

Use of an iron-overexchanged clinoptilolite for the removal of Cu^{2+} ions from heavily contaminated drinking water samples

M.K. Doula^{a,*}, A. Dimirkou^b

^a National Agricultural Research Foundation of Greece, Soil Science Institute of Athens, 1 Sof. Venizelou St., 14123 Lycovrisi, Greece

^b University of Thessaly, Department of Agriculture, Crop Production and Agricultural Environment, Soil Science Laboratory, N. Ionia 38446 Magnesias, Greece

Received 20 December 2006; received in revised form 14 April 2007; accepted 13 June 2007

Available online 17 June 2007

Abstract

Clinoptilolite, a natural zeolite, was used for the synthesis of a high surface area clinoptilolite–iron oxide system, in order to be used for the removal of Cu^{2+} ions from drinking water samples. The solid system was obtained by adding natural clinoptilolite in an iron nitrate solution under strongly basic conditions. The Clin–Fe system has specific surface area equal to $151 \text{ m}^2 \text{ g}^{-1}$ and is fully iron exchanged ($\text{Fe}/\text{Al} = 1.23$). Batch adsorption experiments were carried out to determine the effectiveness of the Clin and the Clin–Fe system in removal of copper from drinking water. Adsorption experiments were conducted by mixing 1.00 g of each of the substrates with certain volume of water samples contaminated with 10 different Cu concentrations (from 3.15×10^{-5} to $315 \times 10^{-2} \text{ M}$ or from 2.00 to 2000 ppm Cu). For our experimental conditions, the maximum adsorbed Cu amount on Clin was 13.6 mg g^{-1} whereas on the Clin–Fe system was 37.5 mg g^{-1} . The main factors that contribute to different adsorption capacities of the two solids are due to new surface species and negative charge of the Clin–Fe system. In addition, the release of counterbalanced ions (i.e. Ca^{2+} , Mg^{2+} , Na^+ and K^+) was examined, as well as the dissolution of framework Si and Al. It was found that for the most of the samples the Clin–Fe system releases lower concentrations of Ca, Mg and Na and higher concentrations of K than Clin, while the dissolution of Si/Al was limited. Changes in the composition of water samples, as well as in their pH and conductivities values were reported and explained.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Clinoptilolite; Clinoptilolite–Fe system; Cu adsorption; Water treatment; Water quality

1. Introduction

The contamination of water resources with heavy metals that can cause serious problems to human beings, to animals and to plants. For this reason numerous researchers work at present on this field and try to find the appropriate solution for each specific aquatic system. Because the elimination and the removal of toxic metals from water resources concentrate the researchers' interest, many different methods and technologies, such as chemical precipitation; ultra filtration; adsorption and ion-exchange; reverse osmosis; electrodialysis, have been tested and developed [1]. Owing to the fact that many of these methods

suffer from some drawbacks, such as high capital and operational costs and problem of disposal of residual metal sludge, many researchers have focused their studies on the synthesis and the use of low cost adsorbent materials to purify water contaminated with metals [1–4].

Zeolites have been widely used in heavy metals adsorption experiments [5] due to their unique physical and chemical properties (crystallinity, thermal stability, well-defined cage structure of molecular size, ion-exchange, etc.). Moreover, they have large specific surface area (SSA) and contain high concentrations of exchangeable cations, which give them high cation exchange capacity (CEC). The advantage of zeolites over resins, apart from their much lower cost, is their ion selectivity. Owing to zeolites structural characteristics and their adsorbent properties, they have been applied as chemical sieves, water softeners and adsorbents [6].

Recently, a very simple and low cost iron-overexchanged clinoptilolite system was synthesized and tested for its effec-

* Corresponding author at: 41 Karaiskaki Str., 13231 Petroupolis, Greece. Tel.: +30 210 5053455.

E-mail addresses: mdoula@otenet.gr (M.K. Doula), adimirkou@uth.gr (A. Dimirkou).

Table 1
Copper adsorption capacities of Clin and of the Clin–Fe system in the presence of KCl at different pH values

Substrate	Cu adsorption capacity (mg g^{-1})		
	$\text{pH}_{\text{KCl}} 2.97$	$\text{pH}_{\text{KCl}} 5.78$	$\text{pH}_{\text{KCl}} 10.12$
Clin	~ 0	7.30	22.0
Clin–Fe system	27.9	39.3	40.3

tiveness in removal of Mn^{2+} ions from drinking water [7] and in Cu^{2+} ions adsorption from KCl solutions with different pH values [8]. This Clin–Fe system has specific surface area equal to $151 \text{ m}^2 \text{ g}^{-1}$, which is almost five times higher than that of untreated clinoptilolite ($30.98 \text{ m}^2 \text{ g}^{-1}$). The experimental results obtained for the removal of Mn^{2+} ions from drinking water revealed that the Clin–Fe system has a noticeably higher Mn adsorption capacity (27.12 mg g^{-1}) than clinoptilolite (7.69 mg g^{-1}) and that, after the treatment with the Clin–Fe system, the water samples had significantly lower hardness because the new system acted simultaneously as water softening material.

In regard with the copper adsorption from KCl solutions [8] under different pH values (2.97, 5.78, and 10.12) the obtained results were also very interesting (Table 1). Copper adsorption was significantly higher for the Clin–Fe system than for untreated clinoptilolite. Owing to the presence of various Fe formations in internal and external positions of Clin, the Clin–Fe system has higher specific surface area and thus, higher adsorption capacity than untreated Clin. As it was shown [8] the Clin–Fe system has also high negative surface charge and this is probably the reason for the adsorption of Cu under acidic conditions ($\text{pH}_{\text{KCl}} = 2.97$). Due to its negative surface charge the Clin–Fe system adsorbed from the acidic solution not only copper ions but also large quantity of H^+ ions stabilizing the solution pH at the basic region. Adsorption of Cu under this pH value was not detected for untreated clinoptilolite.

In the following, we synthesize again this Clin–Fe system in order to test it in removal of Cu^{2+} ions from contaminated drinking water samples.

2. Materials and methods

2.1. Clinoptilolite

The clinoptilolite used in the present investigation comes from a layer situated in Thrace (North Greece). This material has been used in the past for metal adsorption experiments [5,9,10] and consequently its physicochemical properties are well known. The estimated cation exchange capacity (C.E.C.) of Clin, with respect to its formula ($\text{Na}_{0.2}\text{K}_{0.6}\text{Mg}_{0.7}\text{Ca}_{2.0}\text{Al}_{6.2}\text{Si}_{29.8}\text{O}_{72} \cdot 19.6\text{H}_2\text{O}$), is 2.35 mequiv. g^{-1} . The powder XRD study showed that zeolite, feldspars and total micas + clays are present through the tuff whereas, the clinoptilolite used in the present study comes from the layer with the higher clinoptilolite content (up to 90%). Its specific surface area (SSA) is equal to $30.98 \text{ m}^2 \text{ g}^{-1}$ and the average pore diameter is $<20.0 \text{ \AA}$ [5].

Before the synthesis of the new system as well as, the adsorption experiments the zeolite was finely ground and sieved to $<0.02 \text{ mm}$.

2.2. Clinoptilolite–Fe oxide system

The Clin–Fe system was synthesized by following the method of pure goethite preparation, as described by Schwertmann and Cornell [11]. The change made in this study concerns the presence of clinoptilolite, which was added in the experimental flasks.

The system was prepared by mixing 20.0 g of clinoptilolite, 100 ml of freshly prepared 1 M $\text{Fe}(\text{NO}_3)_3$ solution, and 180 ml of 5 M KOH solution in a 2 l polyethylene flask. The addition of KOH solution was rapid and with stirring. The suspension was diluted to 2 l with twice distilled water and was held in a closed polyethylene flask at 70°C for 60 h. After the appropriate period the reaction vessel was removed from the oven, and the precipitate was centrifuged, washed (until free of NO_3^- ions) and finally dried.

After the 60-h period a dark red precipitate was obtained. The specific surface area of the Clin–Fe system is $151 \text{ m}^2 \text{ g}^{-1}$ and the average pore diameter is $\leq 20.0 \text{ \AA}$.

Spectroscopic methods (XRD, EPR, FTIR and TG/DSC) were used for the characterization of the Clin–Fe oxide system and were fully detailed elsewhere [8,12].

Elemental analysis of the Clin–Fe system revealed that it contains 14.1% Fe as amorphous iron species. Its Si/Al ratio is almost equal to the respective ratio of the parent material, and its Fe/Al ratio is equal to 1.23, meaning that the material is fully iron exchanged as well as, it contains an additional fraction of Fe ions that do not act as charge balancing species.

2.3. Water sample

The water sample used comes from the Athens drinking water network and its physicochemical analysis is shown in Table 2.

The concentrations of Na and K were measured by using a Korning 410 flame photometer, while, Si and Al by using a Varian Liberty 220 ICP emission spectrometer. Ca and Mg were volumetrically determined and from these two concentrations the value of sample hardness (in ppm CaCO_3) was estimated.

2.4. Stock copper solutions

Ten stock copper solutions from 40 to 40,000 ppm were prepared by dissolving $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in twice distilled water. Their pH values ranged from 5.56 to 3.08, whereas their conductivities from $157 \mu\text{S cm}^{-1}$ to 80.8 mS cm^{-1} .

2.5. Cu^{2+} adsorption experiment

The adsorption experiment was divided into two stages. Firstly, several samples of 1.00 g of each solid were equilibrated with 95.0 ml of water sample (referred to as “equilibrium period”). This period lasted for 48 h and after this period the sample pH values were measured.

Table 2
Chemical analysis results of water samples before and after their contact with Clin and the Clin–Fe system

	pH	Cond. ^a	Ca	Mg	K	Na	Si	Al	Hardness ^b
Water ^c	7.80	275	7.73×10^{-4}	2.70×10^{-4}	≈0	1.80×10^{-4}	2.97×10^{-5}	1.05×10^{-5}	104
Clin	7.53	293	8.40×10^{-4}	2.78×10^{-4}	4.00×10^{-5}	5.00×10^{-4}	3.36×10^{-4}	1.10×10^{-5}	112
Clin–Fe	8.14	395	1.48×10^{-4}	9.09×10^{-5}	2.86×10^{-3}	2.51×10^{-4}	8.16×10^{-5}	2.41×10^{-6}	23.9

The concentrations of Ca, Mg, Na, K, Si, and Al are in mol l⁻¹.

^a Conductivity in $\mu\text{s cm}^{-1}$

^b In ppm CaCO₃.

^c Water samples before treatment.

Chemical analysis was carried out for some of these equilibrated water samples in order to verify the changes caused by the contact with the adsorbents, as well as to verify the exact solution composition before the addition of the Cu²⁺ solutions.

During the second experimental stage (referred to as “Cu adsorption”) 5.00 ml of each of copper stock solutions were added to the above-mentioned samples, at concentrations such that the total mixture contained 0, 3.15×10^{-5} , 7.87×10^{-5} , 1.58×10^{-4} , 3.15×10^{-4} , 7.87×10^{-4} , 1.58×10^{-3} , 3.15×10^{-3} , 7.87×10^{-3} , 1.58×10^{-2} and 3.15×10^{-2} mol l⁻¹ Cu (or 0, 2.00, 5.00, 10.0, 20.0, 50.0, 100, 200, 500, 1000 and 2000 ppm Cu). The samples at this second stage were equilibrated for 48 h, were centrifuged for 10 min at 15,000 rpm and then their pH values and their conductivities were measured. Copper concentrations were measured in the liquid phase by using a SpectrAA 300 Varian flame atomic spectrometer. The concentrations of adsorbed Cu species were calculated from the difference in measured and initial concentrations of the species in solution. The solution concentrations of Ca, Mg, Na, K, Si and Al were also measured.

All experimental stages took place in triplicate, in a water bath at constant temperature (25 °C), and under a N₂ atmosphere by placing the water bath in a glove box. The relative standard deviations (R.S.D.) for concentration and pH measurements were 0.8 and 2.1%, respectively.

3. Results and discussion

3.1. Equilibrium period

During the equilibrium period the chemical composition of the water samples was changed due to their contact with Clin and Clin–Fe system, as reported in Table 2.

The two substrates changed the composition of the water samples; however the characteristics of these changes were different. The solution concentrations of Ca²⁺, Mg²⁺, Na⁺, K⁺ and framework Si/Al were slightly increased when Clin was used as a substrate. Especially for Na⁺ ions, the increase in their solution concentration is mainly due to the dissolution of zeolites impurities, but also due to ion-exchange process. The limited release of Ca, Mg and K was assumed to occur through ion-exchange reactions, mainly between these surface cations and water molecules as well as with Na⁺ ions from impurities dissolution. Generally, this pro-

cess is a dynamic one and occurs when aluminosilicates materials, such as clinoptilolite, are embedded in aquatic solutions.

The motion of Si and Al, which are framework cations, from the substrate toward solution is a solid dissolution process and can cause a defect to zeolite framework structure and contamination of water samples [13,14].

The new system not only retains its Ca and Mg but also adsorbs these ions from the solution, decreasing so the total hardness of the samples. Na⁺ release as well as the dissolution of Si and Al is also limited. The solution concentration of K⁺ ions is increased due to the dissolution of K⁺ ions deposited on Clin–Fe sites during the synthesis procedure, as it will be better explained in the following. However, despite this process, the new system uses its available active sites to retain Ca and Mg from solution, as well as water molecules. After the equilibration all the samples, treated with the Fe–Clin system, were characterized by basic pH, whereas the final solutions pH values for Clin samples were stabilized at 7.53. The increase in solution pH corresponds to H⁺ adsorption, whereas the decrease in solution pH corresponds to H⁺ release. By considering that the new system adsorbs larger H⁺ amounts, as well as experimental data from previous adsorption experiments [7] we conclude that the negative surface charge of the Fe–Clin system is higher than that of Clin.

Because the K⁺ released concentrations are higher than the retained concentrations of the other cations, a final increase in samples conductivity values were measured for the Clin–Fe system.

3.2. Cu²⁺ adsorption

Copper adsorption by the two substrates was examined by using extent range of Cu initial concentrations. The concentrations used were exceedingly higher than the quality standard of 2.00 ppm (3.15×10^{-5} M) for drinking water (EU Directive 98/83/EK), but the aim of the study was to test the adsorption abilities and capacities of the two substrates under extreme conditions.

Fig. 1 presents the adsorbed Cu amounts in relation to the solution Cu concentrations and Fig. 2 the percentage of adsorbed Cu concentrations for both substrates. It seems that Clin and the Clin–Fe system retain almost the entire Cu concentration from the contaminated water samples when the initial metal concentration is lower than 100 ppm. For Cu concentrations

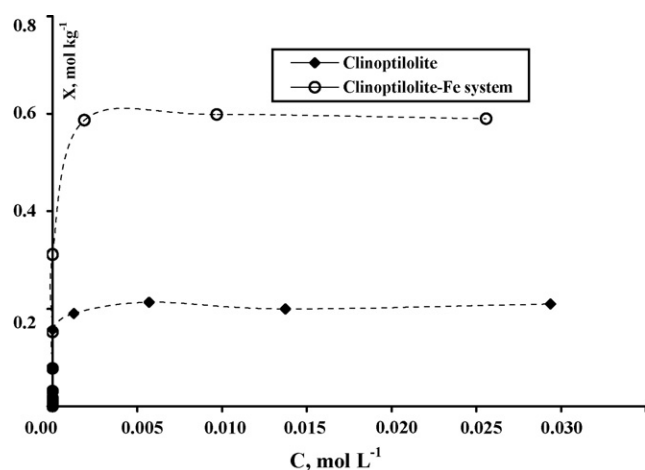


Fig. 1. Adsorbed Cu concentrations (X) in relation to solution Cu concentrations (C) for all samples treated with Clin and the Clin–Fe system.

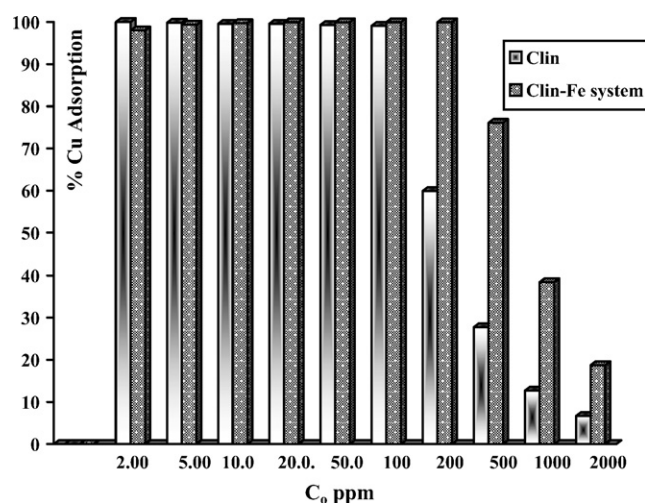


Fig. 2. Percentage adsorption of Cu for Clin and for the Clin–Fe system.

higher than 100 ppm the Clin–Fe system can adsorb significantly larger Cu amounts than its parent material although the percentage of adsorption is gradually decreased for both substrates. This behavior was also revealed from the experimental data of Fig. 1; the samples, with initial Cu concentrations within 2.00 and 200 ppm, which were treated with the Clin–Fe system had

final Cu solution concentrations lower than 2.00 ppm. On the contrary, for the treatment with Clin only the samples with initial Cu concentrations lower than 50.0 ppm had accepted final Cu solution concentrations.

However, clinoptilolite has a satisfactory adsorption behavior and is capable to adsorb Cu^{2+} species from the contaminated samples. The graph of Fig. 1 consists of two regions. In the first, the amount of adsorbed Cu increases gradually up to 0.21 mol kg^{-1} (13.6 mg g^{-1}). The second is a plateau region where Cu adsorption is almost constant. This specific concentration value is considered as the maximum Cu adsorption capacity of clinoptilolite under our experimental conditions. The maximum percentage adsorption of Cu reaches almost 100%, while the lowest is 6.67%.

A two-region graph with a plateau characterizes also the adsorption of Cu by the Clin–Fe system. Its adsorption capacity is equal to 0.59 mol kg^{-1} (37.5 mg g^{-1}) which is almost three times higher than that of Clin.

The adsorption of the Clin–Fe is also higher than that of other natural materials, as they presented in literature; Namontmorillonite has Cu capacity equal to 3.04 mg g^{-1} [2]; clinoptilolite from Western Anatolia has capacity 8.96 mg g^{-1} [1]; sepiolite has 6.90 mg g^{-1} [15]. There are of course materials, mainly synthetic, which have higher Cu capacity than that of the Clin–Fe system, for example zeolite 4A has capacity 49.9 mg g^{-1} and resin Valfor 100 has 51.1 mg g^{-1} [16].

The differences in chemical behavior; in adsorption of Cu^{2+} ions, in counterbalanced ions release and in Si/Al dissolution of the two substrates are owed to the different surface species, which are located on the two substrates. The new material, due to the presence of the Fe oxides located in the zeolite channels or on its external sites, is characterized by the presence of additional active sites ($-\text{Fe}-\text{OH}$), which are influenced by the solution pH and are potential adsorption sites [17]. Owing to the presence of non-crystalline Fe formations located in cationic positions in the zeolite channels, of Fe binuclear and in general iron complexes in extra-framework positions, as well as of amorphous iron oxides FeO_x located at the surface of the zeolite crystal, the Clin–Fe system has higher SSA and thus, higher adsorption capacity than untreated Clin [18]. The higher adsorption detected for the Clin–Fe system is also due to its high negative surface charge [7].

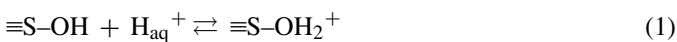
Table 3
Conductivities, pH and hardness values for all water samples treated with Clin and the Clin–Fe system after Cu adsorption

Co (ppm)	Clinoptilolite			Clinoptilolite–Fe system		
	pH	Conductivity ($\mu\text{s cm}^{-1}$)	Hardness (ppm CaCO_3)	pH	Conductivity ($\mu\text{s cm}^{-1}$)	Hardness (ppm CaCO_3)
2.00	7.62	294	109	8.64	428	42.2
5.00	7.62	284	108	8.63	410	37.0
10.0	7.40	304	116	8.51	427	44.1
20.0	7.10	323	120	8.45	471	51.3
50.0	6.53	384	135	8.14	595	85.8
100	5.89	490	150	7.73	786	136
200	5.34	816	161	6.92	1113	255
500	5.02	1812	164	5.41	1941	402
1000	4.89	3400	158	5.06	3490	415
2000	4.76	6240	164	4.87	6390	463

3.3. Conductivity and samples pH

Table 3 presents the conductivities and pH values for all water samples after Cu^{2+} adsorption experiment. For Clin all the samples have pH values between 4.76 and 7.62. The samples' conductivities maintain also low. Extremely high increase in samples conductivities was reported only for the three higher Cu concentrations. The range of solution pH values is wider for the Clin–Fe system than for untreated Clin; the higher pH value is 8.64 while the lower is 4.87. Moreover, all the samples treated with Clin have lower solution pH value than the samples treated with the Clin–Fe system. This different behavior is owed partly to the different surface species, which are located on the two substrates and partly to higher release of H^+ ions from the surface of the Clin–Fe system as a result of the higher Cu^{2+} adsorption (Eqs. (4) and (5)).

Generally, zeolites and zeolite systems tend to neutralize the solutions, acting either as proton acceptors or as proton donors, exhibiting thus an amphoteric character. During Cu adsorption process the H^+ ions participate in many reactions in the solution and in the solid phase. Hydrogen ions were added to the water samples along with Cu^{2+} solutions and their concentrations were increased as higher Cu^{2+} concentrations were used. These H^+ species together with those released from the surface (Eqs. (3)–(5)) as a result of surface reactivity (e.g. H^+ exchange, surface complexation), participate in a lot of solution and surface processes. They are capable to provoke surface protonation (Eqs. (1) and (2)) but also to affect all reactions in which H^+ or OH^- are involved:



where S corresponds to the surface central metal (i.e. Si and Al).

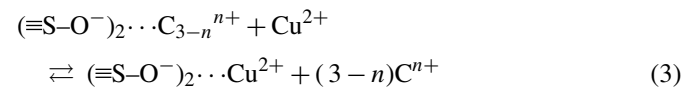
By considering the decrease in solution pH values for both substrates, we could conclude that the two solids release H^+ during Cu adsorption experiments. However, after the appropriate

calculations, and by considering the concentration of H^+ in equilibrated solutions (before and after adsorption), as well as the concentration of H^+ added along with Cu stock solutions [9] it was confirmed that both substrates adsorbed H^+ from solutions. Thus, the continuous decrease in solution pH values is owed to the continuous increase in H_{aq}^+ by external addition. By trying to neutralize the surrounding environments the two solids adsorb H^+ ions from solutions and despite the final decrease in solution pH values, the calculations proved that the predominant process is the adsorption of H^+ .

Especially for the Clin–Fe system, it was calculated that it adsorbs larger amounts of H_{aq}^+ than Clin for all Cu concentrations due to its higher negative surface charge, as it was confirmed also from our previous work [7,8].

3.4. Movement of counterbalanced ions

Figs. 3 and 4 present the amounts of Ca^{2+} , Mg^{2+} , Na^+ and K^+ (in equiv. l^{-1}) released during Cu adsorption, as a function of initial Cu concentrations. They also present the overall release of positively charged ions from the two adsorbents, as well as the overall adsorption of positively charged ions (i.e. H^+ and Cu^{2+}). During adsorption stage, release of the counterbalanced Ca^{2+} , Mg^{2+} , Na^+ and K^+ ions takes place, partly as a consequence of Cu^{2+} adsorption. The retention of Cu^{2+} is undoubtedly the process, which determines and forces directly and indirectly the release of counterbalanced ions. Cu^{2+} species can occupy the exchangeable sites of counterbalanced ions through an ion-exchange process and can form outer-sphere complexes [13]:



where C is the counterbalanced ion with charge $n+$ ($n=+1$ or $+2$).

But metals can also form inner-sphere complexes with surface sites. During inner-sphere complexation, hydrogen ions are

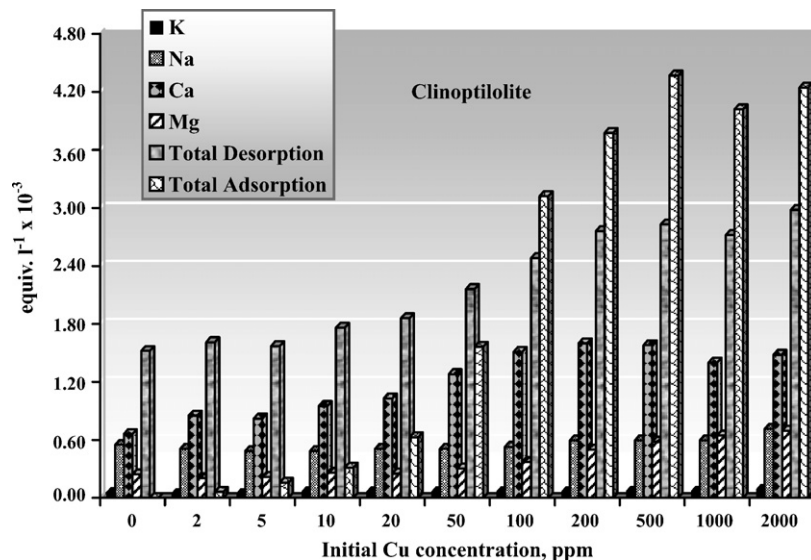


Fig. 3. Concentrations of released Na^+ , Mg^{2+} , Ca^{2+} and K^+ ions, total adsorbed cations (H^+ and Cu^{2+}) and total desorbed cations during Cu adsorption by Clin.

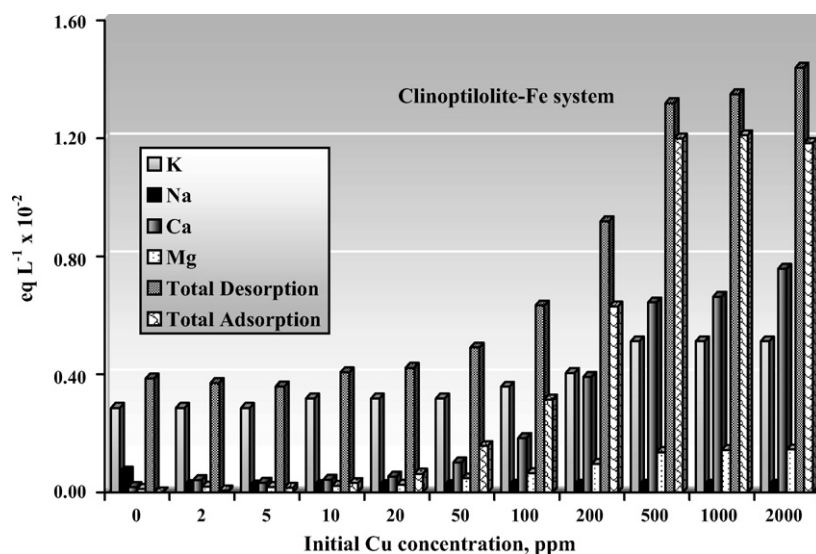
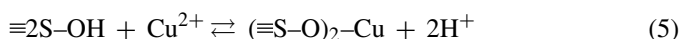
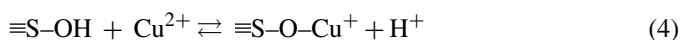


Fig. 4. Concentrations of released Na^+ , Mg^{2+} , Ca^{2+} and K^+ ions, total adsorbed cations (H^+ and Cu^{2+}) and total desorbed cations during Cu adsorption by the Clin–Fe system.

released as products, and the process causes a total decrease in solution pH [13]:



The results obtained from the release of Na^+ and K^+ ions during Cu adsorption are the same with those obtained during Mn adsorption experiments by the two solids [7]. Briefly, the released concentrations of Na^+ and K^+ maintain almost constant during Cu adsorption for all Cu initial concentrations and it is supposed that almost the entire concentrations of these ions were released during equilibrium stage and they do not participate in ion-exchange reactions. Owing to the impurities content of Clin, which are dissolved and enriched the solution with ions, the release of Na^+ ions is higher for Clin. Copper adsorption by the Clin–Fe is characterized by higher release of K^+ ions basically due to the synthesis procedure of this system: the Clin–Fe system was in contact for 60 h with a 5 M KOH solution and thus, high concentrations of this ion were deposited on system sites, which are dissolved mainly during equilibrium stage but also during adsorption. Only for Cu concentrations higher than 100 ppm the release of K^+ ions follows the increase in Cu adsorption (Fig. 4).

The observation that the concentrations of K^+ and Na^+ ions do not significantly vary as a function of Cu adsorption is evidence that they neither influence nor are affected by the adsorption of Cu. This specific behavior of K^+ and Na^+ ions influences also the relation between released and retained equivalents of positive charges which is not stoichiometric (Eqs. (3) and (4)).

For Cu initial concentrations lower than 100 ppm the release of both Ca^{2+} and Mg^{2+} is higher from the surface of Clin than from the surface of the Clin–Fe system. Owing to this limited release the samples treated with the Clin–Fe system have significantly lower values of hardness (Table 3) than the samples treated with Clin, although the two substrates had almost the same behavior in Cu adsorption. For Cu concentra-

tions > 100 ppm the release of Ca^{2+} and Mg^{2+} is increased for the samples treated with the Clin–Fe system with simultaneous increase in the values of samples hardness, although this increase is not noticeably high. The reason for the increase in release of Ca and Mg is the increase in adsorbed Cu concentrations. By increasing initial Cu concentrations, the two solids are forced to adsorb even higher metal concentrations. Clin does not respond satisfactory to this demand whereas, the Clin–Fe system succeeds to adsorb even larger Cu concentrations by simultaneous increase in Ca and Mg release.

Ion-exchange process is more likely to predominate for both substrates when initial concentration of Cu is lower than 7.87×10^{-4} M (or 50.0 ppm) and the release of Ca^{2+} and Mg^{2+} is higher than adsorbed Cu concentrations. When Cu concentration becomes higher than 50.0 ppm the amounts of released Ca and Mg are lower than the adsorbed amounts of Cu. Especially for Clin and $\text{C}_{\text{Cu}} > 100$ ppm, the total adsorbed Cu concentrations are significantly higher than the total amounts of desorbed cations (including K^+ and Na^+ ions). On the contrary, for the Clin–Fe and the same concentration range, the total adsorbed Cu concentrations are higher than the sum of released Ca and Mg concentrations. This observation is probably an indication that Cu ions form inner-sphere complexes with Clin, while the extent of ion-exchange reactions between Cu and the sites of the Clin–Fe are wider than the respective with the sites of Clin. Nevertheless, the fact that the inner-sphere complexation is more obvious for Clin and for high Cu concentrations does not exclude the formation of such complexes for lower Cu concentrations and for both substrates.

By considering that K^+ and Na^+ ions do not significantly affect the adsorption, one concludes that except ion-exchange between Cu^{2+} ions and $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions, there is also another type of Cu retention on system's surface. Thus, it is possible that Cu ions form inner-sphere complexes with surface sites as described by Eqs. (4) and (5).

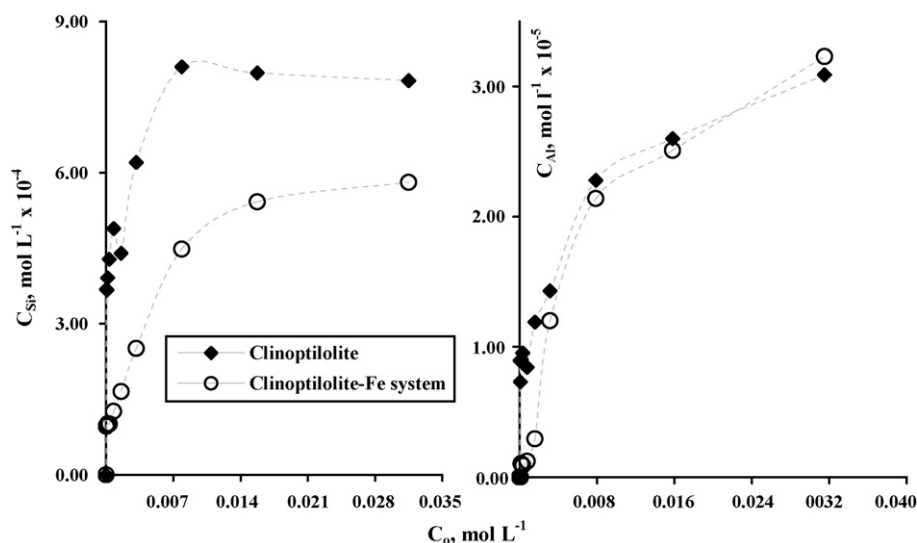


Fig. 5. Dissolution of framework Si and Al for Clin and the Clin–Fe system vs. Cu^{2+} initial concentrations.

The release of Mg^{2+} ions is almost constant for Clin, although there is a slight increase in Mg solution concentration as Cu retention becomes higher. On the contrary, the release of Ca^{2+} is noticeably high for Clin and it seems that the increase in its presence in equilibrated solutions is affected by Cu adsorption. For the Clin–Fe system the release of Ca and Mg is low for low Cu concentrations and increase gradually with the increase in Cu adsorption and in Cu initial concentration.

The dissolution of zeolite framework can also affect and control the presence of Ca and Mg (but also of other cations) in solutions. Under specific experimental conditions Si and Al from the framework move toward solution, and this process is characterized as dissolution and depends mainly on the solution pH, on the extent of surface protonation and on the nature of solution ions [13]. Generally, the dissolution of framework Si and Al causes the local distraction of the framework and the release of more counterbalanced cations. Fig. 5 presents the concentrations of Si and Al found in solutions after Cu adsorption. The dissolutions of Si is higher for Clin than for the Clin–Fe system, whereas the dissolution of Al is higher for low Cu initial concentrations and possibly the increased presence of Ca and Mg ions in solutions is owed to this difference in Al/Si dissolution.

4. Conclusions

The Clin–Fe system used for the adsorption of Cu from drinking water samples was synthesized by mixing clinoptilolite with aquatic solution of $Fe(NO_3)_3$ under strongly basic conditions (5 M KOH).

For one-round purification experiment and for the specific solid/sample ratio used (1/100) the results indicate that both Clin and the Clin–Fe system have a satisfactory adsorption behavior. Thus, for Cu initial concentrations lower than 100 ppm the two substrates adsorb almost the entire quantity of Cu species from solutions, however, the samples treated with the Clin–Fe system had significantly low hardness, and it seems that except the adsorption of Cu^{2+} ions, the Clin–Fe system acts simulta-

neously as water softening material. The adsorption of Cu is decreased for both solids as the initial concentrations of the metal are increased but this decrease is higher for Clin than for the Clin–Fe system.

For the experimental conditions used, the Cu adsorption capacity of Clin was 13.6 mg g^{-1} , while of the Clin–Fe was 37.5 mg g^{-1} .

The high Cu adsorption capacity of the Clin–Fe system is owed to Fe-clusters located on its surface, to high surface negative charge as well as, to its high specific surface area.

Despite the high adsorption of Cu^{2+} ions, the Clin–Fe system maintains the chemical parameters of the water samples to very satisfactory values. One should also point out that these results were obtained from only one-round sample treatment and one expects significantly better results from an integrated water treatment process.

The good behavior in adsorption experiments along with the fact that the Clin–Fe system is inexpensive, easily synthesized and regenerated and harmless for human beings, as well as for the environment could characterize it as a very promising metal adsorbent.

References

- [1] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, *J. Colloid Interf. Sci.* 280 (2004) 309–314.
- [2] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances, *Water Res.* 37 (2003) 1619–1627.
- [3] L.M. Bosco, R.S. Jimenez, W.A. Carvalho, Removal of toxic metals from wastewater by Brazilian natural scolecite, *J. Colloid Interf. Sci.* 281 (2005) 424–431.
- [4] A. Jusoh, W.H. Cheng, W.M. Low, A.N. Aini, M.J.M.M. Noor, Study on the removal of iron and manganese in groundwater by granular activated carbon, *Desalination* 182 (2005) 347–353.
- [5] M. Doula, A. Ioannou, A. Dimirkou, Copper adsorption and Si, Al, Ca, Mg and Na release from Clinoptilolite, *J. Colloid Interf. Sci.* 245 (2002) 237–250.
- [6] H. Ghobarkar, O. Schaf, U. Guth, Zeolites—from kitchen to space, *Prog. Solid State Chem.* 27 (1999) 29–73.

- [7] M. Doula, Removal of Mn^{2+} ions from drinking water by using clinoptilolite and a clinoptilolite–Fe oxide system, *Water Res.* 40 (2006) 3167–3176.
- [8] M. Doula, Synthesis of a clinoptilolite–Fe system with high Cu sorption capacity, *Chemosphere* 67 (2007) 731–740.
- [9] M. Doula, A. Ioannou, The effect of electrolyte anion on Cu adsorption–desorption by clinoptilolite, *Microporous Mesoporous Mater.* 58 (2003) 115–130.
- [10] V.J. Inglezakis, M.M. Loizidou, H.P. Grigoropoulou, Ion exchange studies on natural and modified zeolites and the concept of exchange site accessibility, *J. Colloid Interf. Sci.* 75 (2004) 570–576.
- [11] U. Schwertmann, R.M. Cornell, *Iron Oxides in the Laboratory, Preparation and Characterization*, VCH Verlags-gesellschaft mbH, Germany, 1991.
- [12] M. Doula, Heavy metals adsorption onto inorganic colloids (zeolites), Ph.D. Thesis, National Kapodistrian University of Athens, Athens, Greece, 2003.
- [13] W. Stumm, *Chemistry of the Solid–Water Interface*, J. Wiley & Sons Inc., New York, 1991.
- [14] E.H. Oelkers, I. Schott, Experimental study of anorthite dissolution and the relative mechanism of feldspar hydrolysis, *Geochim. Cosmochim. Acta* 59 (1995) 5039–5053.
- [15] A. García-Sánchez, A. Alastuey, X. Querol, Heavy metal adsorption by different minerals: application to the remediation of polluted soils, *Sci. Total Environ.* 242 (1999) 179–188.
- [16] K.S. Hui, C.Y.H. Chao, S.C. Kot, Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash, *J. Hazard. Mater. B* 127 (2005) 89–101.
- [17] R.M. Cornell, U. Schwertmann, *The Iron Oxides, Structure, Properties, Reactions, Occurrence and Uses*, VCH Verlags-gesellschaft mbH, Germany, 1996.
- [18] J. Pérez-Ramírez, G. Mul, F. Kapteijn, J.A. Moulijn, A.R. Overweg, A. Doménech, A. Ribera, I.W.C.E. Arends, Physicochemical characterization of isomorphously substituted FeZSM-5 during activation, *J. Catal.* 207 (2002) 113–126.