

Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia

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Abstract

The paper presents the results of investigating the treatment of leakage waters from waste dumps using activated carbon and natural zeolite clinoptilolite, known as a very selective and efficient cation exchanger for ammonium ions. The results are presented of chemical and physical analyses of leakage waters characterized by a high content of ammonium (820 mg L^{-1}) and organic pollutants ($1033 \text{ mg L}^{-1} \text{ C}$). Physical and chemical characteristics of zeolite and the exchange of ammonium ions in model and real solutions were determined in laboratory trials. Treatment of leakage water with 0.04–2.5% (w/w) activated carbon (Norit 0.8 Supra) led to a reduction of total organic carbon in leakage water from 1033 to 510 mg L^{-1} . Pretreatment of leakage water with activated carbon did not improve the exchange of ammonium ions on zeolite. Without pretreatment of leakage water, the exchange of ammonium ions amounted to $4.2 \text{ mg NH}_4^+/\text{g zeolite}$. Addition of activated carbon, regardless of its mass, increased the exchange of ammonium ions to only $5.7 \text{ mg NH}_4^+/\text{g zeolite}$. In the model solution of an equal concentration of ammonium as the real solution, $17.70 \text{ mg NH}_4^+/\text{g zeolite}$ was exchanged. Organic pollutants that were not eliminated by activated carbon (most probably components of natural origin) adsorbed to zeolite and prevented the exchange of NH_4^+ ions, which was also reduced due to the presence of K^+ and Ca^{2+} ions.

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1. Introduction

Vast quantities of wastewaters are a typical example of uncontrolled utilization of natural resources. In such waters, nitrogen commonly occurs as organic nitrogen, ammonia or in the form of ammonium, nitrate or nitrite compounds [1].

The traditional method of removing organic compounds and ammonium ions from wastewater is based on biological methods [2–4]. However, as the discharge limits of different pollutants are becoming more stringent, ion exchange is gaining on interest as a potential method for the treatment of waters polluted with ammonium ions.

In the last 20 years, characteristics of natural zeolites have been intensively studied for the needs of wastewater treatment [5–15]. Ion exchange in zeolites is due to

active hydrated cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) in the channels making up the firm anion skeleton. In contrast to the aluminium and silicon structure atoms, which are mutually bound by chemical (covalent) bonds over common oxygen atoms, cations are bound with the aluminosilicate structure mainly by weaker electrostatic bonds, which causes their mobility and capability of being exchanged with solution cations. Organic resins are usually used because of their higher cation-exchange abilities, higher reaction rates and better chemical resistivity. Zeolites, in contrast, possess higher cation-exchange selectivity [5,16]. Mercer (1970) stated that the non-selective nature of convectional cation-exchange resins makes the costs of the process of ammonium ions removal from urban wastewaters too high and suggested the use of clinoptilolite (simplified formula $(\text{Na,K})_6\text{Si}_{130}\text{Al}_6\text{O}_{72}\cdot 24\text{H}_2\text{O}$), the widespread natural zeolite, whose calcium and sodium forms are highly selective for ammonium ions [5]. This recommendation was based on the results of detailed laboratory and pilot investigations.

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This study was, therefore, focused on the possibility of purifying wastewater by using natural zeolite clinoptilolite.

Leakage water samples were taken from the waste dump at Jakuševac, Zagreb, enriched with ammonium ions, synthetic and natural organic compounds (proteins, amines, urea, etc.). The dumped waste is in direct contact with the thick gravely water-bearing deposits and there is a risk of pollution of the sources of drinking water for Zagreb. Leakage waters are collected by means of a drainage system in two specially equipped collection reservoirs with impermeable bottoms. Leakage water is periodically returned from the reservoirs to the waste dump. Water quantity is reduced by recirculation and evaporation of leakage water and the rest is foreseen for purification.

2. Materials and methods

2.1. Zeolite characterization

In the trial use was made of zeolite tuff with the predominant content of the zeolite mineral clinoptilolite from the Krapina region, Croatia. The investigations involved zeolite samples of particle sizes from 0.5 to 2.0 mm.

Identification of mineral components in the zeolite sample was performed using the X-ray diffraction analysis (XRD) on a dust sample (Fig. 1). X-ray analysis of zeolite was performed with a PHILIPS 1710 diffractograph using Cu K α radiation.

Zeolite chemical composition was determined by the classical chemical analysis (Table 1).

Zeolite cation-exchange capacity was measured by successive zeolite saturation with a solution of ammonium ions (concentration 2 mol L⁻¹). Adding up the molal concentrations (x mmol g⁻¹) of Na⁺, K⁺, 0.5 Ca²⁺ and 0.5 Mg²⁺ ions exchanged with NH₄⁺ ions gave the cation-exchange capacity designated Q_1^0 . The obtained sample in the NH₄⁺ form was further saturated with a solution of potassium ions

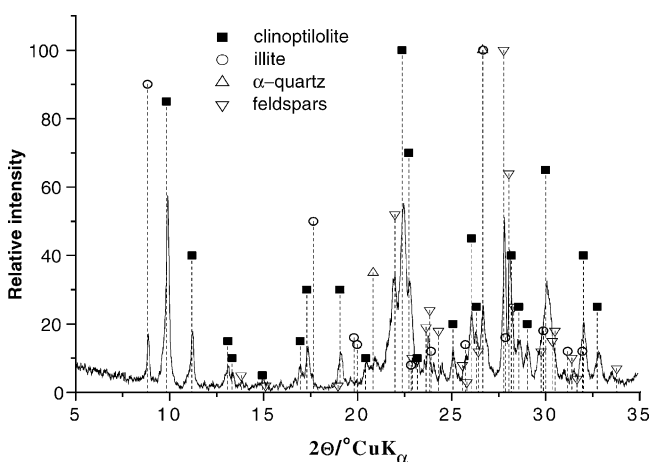


Fig. 1. X-ray of the natural zeolite sample.

Table 1

Chemical composition of the natural zeolite sample

Components	Values (%)
SiO ₂	64.93
Al ₂ O ₃	13.39
Fe ₂ O ₃	2.07
Na ₂ O	2.40
K ₂ O	1.30
CaO	2.00
MgO	1.08
Loss on ignition at 1000 °C	9.63

(concentration 2 mol L⁻¹), and the exchanged NH₄⁺ ions were determined in the eluate. The cation-exchange capacity obtained by determining the molal concentration of exchanged ammonium ions was designated Q_2^0 . Solution of NH₄⁺ ions was prepared by dissolving NH₄Cl, and the solution of K⁺ ions by dissolving KCl in distilled water. The results are given in Table 2. The method of atomic absorption spectrophotometry was used for quantitative determination of Na⁺, K⁺, Ca²⁺ and Mg²⁺ ions. Atomic absorption spectrophotometer PERKIN-ELMER 3110 was used for cation analysis. Ammonium ions were determined using the NH₃ selective electrode METROHM, AG.

The cation-exchange capacity of zeolite was determined in more detail as follows:

- (1) Exactly 0.100 g of sample was weighed into a dry cuvette.
- (2) A 10.0 mL of NH₄⁺ ions solution was poured over the sample.
- (3) The sample was left to stand overnight.
- (4) The following day, the sample was centrifuged at a rate of 3000° min⁻¹.
- (5) Upon centrifuging, the solution above the sediment was decanted into a volumetric flask of 100.0 mL.
- (6) A 10.0 mL of NH₄⁺ ions solution was again poured over the sample, which was then centrifuged. The solution above the sediment was decanted into the volumetric flask.
- (7) Procedure (6) was repeated three more times.
- (8) Upon the last decanting, the volumetric flask was made up to the mark with redistilled water and concentrations of Na⁺, K⁺, Ca²⁺, Mg²⁺ ions were determined in the thus obtained solution. The sample in the cuvette was washed two to three times with distilled water.

Table 2

Cation-exchange capacities Q_1^0 and Q_2^0 of natural zeolite

Cations	x (mmol g ⁻¹)
Na ⁺	0.950
K ⁺	0.312
0.5 Ca ²⁺	0.162
0.5 Mg ²⁺	0.032
Q_1^0	1.456
(Q_2^0)	(1.45)

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