constant temperature oscillator for some time at 30 °C and 200 rpm rotational speed to achieve sorption equilibrium. Then the solution was filtered using a 0.45 μm filter membrane and the concentrations of ammonia-nitrogen and phosphates in the filtered solution were measured. Total amount of adsorbed ammonia-nitrogen and phosphates were divided by the dry weight of zeolite to find out the average amount adsorbed, which were plotted against effluent ammonia-nitrogen and phosphates concentrations to show isotherm tests.

2.7. Adsorption kinetics experiment

Approximately 1.5 g of modified clinoptilolite was weighed. The sample was placed in a 1000 mL solution with 6.0 mg/L ammonia-nitrogen and 1.5 mg/L phosphates. The solution was stirred with speed of 300 rpm. The solution was then filtered using a 0.45 μm filter membrane and the concentrations of ammonia-nitrogen and phosphates in the filtered solution were measured.

2.8. Adsorption thermodynamics experiment

This experiment was conducted in flasks were then placed in a constant temperature oscillator Four equally weighed samples of modified clinoptilolite were placed in a 250 mL solution with 6.0 mg/L ammonia-nitrogen and 1.5 mg/L phosphates. The individual samples were utilized in sorption experiments performed at 20.0, 25.0, 30.0, and 35.0 °C. At the end of the sorption experiment, the solution was filtered using a 0.45 μm filter membrane, and then the concentrations of ammonia-nitrogen and phosphates in the filtered solution were measured.

2.9. Nitrogen and phosphates determination method

The phosphates and ammonia-nitrogen content of the water samples was determined using the ammonium molybdate and the Nessler reagent spectrophotometric methods.

3. Results and discussion

3.1. Results of the sorption experiment

After 3 h sorption, the residual ammonia-nitrogen and phosphates content were 0.80 mg/L and 0.01 mg/L; the ammonia-nitrogen and phosphates removal rate reached to 98.46% and 99.80%, respectively, which had reached equilibrium. Now the pH value changed to 7.5 from the initial 6.0 induced by the hydroxyl on the sorbent releasing into the solution. The observation indicates that the zeolite modified by NaCl-, $FeCl_3$- and thermal treatment has high ammonia-nitrogen and phosphates removal efficiency. The reasons are as follows. Ca^{2+} and Mg^{2+} could be replaced by Na-ions during the NaCl-treatment. The ionic radius of Na^+ is shorter than that of Ca^{2+} and Mg^{2+}, so the effective aperture and exchange capacity of the modified zeolite increased. The ammonia-nitrogen