Available online at www.sciencedirect.com

SCIENCE DIRECT®

Int. J. Miner. Process. 75 (2005) 21–29

INTERNATIONAL JOURNAL OF MINERAL PROCESSING

www.elsevier.com/locate/ijminpro

Characterization and environmental application of a Chilean natural zeolite

A.H. Englert, J. Rubio*

Laboratório de Tecnologia Mineral e Ambiental (LTM), Departamento de Engenharia de Minas, PPGEM-Universidade Federal do Rio Grande do Sul, Av. Osvaldo Aranha 99/512, 90035-190, Porto Alegre, RS, Brazil

Received 22 October 2003; received in revised form 22 January 2004; accepted 22 January 2004

Abstract

The use of natural zeolites for environmental applications is gaining new research interests mainly due to their properties and significant worldwide occurrence. The present work describes the characterization of a natural Chilean zeolite and the results as adsorbent for ammonia from aqueous solutions. The zeolitic-rich tuff sample, mainly composed of clinoptilolite and mordenite, consisted of 13 μm mean volumetric particle diameter, 55 $m^2\ g^{-1}$ (methylene blue adsorption) and 177 $m^2\ g^{-1}$ (nitrogen adsorption) of specific surface area. Particles were negatively charged over a broad pH range (with or without ammonia) and 1.02 meq $NH_4^+\ g^{-1}$ cation-exchange capacity. The ammonia removal appears to proceed through ion-exchange and rapid kinetics (rate constant of 0.3 min^{-1}) at neutral pH value, with removal capacities up to 0.68 meq $NH_4^+\ g^{-1}$. The Langmuir isotherm model provided excellent equilibrium data fitting ($R^2 = 0.97$). Results indicate a significant potential for the Chilean natural zeolite as an adsorbent/ion-exchange material for wastewater treatment and water reuse applications.

Keywords: industrial minerals; natural zeolite; ion exchange; effluent treatment

1. Introduction

Zeolite minerals, also known as natural sedimentary or natural occurring zeolites (Mondale et al., 1995), are mainly composed of aluminosilicates with a three-dimensional framework structure bearing AlO_4 and SiO_4 tetrahedra. These are linked to each other by sharing all of the oxygen to form interconnected cages and channels containing mobile water molecules and alkali (sodium, potassium, lithium, and caesium) and/or alkaline earth (calcium, strontium, barium, and magnesium) cations (Tschernich, 1992). These exchangeable cations give rise to the ion-exchange properties of the material.

Only a few of the existing natural zeolites in the world are found in sufficient quantity and purity as required by industry. Within this group, silica-rich heulandite (clinoptilolite) and mordenite are the most important and play a significant industrial role (Mondale et al., 1995; Tschernich, 1992). Important uses of zeolite minerals include water softening, gas and petroleum processing, mining, sewage treatment, paper products, among others (Tschernich, 1992). Main

* Corresponding author. Tel.: +55-51-33163540; fax: +55-51-33163530.

E-mail address: jrubio@vortex.ufrgs.br (J. Rubio).

URL: http://www.lapes.ufrgs.br/laboratorios/ltm/ltm.html.

0301-7516/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.minpro.2004.01.003

Table 1
Environmental applications of natural zeolites

Wastewater treatment	References
Ammonia removal	Baykal (1998), Cincotti et al. (2001), Demir et al. (2002), Dyer and White (1999), Hlavay et al. (1982), Jorgensen and Weatherley (2003), Klieve and Semmens (1980), Langella et al. (2000), Mercer et al. (1970), Rozic et al. (2000)
Heavy metals removal	Bosso and Enzweiler (2002), Cincotti et al. (2001), Inglezakis et al. (2001), Kesraoui-Ouki et al. (1994), Langella et al. (2000), Mondale et al. (1995), Panayotova (2001)
Organic compounds removal	García et al. (1993), Li et al. (2000)
Radioactive elements removal	Abusafa and Yucel (2002), Dyer and Zubair (1998)

reported environmental applications and related studies, particularly in wastewater treatment, are summarised in Table 1.

The excessive presence of ammonia in water streams and effluents is a problem of great concern for the environment and industrial water systems, mainly due to eutrophication and corrosion/biological fouling problems, respectively (Mercer et al., 1970; Rozic et al., 2000). Existing methods and technologies for the removal of this pollutant/contaminant, i.e. biological and physicochemical, are constantly being either adapted or improved and recent efforts have been made to discover new economically feasible and environmentally friendly alternatives (Rozic et al., 2000). In this context, the use of natural zeolite for the removal of highly loaded ammonia bearing wastewater appear to have potential due to the advantages and peculiarities over some conventional and expensive ion-exchange resins (Demir et al., 2002; Mercer et al., 1970).

Zeolitic-rich tuffs have been studied for the removal of ammonia from aqueous solutions, including material from Hungary (Hlavay et al., 1982), Turkey (Demir et al., 2002), Croatia (Rozic et al., 2000), USA (Klieve and Semmens, 1980), Italy (Cincotti et al., 2001; Langella et al., 2000) and other countries (Dyer and White, 1999). Yet, the number of studies reported on the use of natural zeolites from South America is evident in only a few publications (Bosso and Enzweiler, 2002). Thus, studies of characterization and applications (especially environmental ones) of such minerals available in South America should be of great importance to that region.

Thus, the main objective of this work is to describe the characterization of a natural zeolitic-rich tuff from Chile (Minera Formas™) and to evaluate the use as an ion-exchange material for the removal of ammonia from aqueous solutions.

2. Experimental

2.1. Materials and reagents

A Chilean natural zeolite (designated here as "Ch-zeolite"), from an important and abundant mine in Chile, was provided by Minera Formas™. The sample was homogenized and sieved below 149 μm (100 Mesh Tyler™) before characterization and experimentation. Main physical, mineralogical and chemical properties are summarised in Tables 2 and 3.

Synthetic ammonia solutions were prepared with $(NH_4)_2SO_4$ (analytical purity) for the determination of the cation-exchange capacity of the Ch-zeolite and ion-exchange batch experiments. Methylene blue ($C_{16}H_{18}N_3SCl \cdot 3H_2O$) of analytical purity and ultra pure (>99.999%) nitrogen gas (N_2) were used for surface area determination of the Ch-zeolite. Analytical purity sodium chloride (NaCl) was used for chemical modification of the Ch-zeolite in the determination of its cation-exchange capacity. The pH adjustments for the ion-exchange batch experiments were made using H_2SO_4 and NaOH solutions. Analytical purity potassium nitrate (KNO_3) was used in the zeta potential measurements of the Ch-zeolite. The pH adjustments for zeta potential measurements were made using HNO_3 and KOH solutions. All solutions were prepared with deionised water.

Table 2
Main characteristics of the Ch-zeolite

Cation-exchange capacity (meq g^{-1})	2.05
Specific gravity (g cm^{-3})	2.2
Mineralogical composition	Clinoptilolite (48%), Mordenite (30%), Albite (5%) and Quartz (15%)
Particles size	100% below 149 μm (100 Mesh Tyler™)

Data kindly provided by Minera Formas™.