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Ammonium removal from aqueous solutions by natural Iranian zeolite in the presence of organic acids, cations and anions

Farhad mazloomi*, Mohsen jalali

Department of Soil Science, College of Agriculture, Bu-Ali Sina University, Hamadan, Iran

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ABSTRACT

The present study was conducted to evaluate the possibility of using natural Iranian zeolite for ammonium (NH_4^+) removal from aqueous solutions. Batch experiments were performed as a function of pH, adsorbent dose, contact time, temperature, initial concentration, anions, cations and low-molecular-weight organic acids (LMWOAs). The optimum conditions for the effective adsorption of NH_4^+ ions onto natural zeolite were found to be pH 7.0, temperature 298 °K, and contact time 30 min. The adsorption kinetics was best represented by a pseudo-second-order model and the NH_4^+ adsorption data on natural zeolite fitted better to Langmuir model than Freundlich, Tempkin and D–R models. The presence of other cations and anions in the solution affected the removal of NH_4^+ onto zeolite and the selectivity order was $K > Na > Ca > Mg$, while in presence of anions the order was $Cl > PO_4 > SO_4$. The presence of LMWOAs increased the adsorption of NH_4^+ onto the natural zeolite. The thermodynamic properties of NH_4^+ adsorption indicated that the adsorption was spontaneous and exothermic. Based on these results, it can be concluded that the natural Iranian zeolite can be used to remove NH_4^+ ion from domestic and industrial wastewater.

1. Introduction

Nitrogen (N) is the primary element of plant and animal proteins and is essential for all life forms [10]. However, high concentration of N in surface and groundwater increases oxygen demand and eutrophication [12]. Ammonium (NH_4^+) is the inorganic ion form of N contained in municipal sewage, domestic and industrial wastewater or decomposed from organic N compounds in those wastewater and wastes [16]. NH_4^+ may have harmful effects on animal and human health, and attacks the rubber components of water plumbing systems [7]. Various methods of NH_4^+ removal are biological nitrification-denitrification, air-stripping and ion exchange [27]. The ion exchange method usually utilizes organic resins, which are very selective. However, they are very expensive [11]; therefore, zeolites are preferred [5]. The utilization of zeolites as ion exchanger is one of the efficient methods for removing NH_4^+ in recent years. NH_4^+ ions are removed from aqueous solutions by zeolites via cations exchange or by adsorption in pores of aluminosilicate structures [23]. Natural zeolites have high exchange capacity, molecular sieve properties, and low cost and are available in many parts of the world. They can be used in water and gas purification, adsorption and catalysis, and agriculture and aquaculture [7,23]. Natural zeolite originating from various deposits may differ in purity, chemical composition, crystal size, porosity, pore size and other characteristics [7,8]. The actual wastewater may contain various cations (calcium, magnesium, sodium and potassium), anions (chloride, phosphate and sulfate) and organic acids (oxalic, citric and malic), which may affect NH_4^+ sorption by zeolites. Little research on the use of natural Iranian zeolite for NH_4^+ removal was conducted from wastewater having different quality. Therefore, the purpose of this study was to remove NH_4^+ from aqueous solution using natural Iranian zeolite, by conducting a series batch and kinetics experiments.

2. Materials and methods

2.1. Materials

The natural Iranian clinoptilolite zeolite used in the experiments was obtained from Semnan province, Iran. The chemical composition of natural zeolite is given in Table 1 [22]. The cation exchange capacity (CEC) and effective cation exchange capacity (ECEC) was approximately 440 and 120 mmol kg^{-1}, respectively [22]. The particle size of the zeolite was between 0.25 and 2 mm. The characteristic of the structure was determined using X-ray diffraction (XRD) spectroscopy (Fig. 1). Scanning electron

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* Corresponding author.
E-mail address: Fmazloomi@gmail.com (F. mazloomi).

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Table 1
The chemical analysis of natural zeolite [22].

Constituent	Value (%)
SiO_2	66.50
Al_2O_3	11.81
Na_2O	2.01
Fe_2O_3	1.30
CaO	3.11
MgO	0.72
K_2O	3.12
P_2O_5	0.01
MnO	0.04
TiO_2	0.21
Loss of ignition	12.05

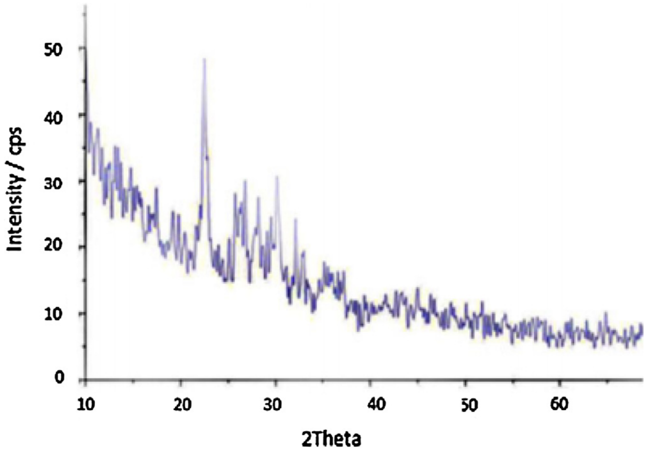

Fig. 1. X-ray diffraction of used natural zeolite [15].

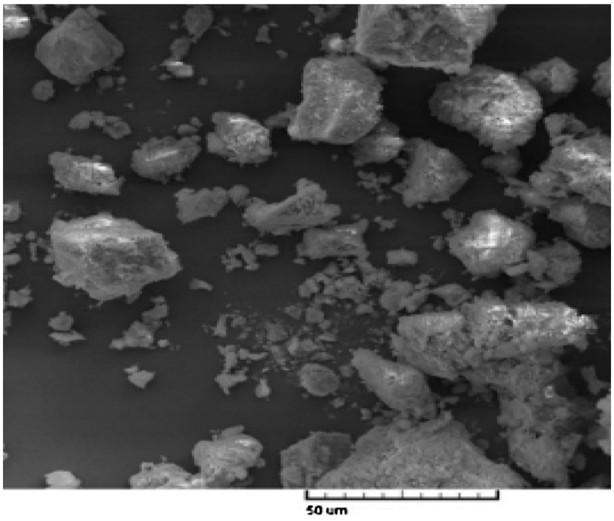

Fig. 2. Scanning electron microscopy of natural zeolite [15].

microscope confirmed that zeolite has weak crystalline structure [15] (Fig. 2). The surface area and average pore diameter of the natural zeolite was 13.8 $m^2 g^{-1}$ and 18.84 nm [15]. The predominant water-extractable component concentrations for the natural zeolite were found to be Na, Ca, and K (Table 2).

2.2. Experimental methods

Batch mode adsorption studies for NH_4^+ have been carried out to investigate the effect of different parameters such as contact time, pH, zeolite dosage, initial NH_4^+ concentration, individual cations (K, Ca, Na and Mg), individual anions (PO4, SO4, Cl), LMWOAs (oxalic, malic and citric) and temperature, on NH_4^+ removal. Stock solution of NH_4^+-N (1000 mg L^{-1}) was prepared by dissolving appropriate amounts of anhydrous NH_4Cl (analytical grade) in deionized water. Batch adsorption experiments were conducted in 50 mL polyethylene tubes. The tubes were shaken in an orbital shaker at 150 rpm for given time. At the end of experiment, the adsorbents were removed from suspension by centrifuging at 5000 rpm for 20 min and solutions containing NH_4^+ were filtered through Whatman filter paper (No. 42). Concentration of NH_4^+ was determined colorimetrically [29]. The percentage removal (R, %) was calculated for each run using the following equation:

$$R = \frac{(C_0 - C_e)}{C_e} \times 100 \tag{1}$$

The amount of NH_4^+ adsorbed (q_e in mg g^{-1}) was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m}. \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentrations of NH_4^+ in solution (mg L^{-1}), V is the volume of solution (L) and m is mass of the adsorbent (g). Freundlich and Langmuir equations were fitted to data. The experimental Freundlich model can be applied to nonideal sorption on heterogeneous surfaces as well as multi-layer sorption and is expressed by the following equation [22]:

$$\mathrm{Log}q_e = \mathrm{Log}k_F + \frac{1}{n}\mathrm{Log}C_e \tag{3}$$

where q_e and C_e have the same definitions as in Eq. (2),k_F is the Freundlich constant representing the adsorption capacity (mg g^{-1}), and n is a constant representing the adsorption intensity. The Langmuir isotherm assumes that adsorption happens at specific homogeneous sites within the adsorbent, and there is no interaction between the adsorbate molecules [28]. The isotherm fitted to the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Mk_L} + \frac{C_e}{M} \tag{4}$$

where q_e and C_e have the same definitions as in Eqs. (2) and (3), M is the maximum adsorption at monolayer coverage (mg g^{-1}), and k_L is the Langmuir constant related to the energy of adsorption that quantitatively reflects the affinity of the binding sites (L mg^{-1}). The adsorption equilibrium data were also analyzed using Tempkin

Table 2
Water-extractable concentrations of cations and anions of the experimental Iranian zeolite.[a]

pH[a]	EC[a] (dS m^{-1})	Solution cations[a] (mg L^{-1})					Solution anions[a] (mg L^{-1})				
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	CO_3^{2-}	PO_4^{3-}	NO_3^-	SO_4^{2-}
7.96	1.82	299	16.6	98.4	15.4	455.7	124.3	00.0	0.612	10.5	197.8

[a] Measured in 5:1 liquid, solid solution.