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Ammonium removal on zeolite modified by ultrasound

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ABSTRACT

This study investigated whether the use of ultrasound-modified zeolite would increase ammonium removal from water. Natural zeolite was used that contained about 70% clinoptilolite and originated from the Sokernitske deposits in Ukraine. The zeolite was modified with 35 kHz ultrasound with a power density of about 5 W/cm^2 for 15, 30, 45, 60, and 90 min. Lab-scale batch experiments showed that, when zeolite was treated by ultrasound, ammonium removal efficiency was up to 14% higher and the rate of ammonium removal was ca. 30% higher than with natural zeolite.

Keywords: Ammonium removal; Zeolite; Ultrasound

1. Introduction

Natural zeolite is a porous mineral described as crystalline hydrated aluminosilicates [1]. The lattice structure of zeolites is formed by AlO_4 and SiO_4 tetrahedra that are connected by an oxygen atom. When an AlO_4 tetrahedron is substituted for a SiO_4 tetrahedron, a negative charge appears which is neutralized by exchangeable cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}). This makes zeolites capable of ion-exchange sorption. Because zeolites have adsorptive and catalytic properties and may act as molecular sieves, they are widely used in many branches of industry, e.g. in the chemical industry, microelectronics, optics, medicine, and agriculture. Studies on the use of zeolites in environmental protection, e.g. to remove radioactive contaminations [2] have been conducted for many years.

Depending on their composition, natural zeolites have different forms. The most widely used natural zeolite is clinoptilolite (simplified formula $(Na, K)_6Si_{30}Al_6O_{72}{\cdot}24H_2O$), whose calcium and sodium forms are highly selective for ammonium ions, independent of NH_4^+-N concentration [3,4]. For this reason, the most extensive studies have been carried out on the use of zeolites to remove ammonium from water and wastewater [5,6]. Zeolites have been used to purify concentrated piggery wastewater [7] and aquaculture wastewater [8] of relatively low concentrations of ammonium.

In order to improve the ion exchange and adsorption capacity of natural zeolites, they are modified by physical and chemical methods [9–11]. The procedures most frequently used include ion exchange, thermal treatment, treatment with acids, alkalis, and salt solutions (NaCl). These procedures give natural zeolite a one-ion (usually sodium) structure that is better for

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adsorption and selective for a specific type of ion. The structure also has improved ion exchange capacity and increased resistance to mechanical, thermal, and acidic degradation. These features largely determine the effectiveness of the material in purifying water and wastewater. Although the use of chemically treated zeolite causes high ammonium adsorption per gram of zeolite [11], periodic regeneration of zeolite, often in the conditions of very high pH, and the disposal of washing solutions are necessary.

In a search for waste-free and inexpensive technology, we examined the possibility of enhancing the sorption capacity of zeolite using ultrasound. The application of ultrasonic waves in water purification and sewage treatment is becoming more and more common. This is due to the discovery and explanation of many phenomena directly related to the mechanism of ultrasonic wave effects. Numerous publications have presented broad application possibilities and successful technological solutions based on the use of ultrasound [12–14]. Ultrasound has been used in the processes of sewage treatment [15] to improve the susceptibility of organic compounds to biological degradation [16], water disinfection [17], treatment of sludge before its fermentation or draining [18,19], to support the process of membrane filtration [20,21], and for other purposes [22–24]. However, there is little information on improving the removal of ammonium from water by modifying a zeolite sorbent with ultrasonication. Therefore, the aim of this pilot study was to determine whether treatment of zeolite with ultrasound before sorption would increase ammonium removal from water. The study determined the duration of ultrasound modification that gave the most effective removal of ammonium from water solutions.

2. Materials and methods

The study was conducted at laboratory scale in two stages. In the first stage, the zeolite was exposed to ultrasonic waves. In the second stage, the effectiveness of ammonium removal from an aqueous solution by ultrasound-treated zeolite was examined. Natural zeolite ($Na_6[(AlO_2)_6(SiO_2)_{30}]\cdot 24H_2O$), containing about 70% of clinoptilolite, from Sokernitske deposits in Ukraine, was used in the experiment (Table 1). The characteristics of the zeolite were as follows: average particle diameter (D90) 3 mm, pore size 0.4 ± 0.9 nm, porosity 34%, density 2.54 g/mL, and specific surface area 316 m^2/g.

In the first stage, 50 g of zeolite with 1 L of distilled water was put into an ultrasound generator (InterSonic, Poland) that generated 35 kHz ultrasound with a power density of about 5 W/cm^2. The time of direct exposure of zeolite to ultrasound, depending on the series, was 15, 30, 45, 60, and 90 min. The generator was equipped with a thermostat that kept the temperature at a constant level of 20°C.

Table 1
Mineralogical composition of the natural zeolite used in this study

Component	Value (wt%)
SiO_2	69.43
Al_2O_3	13.04
Fe_2O_3	1.05
FeO	0.78
TiO_2	0.18
MnO	0.03
CaO	2.10
MgO	0.87
P_2O_3	0.03
K_2O	2.64
Na_2O	2.06
Loss on ignition at 1,000°C	7.79

In the second stage, the flasks with 50 ml of ammonium solution were supplied with 1 and 2 g of the modified zeolite (zeolite dosage 20–40 g/L, respectively). The ammonium solution was prepared by dissolving NH_4Cl in distilled water to obtain a concentration of 50 mg $N\text{-}NH_4$/L. This initial ammonium concentration corresponds to the average ammonium concentration in eutrophic watercourses in our region. The flasks were shaken for 60 min with a shaker (Laboshake Gerhardt GmbH&Co., Germany) at 60 rpm, a temperature of 20°C, and a pH of 7.0. To calculate the ammonium removal rate, every 15 min a sample was collected and filtered to separate zeolite from the liquid before measuring ammonium concentrations in the liquid with a Hach DR 2010 spectrophotometer using the 10,031 test tube method (HACH LANGE, US, Analytical procedures). Control experiments were also conducted with unmodified zeolite under the same experimental conditions. For control, the zeolite was washed with distilled water for 90 min at 20°C. The washing was performed in a 1 L vessel and the whole solution was stirred with a magnetic stirrer.

Sieving was used to determine the average particle diameter of the zeolite (D90). In each series, this measurement was repeated five times both before and after ultrasound modification. All other information about the composition and characteristics of zeolite was provided by the manufacturer.

To find the average sorption capacity of the zeolite (q_S) (mg NH_4^+-N/g zeolite), the total amount of sorbed ammonium was divided by the dry weight of zeolite, using Eq. (1):

$$q_S = \frac{(C_{inf} - C_{eff}) \cdot V}{m} \quad (1)$$

Kinetic studies showed that ammonium sorption on zeolite proceeded according to pseudo-first-order kinetic, and it was expressed by Eq. (2):

$$y = (C_{inf} - C_{eff}) \cdot \exp(-k \cdot t) \quad (2)$$

The rate of ammonium sorption (r) (mg/(L h)) was calculated as expressed by Eq. (3):

$$r = k \cdot (C_{inf} - C_{eff}) \quad (3)$$

Each of the series was repeated five times. The results presented in the paper are the arithmetic averages of these five measurements. Statistical analyses were performed with STATISTICA 7.1 PL software pack. The normality of distribution of each of the examined variables was verified by the W Shapiro–Wilk test. The significance of differences between the variables was determined with a single-factor analysis of variance (ANOVA). The uniformity of variance in groups was examined by a Levene test. The significance of differences between the variables was determined with a RIR Tukey test (t-test value). A level of significance of $p < 0.05$ was adopted in the tests. In kinetic analyses, determination coefficient (R^2) was used to select the most fitting model of ammonium sorption.

3. Results and discussion

Although unmodified zeolite sorbed ammonium from the solution, the exposure of zeolite to ultrasound improved the efficiency of ammonium removal. When 20 g/L of unmodified zeolite was used, the final (after 60 min of the experiment) average concentration of ammonium was 15.1 mg N-NH_4/L with a process efficiency of 69.8%. With 40 g/L of unmodified zeolite, the final concentration was 7.7 mg N-NH_4/L with an efficiency of 84.6% (Fig. 1). Treatment of zeolite with ultrasound for 90 min led to the lowest concentrations of ammonium in the solution. When 20 g/L of modified zeolite was used, the ammonium concentration was 8.4 mg N-NH_4/L. When 40 g/L was used, it was 3.3 mg N-NH_4/L. With treatment times of 45 min or longer, significantly more ammonium was removed than with treatment times of 30 min or shorter ($t = 0.002$, $p < 0.05$). However, the effectiveness of removal did not differ significantly between the treatment times of 45 min or longer, nor between the

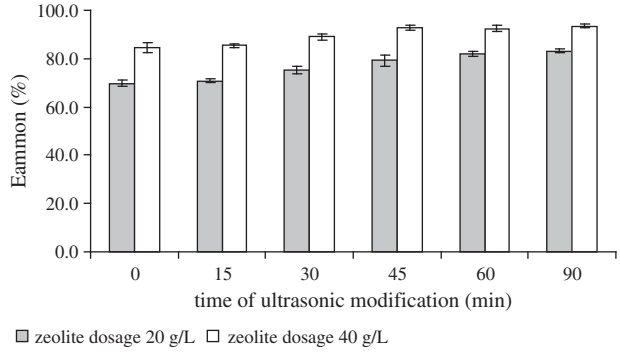

Fig. 1. Efficiency of ammonium removal (E_{ammon}) in relation to duration of ultrasonic treatment of zeolite.

treatment times of 30 min or less. Therefore, it is not necessary to extend ultrasound modification beyond 45 min with these conditions.

Independent of the sonification time, the efficiency of ammonium sorption was significantly higher with the zeolite dosage of 40 g/L than with 20 g/L ($t = 0.001$, $p < 0.05$) (Fig. 1). Similarly, Huang et al. [25] showed an increase in ammonium removal efficiency from 61.4 to 96.0% with the increase in adsorbent dosages ranging from 8 to 64 g/L. However, in the current study, the maximum sorption capacity (q_S) was lower when more of both natural zeolite (1.7 ± 0.2 mg/g at 20 g/L; 1.1 ± 0.1 mg/g at 40 g/L) and modified zeolite were used (2.1 ± 0.1 mg/g at 20 g/L; 1.2 ± 0.1 mg/g at 40 g/L, for zeolite modified for 90 min) ($t = 0.0002$, $p < 0.05$). This suggests that sorption sites were not completely used when a greater amount of zeolite was present in the vessels, despite the same particle size of zeolite throughout the experiment. This may be attributed to the formation of particle aggregates at higher solid/liquid ratios or to precipitation of particles [26]. The lengthening of the adsorption time would not improve the q_S, since from Fig. 2 it can be seen that the concentration of ammonium in the solution reached stable level after ca. 45 min. This may be ascribed to the fast utilization of the most readily available adsorbing sites of the zeolite leading to rapid equilibrium [27].

Changes of the ammonium concentration in the solution and kinetic parameters of a pseudo-first-order kinetic that represented the changes of ammonium adsorption on zeolite are depicted in Fig. 2. For zeolite dosage of 20 g/L, the ammonium removal rate ranged from 174 to 233 mg/(L h), independent of the duration of ultrasound treatment. For zeolite dosage of 40 g/L, the process rate was significantly higher ($t = 0.0004$, $p < 0.05$) and ranged from 233 to 307 mg/(L h). In the experiment with 40 g/L of zeolite, the highest

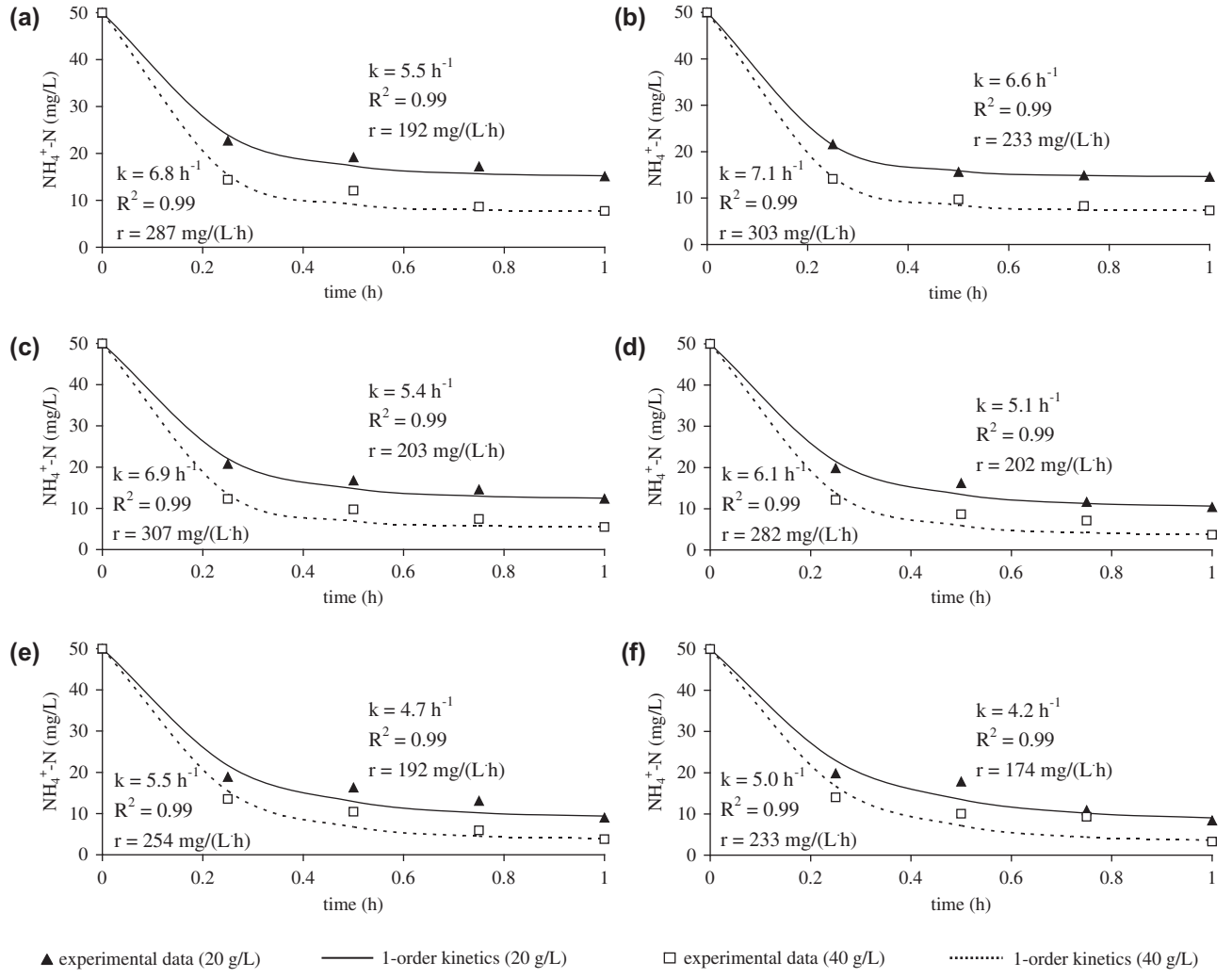

Fig. 2. Change in ammonium concentration with reaction time at different zeolite dosage (20–40 g/L). Ultrasonic pre-treatment duration: (a) 0 min, (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min, and (f) 90 min (k—reaction rate constant, r—reaction rate, R^2—determination coefficient).

ammonium removal rate was obtained with 30 min of ultrasonic modification of zeolite. A lot of studies have been conducted into improving the sorption capacity of zeolites by means of different pre-treatment procedures. Our study of the application of ultrasound to improve this capacity was based on data concerning the characteristics of ultrasonic waves and previous applications of this technology. For example, the positive effect of ultrasound on adsorption cadmium ion has been examined [28]. It has been proposed that these positive effects can be explained by the cavitation phenomenon, in which the formation, growth, and implosive collapse of bubbles in liquids result in the release of large amounts of highly localized energy [29]. Lower frequencies of ultrasound, as in our experiment, favor mechanical effects and produce violent agitation, which can be utilized to disperse particles [30]. In our study, the cavitational effect could have cleaned the zeolite surface, thus facilitating adsorption. Cavitational bubbles affect all surfaces and infiltrate hollows and pores, which results in removal of all impurities from these surfaces, which cannot be purified by ordinary methods because access is difficult [12]. Thus, after cavitation the active sites for adsorption are available again [31], so ultrasound modification is a potential method for regenerating the adsorbent. In addition, Breitbach and Bathen [31] and Entezari and Bastami [28] report that ultrasound improves mass transfer in pores of the adsorbent during sorption. These authors attribute this phenomenon to the induced turbulence and additional convective mass transport inside the pores of the adsorbent.

They also found that ultrasound influenced the morphology and size distribution of sorbent particles through the cavitation process and therefore affected the amount of sorbed pollutant. In the present study, modification of zeolite could has changed the zeolite structure, making its surface less coarse, which increases ammonium sorption, according to Sprynskyy et al. [32]. In the current study, statistical analysis revealed no significant difference between the average particle sizes of the natural zeolite and modified zeolite, irrespective of the time of sonication. In contrast, in the study by Entezari and Bastami [28], size distribution was more homogenous after sonication. Our study found that ultrasonic treatment can increase the adsorptive effectiveness of zeolite. However, to gain deeper knowledge about the workings of this phenomenon, further research is necessary to describe how the zeolite structure is changed by ultrasonic treatment.

4. Conclusions

This study found that ultrasound modification of zeolite has substantial potential for improving ammonium removal from water. When the zeolite was modified with 35 kHz ultrasound with a power density of about 5 W/cm^2 for 45 min, ammonium removal was significantly greater than with untreated zeolite or with zeolite treated for 15–30 min. However, extending treatment time to 60–90 min did not significantly increase ammonium removal, indicating that 45 min was the most energy efficient duration of treatment. To gain deeper knowledge of this phenomenon, research can be done to investigate how the zeolite structure is modified by ultrasound treatment.

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List of symbols

C_{eff} — ammonium concentration after 60 min of treatment (mg/L)
C_{inf} — initial ammonium concentration (mg/L)
k — reaction rate constant (h^{-1})
m — mass of zeolite (g)
q_S — amount of ammonium sorbed on zeolite (mg/g)
r — rate of ammonium sorption (mg/L h)
t — time (h)
V — solution volume (L)

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