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Ammonium exchange in aqueous solution using Chinese natural clinoptilolite and modified zeolite

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Abstract

In this study, the Chinese natural clinoptilolite (sample 1) was fused with sodium hydroxide prior to hydrothermal reaction, and it was transformed to modified zeolite Na–Y (sample 2). The uptake of ammonium ion from aqueous solutions in the concentration range 50–250 mg NH_4^+/l on to the two samples was compared and the equilibrium isotherms have been got. The influence of other cations present in water upon the ammonia uptake was also determined. The cations studied were potassium, calcium and magnesium. In all cases the anionic counterion present was chloride. The results showed that sample 2 exhibited much higher uptake capacity compared with sample 1. At the initial concentration of 250 mg NH_4^+/l, the ammonium ion uptake value of sample 2 was 19.29 mg NH_4^+ g^{-1} adsorbent, while sample 1 was only 10.49 mg NH_4^+ g^{-1} adsorbent. For the natural clinoptilolite, the effect of the metal ions suggested an order of preference $K^+ > Ca^{2+} > Mg^{2+}$. These contrasted with the modified zeolite, where the order appeared to be $Mg^{2+} > Ca^{2+} > K^+$.

Keywords: Clinoptilolite; Zeolite Na–Y; Ion exchange; Ammonium uptake

1. Introduction

Nowadays, the presence of nitrogen and phosphorus excess in the environment has caused eutrophication. Ammonia is usually found as ammonium ion (NH_4^+) in aqueous solution. Common method for NH_4^+ removal in wastewater is by air stripping and biological treatment [1,2]. However, as the discharge limits of different pollutants are more stringent, ion exchange is gaining on interest as available method for the treatment of waters polluted with ammonium ions.

Natural zeolites are the most important inorganic cation exchangers that exhibit high ion exchange capacity, selectivity and compatibility with the natural environment. Zeolites are hydrated aluminosilicates that possess a three-dimensional framework structure. This structure is formed by AlO_4 and SiO_4 tetrahedra that are connected by sharing an oxygen atom. When an AlO_4 tetrahedron is substituted for a SiO_4 tetrahedron, a negative charge appears which is neutralized by the exchangeable cations (Na^+, K^+, Ca^{2+}, Mg^{2+}). The discovery of natural zeolite deposits has lead to an increasing use of these minerals for the purpose of eliminating, or at least reducing, many long standing pollution problems [3–6].

Among natural zeolites, clinoptilolite occurs most frequently. Clinoptilolite is a silica-rich zeolite and has a lower ion exchange capacity. Further more, there are impurities like quartz in most of the clinoptilolite deposits. These factors reduce the uptake of ammonium ion onto natural clinoptilolite. Fusion with sodium hydroxide prior to hydrothermal reaction is the method to transform low-grade natural materials to high cation exchanger, which has been reported in several reports [7–9]. This method can dissolve the natural zeolites including impurities into silicate and aluminate with fusion, and get some high purity of zeolites with new frameworks after hydrothermal synthesis.

Besides ion exchange capacity, selectivity is also an important character for zeolites. The significant uptake of ions other than ammonium will reduce the effective uptake capacity for ammonium ion and thus the economics of the process. The cations chosen for this study were potassium, calcium and magnesium.

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They are always found in many natural waters and the water used in industrial recycle operations. Furthermore the ammonium ions coexist with them frequently in waste waters.

A range of studies has shown that clinoptilolite can be effective in removing ammonia from waste water [6,10,11]. Although the ion exchange capacity of clinoptilolite is lower than some other zeolites, it generally exhibits a high selectivity for NH_4^+ ion. However, there is some uncertainty on the selectivity differences between potassium, calcium and magnesium. Mc Veigh and Farkaš provided an order of preference $K^+ > Ca^{2+} > Mg^{2+}$ [10,12], whereas Weatherley and Miladinovic suggested $Ca^{2+} > K^+ > Mg^{2+}$ [6]. It seems that natural clinoptilolites from various places have different characters.

The aim of the research here was first to transform lowed-grade Chinese natural zeolite to high cation exchanger, then to measure and compare the equilibrium uptake of ammonium ion onto the two materials. The effect of the individual presence of potassium, calcium and magnesium ion upon ammonium ion uptake onto each sample was also investigated.

2. Materials and methods

2.1. Reagents

All chemicals were of analytical grade. NH_4Cl, KCl, $CaCl_2$, and $MgCl_2$ were all prepared into 1000 mg cations/l stock solution. Deionized water was used throughout the experiments.

2.2. Zeolites characterization

The natural clinoptilolite (light grayish white) was collected at Jinyun, Zhejiang, PR China. The chemical composition of the mineral is shown in Table 1 [13]. The natural zeolite was prepared as a sample for the present experiment after crushing, air-drying and passing through a 74 μm sieve.

Under investigation, we choose the optimal condition to synthesize the modified zeolite [9]. 7.5 g of the natural zeolite powder was placed in a Ni crucible and fused with 9 g of NaOH powder at 550 °C for 2 h. The melt was ground and 75 ml of water was added so as to prepare the NaOH solution of 3 mol/l. The mixture was homogenized, transferred into a Teflon-lined stainless-steel autoclave and heated at 100 °C for 8 h. The products were filtrated and stirred with 50 ml 1 mol/l NaCl. In order to remove the alkali absorbed by the zeolite, 1 mol/l HCl was dropped into the mixture until the pH got to 6. The products were filtrated and dried.

Table 1
Chesmical composition of the natural zeolite (wt%)

SiO_2	65.52
TiO_2	0.21
Al_2O_3	9.89
Fe_2O_3	1.04
MnO	0.06
MgO	0.61
CaO	3.17
Na_2O	2.31
K_2O	0.88
H_2O	7.25
LOI	10.02

2.3. Analytical methods

Identification of mineral species in the zeolite samples was carried out by X-ray diffraction (XRD) of the random-oriented powder samples using Siemens X-ray diffractometer D5005 (Cu Kα radiation, $2\theta = 5$–$40°$).

An IRIS Intrepid II XSP Inductively Coupled Plasma Atomic Emission Spectroscopy determined the content of Si and Al in samples 1 and 2.

The exact concentrations of ammonium ions in the solutions were determined by Nesslerization [14]. And the solid-phase concentrations determined by mass balance, according to Eq. (1):

$$Q_e = \frac{V}{M}(C_0 - C_e) \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of ammonium in the liquid phase (mg/l), respectively, Q_e the solid-phase concentration of ammonium (mg/g), V the volume of solution (l), and M is the mass of dry zeolite (g).

2.4. Equilibrium batch experiments

All sorption studies were carried out in beakers of 250 ml by subjecting a given dose of sorbent to a period of stirring with ammonium solution on a magnetic stirrer (800 turns/min). After adsorption, the sorbent was separated by centrifugal machine (2000 turns/min).

The scope of the experimental work was confined to determination of the equilibrium uptake behaviour of ammonium ion on to natural and modified zeolites in the presence of chloride co-ion. During all experimental work the pH was maintained at a value of 6–7. It was assumed that all ammonia existed in the ionic form and was available for ion exchange.

2.4.1. Equilibrium studies

One gram samples of zeolite were continuously stirred with 100 ml of ammonium chloride solution, having concentrations in the range 50–250 mg NH_4^+/l. The ammonia levels were measured every 1 h over a period of 8 h. Preliminary experiments showed that up to 5 h contact were required for equilibrium to be reached.

2.4.2. Influence of individual presence of K^+, Ca^{2+} and Mg^{2+} ions

In order to establish the extent to which the presence of potassium, calcium and magnesium ions influenced ammonium ion uptake, further equilibration experiments were conducted. These were confined to determination of the effect of each individual ion alone upon ammonium ion uptake. The starting solutions were dosed with the appropriate metal cation at a concentration of 100 mg/l and equilibration in the presence of ammonium ion