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Separation and Purification Technology 46 (2005) 202–207

Separation and Purification Technology

www.elsevier.com/locate/seppur

The effect of competitive cations and anions on ion exchange of heavy metals

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Received 26 November 2004; received in revised form 18 May 2005; accepted 23 May 2005

Abstract

In the present study, the effects of competitive cations NH_4^+, K^+, Ca^{2+}, Na^+, Mg^{2+} and Li^+ and co-anions Cl^- and Br^- on ion exchange of heavy metals Pb^{2+}, Fe^{3+}, Cr^{3+} and Cu^{2+} on clinoptilolite is examined. The presence of cations and anions in the solutions of heavy metals is reducing the removal of the latter and the order of decreasing negative effect is the following: $NH_4^+ > Mg^{2+} > Ca^{2+} > Na^+ > K^+ > Li^+$ and $Br^- > Cl^-$ for Pb^{2+}, $NH_4^+ > K^+ > Ca^{2+} > Na^+$, $Mg^{2+} \approx Li^+$ and $Br^- > Cl^-$ for Cr^{3+}, $NH_4^+ > K^+ > Na^+ > Ca^{2+} > Li^+ > Mg^{2+}$ and $Cl^- > Br^-$ for Fe^{3+} and $Ca^{2+} > NH_4^+ > Li^+ > K^+ > Na^+ > Mg^{2+}$ and $Cl^- > Br^-$ for Cu^{2+}. In all cases, the selectivity of clinoptilolite for heavy metals is the following: $Pb^{2+} > Fe^{3+} > Cr^{3+} \geq Cu^{2+}$.

Keywords: Clinoptilolite; Heavy metals; Ion exchange; Competitive cations; Anion complexes

1. Introduction

Heavy metal contamination exists in aqueous wastewaters of many industries, such as tanneries, metal plating facilities and mining operations. Especially Pb^{2+}, Cu^{2+}, Fe^{3+} and Cr^{3+} are common metals found in many industrial wastewaters. Ion exchange is one of the most promising technologies for the removal of such metals from waste streams. In ion exchange, a solid either synthetic or natural is used, which has the specific ability to exchange its cations, most commonly Na^+, Ca^{2+} and K^+, with the metals initially present in the waste stream. One species of these materials are zeolites, which are naturally occurring silicate minerals. Zeolite clinoptilolite has received extensive attention due to its attractive selectivity for several cations and especially for heavy metals [1–4].

Ion exchange of a specific cation is strongly influenced by the presence of competitive cations and complexing reagents, such as anions [5]. It is expected that in municipal and industrial waste liquors, where the complexity of the system is high, several cations and anions could influence the removal of specific target metals.

The negative effect of competing cations such as NH_4^+, Ca^{2+} and Na^+ on the ion exchange of some metals on several forms of clinoptilolite has been investigated in the related literature [6–8]. However, the main work has been limited on the ion exchange of Cs^+ [7].

It is well known that ion exchange is strongly affected by complex formation of the various mobile species with one another [5]. Furthermore, transition metals can form stable complexes due to their electronic structure (availability of d orbital, as well as s and p orbital) [9–11]. It is true that Fe^{3+}, Cr^{3+} and Cu^{2+} can form stable complexes with water molecules, inorganic anions and NH_4^+, which are charged and are frequently giving colour to their solutions. It is obvious then that the heavy metal species can be more than one simple cation and this species influences the ion exchange process.

The relatively poor removal of Ni^{2+}, Hg^{2+}, Cu^{2+}, Fe^{3+} and Cr^{3+} in the presence of Cl^-, SO_4^{2-}, HPO_4^{2-} and NO_3^- by several zeolites including clinoptilolite, has been attributed to the high stability of several complexes formed in the solution [12–15]. However, the main work on anion effects is on the

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doi:10.1016/j.seppur.2005.05.008

formation of precipitates in zeolite pores or on the surface, leading to pore clogging [16–18]. Surface precipitation most probably reduces the zeolite ion exchange ability due to the blockage of the microprores by the precipitated phase [16].

In the present study, the effects of cations Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+ and anions Cl^- and Br^- on ion exchange of Pb^{2+}, Cu^{2+}, Fe^{3+} and Cr^{3+} on natural clinoptilolite is examined. The aim of the present work is to study the specific effects of anion and cation competition on ion exchange of the above heavy metals.

2. Materials and methods

2.1. Clinoptilolite samples

The mineral used was collected from a deposit in the northern part of Greece. The raw material was sieved to different fractions, of which 1.4–1.7 mm was used in the study. The samples were washed prior to the ion exchange experiments in order to remove the surface dust. The chemical composition of the material was determined by scanning electron microscopy (SEM)/EDS measurements, using the model JSM-6100 of Jeol Scanning Microscope. Furthermore, X-ray diffraction and N_2 porosimetry were performed using XRD diffractometer (D500 of Siemens) and Soprtomatic 1900 model (Carlo Erba Instruments), respectively.

2.2. Effect of competitive cations

Six grams of clinoptilolite particles of size 1.4–1.7 mm and 100 mL portions of heavy metal solution (single-metal solutions) were placed in a suitable container. The corresponding concentration of each metal is 1000 mg L^{-1} for Pb^{2+}, 310 mg L^{-1} for Cu^{2+}, 182 mg L^{-1} for Fe^{3+} and 170 mg L^{-1} for Cr^{3+} (normality of 0.01N). For all metal solutions, nitric salts were used. To examine the effect of the competitive cations, the appropriate mass of its nitrate salt was dissolved in the metal-containing solutions to produce a competitive cation concentration of 0.01N and consequently the concentration ratio was set equal to 1. Concentration ratio (C_R) is defined here as the ratio of competitive cation concentration to metal concentration, all in eq L^{-1} (N) scale. Since ion exchange is a stoichiometric process [5], the effect of cations should be investigated under equal normality or $C_R = 1$ for all metals and cations.

The solutions were initially acidified to avoid precipitation of hydroxides with HNO_3, at a pH value of 2. In Table 1, competitive cation concentration is presented in mg L^{-1} scale.

Table 1
Cation concentration (mg L^{-1})

Cation	C_o
NH_4^+	180
K^+	390
Na^+	223
Mg^{2+}	121
Ca^{2+}	200
Li^+	70

[*] Common concentration of NO_3^- anion equal to 1220 mg L^{-1}.

After the preparation of the samples, the mixtures were equilibrated for 4 days. At the end of this period, final pH was recorded and heavy metal concentration was measured using atomic absorption spectrometry (AAS). The solutions were separated by solid phase by centrifugation (4000 rpm/10 min) before chemical analysis. Metal removal from the solution is determined as follows:

$$\text{Uptake}\,(\%) = \frac{C_o - C}{C_o}100 \tag{1}$$

where C_o and C are the initial and final metal concentrations (meq L^{-1}).

Control zeolite-heavy metal solutions were prepared, under the same normality and pH, without competitive cations in order to examine the effect of the latter on ion exchange of heavy metals.

All the experiments were performed three times and the average experimental relative error was found to be 3.5% for metal concentration measurements.

2.3. Effect of anions

In a suitable container were placed 6 g of clinoptilolite particles of size 1.4–1.7 mm and 100 mL portions of heavy metal solution (single-metal solution), under normality of 0.01N. For all metal solutions, nitric salts were used. To examine the effect of the anions, the appropriate mass of the appropriate potassium salt was dissolved in the metal-containing solutions to produce a potassium concentration of 0.01N. The objective of K^+ presence in the same normality for all mixtures is to eliminate the effect of different cation concentration on ion exchange of metals. The solutions were initially acidified to avoid precipitation of hydroxides with HNO_3, at pH value of 2.

In Table 2, anion concentration in metal–anion solution is presented in mg L^{-1} scale.

After the preparation of the samples, the mixtures were equilibrated for 4 days. At the end of this period, final pH was recorded and heavy metal concentration was measured using atomic absorption spectrometry. The solutions were separated by solid phases by centrifugation (4000 rpm/10 min)

Table 2
Anion concentration[a] (mg L^{-1})

Anion	C_o
NO_3^-	1220[b]
Cl^-	352
Br^-	792

[a] Common concentration of K^+ cation equal to 390 mg L^{-1}.

[b] All solutions except this contains a common concentration of NO_3^- equal to 610 mg L^{-1}.