Simultaneous removal of metals Cu^{2+}, Fe^{3+} and Cr^{3+} with anions SO_4^{2-} and HPO_4^{2-} using clinoptilolite

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Abstract

In the present study the effect of SO_4^{2-} and HPO_4^{2-} on ion exchange of Cu^{2+}, Fe^{3+} and Cr^{3+} on natural clinoptilolite is examined under normality of 0.01 N, temperature of 25 ± 2 °C and pH 2–2.5 after four days of equilibration. It is observed that Cu^{2+} uptake is significantly decreased in the presence of HPO_4^{2-} and SO_4^{2}. The observed effect is less significant for Fe^{3+} and Cr^{3+} in the presence of SO_4^{2-} and HPO_4^{2-} respectively. This could possibly be due to the metal–anion complex formation and the nature and charges of the complex species present. Blank solutions show precipitation in the case of Fe^{3+}/HPO_4^{2-} solution, leading in complete removal of Fe^{3+} from solutions. Precipitation along with ion exchange is resulting in higher removal of Fe^{3+} from the solution than ion exchange or precipitation alone. Finally, anion co-removal is significant, reaching 80% for HPO_4^{2-} ions.
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1. Introduction

Heavy metal contamination, especially Cu^{2+}, Fe^{3+} and Cr^{3+}, occurs in aqueous wastewater of many industries, such as tanneries, metal plating facilities and mining operations. Ion exchange is among the most promising technologies for the removal of such metals from waste streams. Natural silicate minerals such as zeolites are common ion exchangers, clinoptilolite being probably the most abundant among more than 40 natural zeolite species. Clinoptilolite has received extensive attention due to its selectivity for heavy metal cations such as lead, cadmium and nickel [1–4].

Ion exchange of a specific cation is strongly influenced by complexing reagents such as anions [5]. Very large inorganic complexes may be mechanically excluded by sieve action. Such exclusion occurs if the openings in the zeolite matrix are too narrow to accommodate the incoming ion. The relative strength of the complex controverts then the attraction strength of the exchange site. On the other hand, the stronger the complexes and the higher the concentration of the free anion, the larger is the fraction of the cation present in the form of complexes of lower positive or even of negative charge, and thus the exchanger affinity for the cation is lowered.

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It is expected that in municipal and industrial wastewater, where the complexity of the system is high, several anions could influence the removal of specific target metals. It is well known that transition metals can form stable complexes due to their electronic structure [6]. It is true that Fe^{3+}, Cr^{3+} and Cu^{2+} can form stable and charged complexes with water molecules, inorganic anions and NH_4^+. It is obvious then that the heavy metal species found in wastewater can be present in various ionic forms and these species may influence the ion exchange process.

Ion exchange behavior of Na-clinoptilolite towards Ni^{2+} in the presence of Cl^-, SO_4^{2-} and NO_3^- was investigated and the exchange process was influenced by the presence of anions, following the order $Cl^- > SO_4^{2-} > NO_3^-$ [7]. However, these results were not attributed to complex formation, but to the solution non-ideality. On the other hand, the relatively poor removal of Ni^{2+} and Hg^{2+} by several zeolites, including clinoptilolite, has been attributed to the high stability of the respective aqueous complexes and to the strong coordination of Cl^- around the central Hg^{2+} ion [8]. Cr^{3+} complexes with water or chloride ions are strong and big enough, hence the majority of these ions are excluded from the clinoptilolite micropores, where the exchange sites of the material are located [9].

Finally, research has focused on the formation of precipitates in zeolite pores or surface, leading to pore clogging [9–12]. The meso- and macropores as well as the irregular surface of the material could be considered as an appropriate environment for surface precipitation. Surface precipitation most probably reduces the ion-exchange ability of the zeolite due to the blockage of the micropores. For example, Cu^{2+} is forming $CuCl_2 \cdot 2Cu(OH)_2$, Ni^{2+} amorphous $NiCO_3$ and U^{2+}, Th^{4+}, Cu^{2+} and Zn^{2+} several hydroxides, due to hydrolysis, in clinoptilolite pores [11–13].

In the present study the effects of SO_4^{2-} and HPO_4^{2-} on ion exchange of Cu^{2+}, Fe^{3+} and Cr^{3+} on natural clinoptilolite is examined. The aim of the present work is to study the effects of complex formation on the ion exchange process and examine the ability of clinoptilolite to exchange complex forms of metal species and anions.

2. Experimental

2.1. Clinoptilolite samples

The mineral used was collected from the Metaxades deposit in the northern part of Greece. It was ground and sieved. Chemical composition was determined through SEM/EDS analysis: the samples were coated with graphite under vacuum and irradiated by a low-energy electron beam (250 eV), using the Jeol Scanning Microscope, model JSM-6100.

2.2. Ion exchange studies

Six grams of clinoptilolite particles in size of 1.4–1.7 mm and 100 ml portions of heavy metal solution were placed in a suitable container under normality of 0.01 N, and temperature of 25 ± 2 °C. For all metal solutions nitric salts were used. In Table 1 the composition of the test solutions is

Table 1
Test solutions and corresponding concentrations (g/m^3)

No	Solution[a]	C_o (anion)	C_o (metal)
1	$Cu(NO_3)_2 + KNO_3$	1220 (NO_3^-)	310
2	$Cr(NO_3)_3 + KNO_3$	1220 (NO_3^-)	170
3	$Fe(NO_3)_3 + KNO_3$	1220 (NO_3^-)	182
4	$Cu(NO_3)_2 + K_2SO_4$	610 (NO_3^-) + 480 (SO_4^{2-})	310
5	$Cu(NO_3)_2 + K_2HPO_4$	610 (NO_3^-) + 480 (HPO_4^{2-})	310
6	$Cr(NO_3)_3 + K_2SO_4$	610 (NO_3^-) + 480 (SO_4^{2-})	170
7	$Cr(NO_3)_3 + K_2HPO_4$	610 (NO_3^-) + 480 (HPO_4^{2-})	170
8	$Fe(NO_3)_3 + K_2SO_4$	610 (NO_3^-) + 480 (SO_4^{2-})	182
9	$Fe(NO_3)_3 + K_2HPO_4$	610 (NO_3^-) + 480 (HPO_4^{2-})	182

[a] Common concentration of K^+ equal to 390 g/m^3.

presented. The test solutions 4–9 were prepared using the appropriate quantity of potassium salt (K_2SO_4/K_2HPO_4) which was dissolved in the metal-containing solutions. To examine the effect of the anions (SO_4^{2-}/HPO_4^{2-}), anion-free solutions were prepared (solutions 1–3). All solutions were prepared in such a way to contain a potassium concentration of 0.01 N in order to avoid the effect of the competitive exchange of K^+. Anion-free solutions were prepared using potassium nitrate since nitrate anions are not forming precipitates or complexes with the corresponding metals and are considered to be inert [14]. Finally, a series of blank zeolite-free solutions were used in order to examine the possible precipitation of metals in the presence of SO_4^{2-} and HPO_4^{2-} in solutions.

The solutions were acidified to avoid precipitation of hydroxides with HNO_3, at pH 2 ± 0.1. After ion exchange the pH of the filtrates was measured to be in the range of 2.23–2.49 for all test solutions.

After the preparation of the samples the mixtures were equilibrated for four days. At the end of this period the final pH was recorded. The solutions were separated from solid phases by centrifugation (4000 rpm/10 min) before chemical analysis. Heavy metal concentrations were measured by atomic absorption spectrometry (AAS), using a Perkin Elmer model 350B spectrophotometer. The corresponding wavelengths/slit settings were 283 nm/0.7 nm for Pb^{2+}, 324.7 nm/0.7 nm for Cu^{2+}, 358 nm/0.7 nm for Cr^{3+} and 248 nm/0.2 nm for Fe^{3+}. Hollow cathode lamps and air-acetylene flame were used.

SO_4^{2-} were measured by nephelometry using a HACH 2100P nephelometer and HPO_4^{2-} by UV–vis spectrophotometry using a Camspec Spectrophotometer and 470 nm wavelength [15].

All experiments were repeated three times. The standard error was 3.5% for metal concentration and 13% for anion concentration measurements.

3. Results and discussion

3.1. Clinoptilolite samples

In Table 2 the chemical composition of natural clinoptilolite is presented.

Table 2
Chemical composition of natural clinoptilolite

Oxide	% w/w
SiO_2	66.5 ± 0.8
Al_2O_3	12.8 ± 1.3
Na_2O	1.2 ± 0.4
K_2O	1.4 ± 0.3
CaO	2.7 ± 0.6
MgO	1.5 ± 0.2
FeO	1.2 ± 0.4
H_2O[a]	12.1 ± 0.2

[a] Water content was measured by complete dehydration of the original material.

According to the chemical analysis, the theoretical or maximum exchange capacity of the material is 2.62 ± 0.26 meq/g, calculated as the sum of Mg, Ca, K and Na cations [16,17]. The ratio Si/Al is 4.29 (mol/mol) and the corresponding ratio of (Na + K)/Ca is 1. The chemical composition and the ratio Si/Al, generally ranging from 4 to 5.5, are typical for clinoptilolite [1].

3.2. Ion exchange studies

In Fig. 1 the percent metal removal is presented. It can be seen that both SO_4^{2-} and HPO_4^{2-} lower metal uptake, for the three metals tested, with the possible exception for the system Fe^{3+}/HPO_4^{2-}. However, the blank solutions tested showed precipitation in the case of Fe^{3+}/HPO_4^{2-} solution, leading in a 99% removal of Fe^{3+} from solutions. The white precipitates formed are probably $FePO_4$
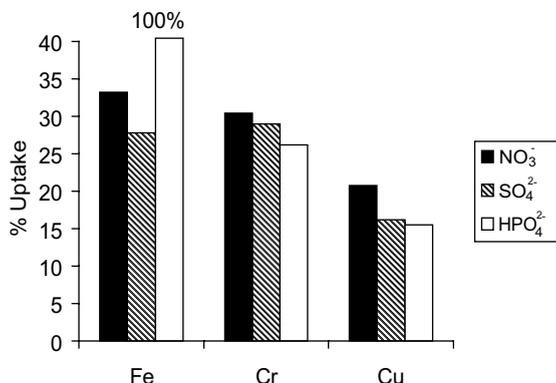

Fig. 1. % Metal removal on natural clinoptilolite after four days at pH 2, $T = 25$ °C and concentration $C = 0.01$ N.

and $Fe_2(HPO_4)_3$ [14]. In the absence of precipitation Fe^{3+}/HPO_4^{2-} case), the HPO_4^{2-} anions are found to have a stronger influence on the metal removal than SO_4^{2-} anions. The decrease in uptake is more pronounced for Cu^{2+} compared to Fe^{3+} and Cr^3. This effect is considered to be a result of metal–anion complex formation.

During cationic exchange using a resin between K^+ and Na^+ at high concentrations in the presence of Cl^- and SO_4^{2-} anions in solutions, an anionic exchange together with the cationic one was noticed. This process, considered as different from electrolyte sorption, was explained in terms of the retention of some ionic pair or ion complex formed in solution due to the high concentration [18].

In Table 3 anion removal and the respective decrease of metal removal (as calculated from Fig. 1) in the HPO_4^{2-} and SO_4^{2-}-containing test solutions with respect to the NO_3^--containing ones is presented. Anion co-removal is significant, especially for HPO_4^{2-} ions. It is known that common complex species formed in acidic solutions in the presence of Cu^{2+}, Fe^{3+}, Cr^3, SO_4^{2-} and HPO_4^{2-} ions are $[Cu(SO_4)]$, $[Cu(SO_4)_2]^{2-}$, $[Cu(SO_4)_3]^{4-}$, $[Cu-HPO_4]$, $[Cu(HPO_4)_2]^{2-}$, $[Cu(HPO_4)_3]^{4-}$, $[Fe-HSO_4]^{2+}$, $[FeSO_4]^+$, $[Fe(SO_4)_2]^{2-}$, $[FeHPO_4]^+$, $[Fe(HPO_4)_2]^-$, $[Cr(H_2O)_6SO_4]^+$, $[Cr(SO_4)_2]^{2-}$, $[Cr(OH)(SO_4)(H_2O)_3]$, $[CrHPO_4]^+$, $[Cr(OH)_3(H_2PO_4)]^-$ and $[Cr(OH)_3(HPO_4)]^{2-}$ [19–27]. The data in Table 3 are in accordance with these findings, since less positive, neutral and negative complex species should influence metal uptake and this effect should increase with a decrease of the effective charge.

Internal precipitation of metal–anion compounds is not considered to take place, due to the fact that in control solutions no such precipitates

Table 3
Anion removal and decrease of metal removal in test solutions

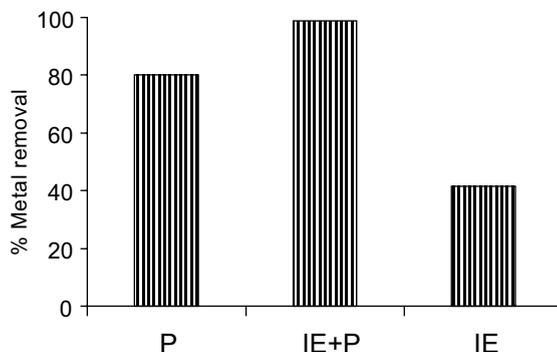| Couple	% Anion removal	% Decrease of metal removal
Cu–HPO$_4$	80	25
Cu–SO$_4$	61	22
Fe–SO$_4$	33	16
Cr–HPO$_4$	80	14
Cr–SO$_4$	15	5

Fig. 2. Metal removal for the case of Fe^{3+}/HPO_4^{2-} on natural clinoptilolite due to different removal patterns (IE: ion exchange, P: precipitation, IE + P: ion exchange and precipitation).

are formed, in the pH range of 2–2.5. However, removal of anions via adsorption, along with ion exchange of their complex form, could be a possible explanation and should not be rejected.

In Fig. 2 metal removal with respect to different removal patterns is presented, for the case of Fe^{3+}/HPO_4^{2-} solutions. As it can be seen, precipitation along with ion exchange (P + IE) is resulting in higher removal (99%) of Fe^{3+} from the solution than ion exchange (IE, 40%) or precipitation (P, 80%) alone. The observation that Fe^{3+} is better removed by precipitation alone than ion exchange is probably due to the relatively low selectivity of clinoptilolite for Fe^{3+} [28] and low K_{sp} value of $FePO_4$ ($pK_{sp} = 21.9$) [14]. Furthermore, precipitate dissolution is probably taking place in the presence of zeolite, along with some exchange of the anions in the metal-complex form. It is known that ion exchangers are able to dissolve slightly soluble solids, which dissociate enough to give traces of ions [5]. For example, calcium carbonate, lead sulfate and silver chloride can be dissolved using ion exchange materials, according to the following mechanism: The supernatant solution in the equilibrium with the slightly soluble solid contains a certain, though very small, amount of ions. The equilibrium between the solid and the dissolved ions is disturbed when the latter are removed from the solution by ion exchange, and re-established by further dissociation of the solid. In this way the precipitate can be completely dissolved, provided

that a sufficiently large excess of the ion exchanger is added.

4. Conclusions

In the present study the effect of SO_4^{2-} and HPO_4^{2-} on ion exchange of Cu^{2+}, Fe^{3+} and Cr^{3+} on natural clinoptilolite is examined. It is observed that mainly Cu^{2+} uptake is lowered in the presence of HPO_4^{2-} and SO_4^{2-}. The observed effect is less significant for Fe^{3+} and Cr^{3+} in the presence of SO_4^{2-} and HPO_4^{2-}, respectively. This could be explained by means of metal–anion complex formation. The stronger the cation–anion complexes and the higher the concentration of the free anion, the larger is the fraction of the complexing cation present in the form of complexes of lower positive or even of negative charge, and thus the affinity of exchanger for the cation is lowered. The observed effect is less significant for Fe^{3+} in the presence of SO_4^{2-}.

Blank solutions showed precipitation in the case of Fe^{3+}/HPO_4^{2-} solution, leading in complete removal of Fe^{3+} from solutions. Precipitation along with ion exchange is resulting in higher removal of Fe^{3+} from the solution than ion exchange or precipitation alone. The observation that Fe^{3+} is better removed by precipitation alone than ion exchange is probably due to the low selectivity of clinoptilolite for Fe^{3+}.

It is also clear that anion co-removal is significant, especially for HPO_4^{2-} ions. This can be explained by metal–anion complexing. However, anion adsorption, along with ion exchange of anion–metal complexes, should not be rejected. Finally, the possibility of removing anions such as SO_4^{2-} and HPO_4^{2-} using clinoptilolite and heavy metals as complexing agents seems realistic and could be further investigated.

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