



Ammonium modified natural clinoptilolite to remove manganese, cobalt and nickel ions from wastewater: Favorable conditions to the modification and selectivity to the cations



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ABSTRACT

The removal of manganese, cobalt and nickel from industrial ammoniacal wastewaters has been studied using natural Cuban clinoptilolite modified to ammonium form. Favorable conditions to obtain the ammonium-clinoptilolite form (NH₄-CLI) were determined from detailed kinetic studies of NH₄⁺ ion-exchange in the clinoptilolite (CLI). Obtained NH₄-CLI was characterized by IR spectroscopy and X-ray diffraction. NH₄-CLI was used to remove Mn²⁺, Co²⁺ and Ni²⁺ from mixed aqueous solutions. The thermodynamic study on ion-exchange equilibrium between NH₄⁺ in solution and these metallic cations from metal-clinoptilolite forms was performed. Increasing the temperature promotes the NH₄⁺ exchange, which is controlled by the intracrystalline diffusion of ions inside the clinoptilolite. However, the activation energy of this process is not very high. This provides a wide temperature interval for the NH₄-CLI efficient production. NH₄-CLI removes Co²⁺ and Mn²⁺ by ion-exchange selectively at room temperature, being poorly selective to Ni²⁺, producing a well ions separation. Increasing the temperature greatly enhances the NH₄-CLI capacity to remove these metal cations, which is substantially higher to Ni²⁺. The obtained values for the free energy variation and equilibrium constant lead to outline that the selectivity order of the metal-clinoptilolite forms by NH₄⁺ at room temperature is Mn-CLI > Co-CLI > Ni-CLI. Divergences in the behavior to these exchange processes are associated with difference in the interaction of cations with their ligands in solution as well as into zeolite framework, and accessibility at ion-exchange sites inside clinoptilolite.

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1. Introduction

Zeolites are nanostructured materials with a crystalline structure negatively charged. This structure is formed by interconnected cavities and channels, which contain adsorbed molecules and cations with movement freedom. Ion-exchange is one of their most important properties, which has allowed the development of new materials and different applications such as the harmful heavy-metal removal from industrial wastewaters. This property allows removing and recovering the cations from very low concentration in solutions, which is very outstanding with respect to others used

techniques such as the precipitation of low-soluble substances [1–6].

Generally, the treatment of residual industrial effluents has required great amounts of material. Natural zeolites are effective and low-cost materials with great availability and selectivity by cations, which make them the suitable materials for this purpose.

To know the characteristics of the wastewaters to be treated and the behavior of the zeolite during this use are essential aspects to resolve before starting the applications. This has incidence on a possible zeolite modification to increase the treatment effectiveness. Then, the study on its modification (cationic, surface, etc.) should be performed to design an efficient treatment process. However, deep studies about the zeolite modification for this purpose are not usually shown or referred. Also, the reported studies on cations removal are commonly performed using single ion solutions. However, the cations are normally presented inside multi-

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component or mixed solutions for the real conditions. In addition, integrated studies about the cation removal from aqueous solution and later its elution (recuperation) from exchanger where they were retained are scarce. The majority of the studies have been carried out in a separated or nonintegrated mode, i.e., either as removal or elution studies.

Studies on Ni^{2+} removal from aqueous solutions using natural clinoptilolite modified to its Na^+ , K^+ and Ca^{2+} forms have reported that only monovalent ion forms enhances the nickel removal efficiency [7]. Natural zeolite (mixed clinoptilolite and mordenite) modified with NaCl , Na_2CO_3 , NH_4Cl and NaOH solutions was used to remove manganese ions from aqueous solutions. The modifications increase the removal capacity, however, the treatments with NaOH and Na_2CO_3 cause zeolite desilication. This can come united with low-soluble manganese-phases formation [8]. Nickel and copper removal from saline (NaCl) solutions has been studied using natural clinoptilolite, being reported that zeolite selectivity is higher for Na^+ than for nickel and copper cations [9]. Natural and NaCl pre-treated clinoptilolite have been used to removal ammonium from aqueous solutions. This treatment improves its removal efficiency, however, it is affected by presence of calcium [10,11]. Studies on Ni^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+} removal using natural clinoptilolite have reported that modification of this zeolite to a homoionic (Na) form lead to increase its capacity to remove these metal cations from their single-ion and multi-component solutions, mainly when the water hardness due to Ca^{2+} presence is not high. Zeolite modification practically does not change the selectivity sequence for these ions [12]. The removal of Mn^{2+} , Zn^{2+} , Pb^{2+} and Cu^{2+} from mixed solutions, using natural clinoptilolite was studied. It has been reported that cations removal from multi-component solution was affected significantly with respect to those observed in solutions from single cation, except for Pb^{2+} , also differences to Mn^{2+} and Zn^{2+} selectivity were observed [13].

In previous studies, we have reported the removal of nickel and other heavy metals from wastewater of nickel hydrometallurgy industry using natural Cuban clinoptilolite. The effect of the presence of metal amino-complexes, carbonate anions, temperature, ion concentration and formation of low-soluble phases during the ion-exchange with watery solutions of metal single salts (no mixed) has been the subject of such studies [14–17]. However, these wastewaters or industrial liquors have numerous mixed ions, such as nickel, cobalt, manganese and ammonium; a quite complex solutions for the deep study of the metal cations removal using a natural zeolite that has not been reported yet. It is a subject to be resolved in order to enhance the removal and recovery efficiency of nickel and other heavy metals.

The present study was performed to acquire information on the modification of the clinoptilolite from Caimanes deposit, Cuba, to obtain its ammonium form, and to study their behavior in the removal of nickel, cobalt and manganese cations by ion exchange. The kinetic of NH_4^+ ion-exchange in the natural clinoptilolite and the favorable conditions to obtain the ammonium-clinoptilolite were studied. Obtained NH_4 -clinoptilolite was applied for the removal of Ni^{2+} , Co^{2+} and Mn^{2+} cations from mixed aqueous solutions at different temperatures. Also, the thermodynamic study on the ion-exchange between NH_4^+ in solution and these metallic cations from homoionic metal forms of clinoptilolite was carried out in order to establish the selectivity of this zeolite to these metal cations as well as to get information on their elution from zeolite, where they were retained, to the solution phase.

2. Experimental

Purified zeolite samples were obtained from the zeolitic rock of Caimanes deposit (Cuba) by application of a procedure similar to

described elsewhere [16]. This zeolite, with particles size class +0.25–0.5 mm, resulted in a mixture of clinoptilolite (85%) mordenite, quartz and other phases (montmorillonite, feldspar, etc.). Their elemental chemical composition in oxide form is: 63.2% SiO_2 , 10.13% Al_2O_3 , 3.92% CaO , 3.05% Fe_2O_3 , 1.3% MgO , 1.42% K_2O , 0.93% Na_2O and 13.9% H_2O . Herein this purified zeolite is referred to as clinoptilolite (CLI).

2.1. Preparation of ammonium-clinoptilolite form

The modification of the clinoptilolite to its ammonium form (NH_4 -CLI) was preceded by the study of NH_4^+ ion-exchange in CLI to obtain favorable conditions to prepare this form.

Study of NH_4^+ ion-exchange in natural clinoptilolite: CLI samples were combined with 0.15 mol/L NH_4Cl solutions in a relation of 1 g of CLI by 20 mL of solution and applying agitation. The experiments were conducted at 25 °C, 80 °C and 100 °C. At different times, the liquid and solid phases were separated by filtration. The Na, Ca, K and Mg concentrations in the liquid phase after the treatment were determined by atomic absorption spectrometry (AAS), while the ammonium concentration was determined using the Nessler reagent. The main kinetic parameters associated with this exchange were determined. Using the favorable conditions (temperature, time, etc.; which will be presented afterward) obtained to the NH_4^+ exchange in clinoptilolite, the NH_4 -CLI was prepared as nearly as possible to the homoionic ammonium form.

X-ray diffraction (XRD) patterns and Infrared (IR) spectra of the samples, before and after the treatments, were obtained. XRD patterns were recorded in a Philips PW 1218 diffractometer equipped with a curved graphite monochromator, using $\text{CoK}\alpha$ ($\lambda = 0.179026$ nm) radiation at 2° min^{-1} with a time constant of 3 s. IR spectra were obtained with a FTIR PU9600 Pye Unicam Spectrometer; the samples were prepared using the KBr pressed-disk technique with 1% inclusions of the samples.

2.2. Removal of Mn^{2+} , Co^{2+} and Ni^{2+} cations from aqueous solutions using NH_4 -CLI

Studies were performed in dynamic form into a tubular column with dimensions of 1 cm diameter and 20 cm high. Through this column with 1 g of NH_4 -CLI, mixed aqueous solutions of NiCl_2 , MnCl_2 and CoCl_2 (containing 25 mg/L Ni and 1 mg/L to Co and Mn) were made to flow at a 2 mL/min rate. In the case of nickel, another single NiCl_2 solution (25 mg/L Ni) was used too. The experiments were performed at 25 °C and 80 °C, and the resulting eluate solutions were collected over time. The heights of the zeolite bed and of the total bed (zeolite + solution) in the column were 2 and 3 cm, respectively. The nickel, cobalt and manganese concentrations in the solutions after the treatments were determined by AAS.

2.3. Isotherms of NH_4^+ ion-exchange with Mn^{2+} , Co^{2+} and Ni^{2+} cations

Isotherms of the ion exchanges between NH_4^+ in solution and these metal cations from homoionic metal forms of clinoptilolite (Mn -CLI, Co -CLI and Ni -CLI) were constructed at 25 °C by contacting 20 mL of 0.1 mol/L NH_4Cl solution with predetermined mass (0.05–10 g) of these metal forms. The treatment was conducted for 15 days, with agitation of 120 jolts per minute using a universal agitator. This exchange period is very superior with respect to the equilibrium time (four to five days) indicated by kinetic test for the less favored exchange (Ni^{2+} exchange). After the treatment the concentration of ammonium, Mn^{2+} , Co^{2+} and Ni^{2+} cations in both liquid and solid phases were determined using the previously described techniques.

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