ELSEVIER

Water Research 39 (2005) 1527–1532

WATER RESEARCH

www.elsevier.com/locate/watres

Influence of chemical conditioning on the ion exchange capacity and on kinetic of zinc uptake by clinoptilolite

Konstantinos Athanasiadis*, Brigitte Helmreich

Institute of Water Quality Control and Waste Management, Technical University of Munich, Am Coulombwall, 85748 Garching, Germany

Received 2 September 2004; received in revised form 24 January 2005; accepted 26 January 2005
Available online 17 March 2005

Abstract

Aim of this study was to evaluate the feasibility of the use of clinoptilolite as a barrier material to eliminate heavy metals from roof runoff. The effect of chemical conditioning with 1 M NaCl solution upon the ion exchange capacity and on kinetic of zinc uptake by clinoptilolite has been investigated. According to the batch experiments the modified clinoptilolite has up to 100% higher sorption capacity, regarding Zn than the natural material. The pre-treatment of clinoptilolite results in an acceleration of the ion exchange process up to 40% regarding zinc. In order to define the reasons of this behaviour, both materials, modified and natural, were analysed for: (i) chemical composition, (ii) density, (iii) pore size distribution and (iv) zeta potential. The clogging of the pores, the charge of the grain surface, the pH of the initial metal solution and the ion metal concentration are the factors which are mainly affecting the ion exchange capacity and the rate of zinc uptake by clinoptilolite.

Keywords: Ion exchange capacity; Clinoptilolite; Heavy metals; Roof runoff; Pore size distribution; Zeta potential

1. Introduction

Roof surfaces account for about half of the total area of impermeable surfaces in urban areas. Traditionally, the roof runoff is sent to sewers through which the rainwater is either directly transported to the receiving water or, in case of combined sewer systems, sent to wastewater treatment facilities. From an economical point of view, this approach is far from being optimal because of the high costs for providing sewer capacity which is rarely exploited. Ecologically, the traditional urban dewatering concept is to be critically assessed as well, since it leads to two negative effects, pollution of the receiving water by direct discharge of the storm water or by sewer overflow, and lowering of the groundwater table underneath the urban area.

On-site infiltration may be considered as the promising way of managing roof rain water situations in urban areas, provided the hydrological and geological conditions allow infiltration, and provided the pollutants contained in the collected water are effectively removed before the rain runoff enters the soil and the groundwater. Otherwise, the pollutants may accumulate in the soil leading eventually to highly contaminated sites. Additionally, pollutants contribute to further deterioration of the groundwater quality. Major pollutants of concern are heavy metals (Zn and Cu) stemming from

---

*Corresponding author. Tel.: +49 89 289 13708; fax: +49 89 289 13718.
E-mail address: k.athanasiadis@bv.tum.de (K. Athanasiadis).

0043-1354/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2005.01.024

the roof material and from piping. The phase distribution of copper and zinc in the roof runoff is dominated by the dissolved phase (Förster, 1996).

To avoid such a negative effect it is proposed to pass the roof runoff through an artificial barrier before it will enter soil and groundwater (Boller and Steiner, 2002; Matsui et al., 2003). The problem is that only very little contact time between the rainwater and the barrier material is available. The pollution removal rate has to be very high. Secondly, one must consider that the barrier material has to be highly efficient during rain events which are following long dry periods. Thirdly, it has to be realized that pollutants may appear in enhanced concentration at the beginning of a rain event, whereas pollutants from roof runoff, particularly heavy metals, may remain in enhanced concentrations for a prolonged period of time. The use of clinoptilolite as a barrier material could be the solution of these problems.

Clinoptilolite is a mineral zeolite of the heulandite group. The structures of zeolites consist of a three-dimensional framework, having a negatively charged lattice. The negative charge is balanced by cations, most frequently sodium, potassium, calcium and magnesium which are exchangeable with certain cations in solutions such as heavy metals. Clinoptilolite, one of the most frequently studied natural zeolites, was shown to have high selectivity for certain heavy metals such as copper, zinc, lead, cadmium and nickel (Athanasiadis et al., 2004; Kesraoui-Ouki et al., 1994; Tsitsishvili et al., 1992).

The theoretical ion exchange capacity is defined as the total amount of exchangeable cations per unit quantity of the material. This capacity is independent of any pre-treatment applied. The effective ion exchange capacity refers to the amount of cations, which can be exchanged, contained in a specific quantity of the material under specific experimental conditions (Hellferich, 1995). The theoretical ion exchange capacity is determined by chemical analysis of the zeolites (Pabalan, 1994). The pre-treatment aims to remove certain cations from the structure of the zeolite and locates more easily removable ones, prior to any ion exchange application of it. The final homoionic or near-homoionic state of the zeolites was found to improve their effective exchange capacity and performance in ion exchange applications (Cmielewska and Lesny, 1995; Kesraoui-Ouki et al., 1993; Semmens and Martin, 1988; Bremmer and Schultze, 1995; Gradev et al., 1988).

It has been also known that zeolites are increasing the acidity of their solution. This is the result of the ion exchange process, as H^+ ions are exchanged with cations from the zeolite structure. Therefore, the pH-profile during the ion exchange process must be reported (Kesraoui-Ouki and Kavannagh, 1997; Curkovic et al., 1997; Rozic et al., 2000).

Aim of this study is to explain the influence of chemical conditioning on the ion exchange capacity and on kinetic of zinc uptake by clinoptilolite under different pH values. For this reason, both materials, in their original state and after conditioning, were analysed for: (i) chemical composition, (ii) density, (iii) pore size distribution and (iv) zeta potential. The results obtained will be presented and discussed in this paper.

2. Methods

2.1. Chemical conditioning of clinoptilolite

The clinoptilolite used was supplied by Silver & Baryte Ores Mining Co.S.A, Greece. The particle size of the sieved material was in the range of 0.5–1 mm. A 100 g of it was treated with 1 M NaCl solution at room temperature over a period of 24 h. Afterwards, the clinoptilolite was washed with ultra pure water (18.2 MΩ) water by ultrasonication (SONOREX SUPER RK 514 BH), several times, until the fine fraction was removed. Then the sample was dried at 105 °C for 24 h.

The chemical composition of the natural and modified clinoptilolite was determined by X-ray fluorescence analysis measurements, using the model SRS 303 from Siemens.

The density was determined by an autopycnometer from Quantachrome Corporation (Ultrapycnometer 1000 Version 2.2). The pore size distribution of the natural and modified clinoptilolite was established with a Mercury-Porosimeter from Porous Materials Inc, Ithaca—New York. For the determination of the zeta potential, the electroacoustic method from Acousto-Phor, PENKEM was applied (Beattie et al., 2003).

2.2. Equilibrium experiments

The equilibrium studies with natural and modified clinoptilolite were conducted as follows: a constant amount of clinoptilolite (1 g) was added into a tube (50 ml) containing measured volumes of zinc solutions (40 ml). The following concentrations of Zn^{2+} were used: 1, 2, 3, 4, 5 and 10 mM. The experiments were carried out for initial pH values of 5.0 and 3.0 at room temperature. The suspension was mixed for a period of 24 h with a vertically rotary shaker at a speed of 40 rpm (Athanasiadis et al., 2004). Afterwards, 30 ml of every sample was filtrated (0.45 μm membrane filter pore diameter) and pH and temperature values recorded prior to analysis. Analysis of Zn^{2+} was performed on the collected samples by means of flame atomic adsorption spectrometry (VARIAN SPECTRA A-40). In order to check for precipitation of metal hydroxides, control samples were acidified at the end of each