

The investigation on cationic exchange capacity of zeolites: The use as selective ion trappers in the electrokinetic soil technique

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Abstract

The cation exchange capacity (CEC) of porous zeolites allows to adsorb in the framework cavities the cations as pollutant heavy metal ions. We investigate the CEC behaviour of different zeolites in different experimental conditions; in solution where the ion's mobility is spontaneous and free and in the electrokinetic system where the ion's mobility is driven by the electric field. The aim of this study is to investigate if the CEC is a useful property to create a special interface region of zeolites, that if placed in the electrokinetic cell, just before the cathode, could allow to capture and concentrate the heavy metallic ions, during their migrating process. The zeolite 13X investigated in the electrokinetic proofs, retains a good high ions adsorption, even if quite smaller than the relevant free solution condition and well acts as confined trap for the heavy metal ions. In fact no trace of metallic deposition are present on the electrode's surface.

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1. Introduction

1.1. Background of the zeolite

Zeolites, in a narrow definition, are porous crystalline aluminosilicate having an uniform pore structure and exhibiting an ion-exchange behaviour. The zeolites are characterized by:

- three-dimensional and regular framework,
- channels and cavities with molecular sizes which can host the charge-compensating cations, and water molecules.

One of the peculiar characteristic of the zeolite is the ion-exchange capacity defined as the capacity to locate specific cations in the framework of zeolites.

The ion-exchange capacity of a zeolite depends on the chemical composition and varies with the structure of the zeolite and with the cation nature. The CEC (cation exchange capacity) depends on the number of exchangeable positions and these values depend on the ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$.

1.2. The aim of our study

The aim of this study is to investigate and to measure the CEC of different zeolites in different experimental conditions; first of all in solution where the ion's mobility is spontaneous and free and then in the electrokinetic system where the ion's mobility is induced by the electric field. In the aqueous systems the cations adsorption depends on the charge density and the reticular structure of the zeolite's framework, and comes from the size and charge of the cations. Afterwards, we have followed the CEC changes in the electrokinetic process where the ion's mobility is induced by electric field and where the mechanism that controls this process could influence the adsorption capacity. The CEC of zeolites are an useful property in the electrokinetic process? It is possible use these selective porous materials to create a special interface region, that if placed in the electrokinetic cell, could allows to locate and to concentrate the heavy metallic ions. In this paper, we investigated the zeolite's CEC behaviour of copper ions.

1.3. Background of the electrokinetic process

The electrokinetic soil remediation is a well-established decontamination technique for removal of heavy metals from

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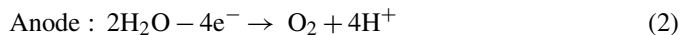
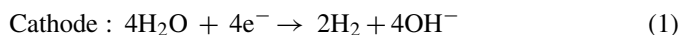
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polluted sites. This method aims to remove heavy metallic contaminants from low permeability contaminated soils under the influence of an applied direct current. When dc electric fields are applied to contaminated soils via electrodes placed into the ground, migration of charged ions occurs. The interest for the electrokinetic process is based on the proper nature of the “in situ” remediation technology.

The main mechanisms, that control the electrokinetic process, [1–3] are electroosmosis, electromigration, electrophoresis and diffusion. Electroosmosis [3,4] in water-saturated soil is the movement of water relative to the soil under the influence of an imposed electric gradient, i.e. the net movement of pore water from the anode to the cathode. Electromigration is the transport of ions to the electrode of opposite charge. Electrophoresis is the transport of charged particles or colloids under the influence of an electric field.

The contaminant transport due to the electromigration is one to two order greater than the contaminant transport due to the other mechanisms, therefore, electromigration is considered the dominant transport mechanism for ionic species.

An important aspect of this method is the presence of water in the soil that can facilitate the ion migration. At the cathode, negative electrode, the reduction of water's molecule produce hydroxyl ions and hydrogen gas. At the anode, positive electrode, occurs the oxidation of water with development of oxygen gas and production of protons H^+ . The protons travel through the phase toward the cathode. The metallic positive ions present in the medium are attracted to the negatively charged cathode, and travel through the medium transported by electric field.



So at the cathode, the metallic ions migrating under the electric field are reduced in neutral form. (Eq. (3))



So, the extraction and removal of heavy metal contaminants occurs by the electrodeposition of the metal on the cathode.

Many authors [5,6] support that positioning the electrodes directly into soil is the method to have most reliable and effective results. This is an open controversy object of many studies.

2. Experimental section

The cation exchange capacity (CEC) of the 13X, 5A and CBV-100 zeolites, was estimated following the procedure that involved the equilibration of zeolites, 6.6 g portions, with 250 mL of 0.24 M solutions prepared with different copper salts.

The process was followed for 7 h or 24 h with constant stirring at room temperature. The amount of copper, captured in the zeolites, was measured dissolving the crystalline material in HF 10% v/v. The dissolution was taken for 10 min at room temperature, followed by HF solution evaporation at 70 °C till the completed drying process. After the acid's evaporation the sample was ready for the AAS measurements. The AAS instrument is a Shimadzu AA 6300 with deuterium background correction. We carried out flame analyses. The residual copper in solution was also checked by AAS.

To investigate the behaviour of the zeolite slice in the electrokinetic remediation we used a home-built electrochemical cell of polycarbonate acid-proof polymer. The dimension of cell used for the aqueous experiments are: length 20 cm, width 13 cm and height 15 cm. The cell is equipped with two graphite dish-shaped electrodes with a diameter of about 6 cm. For the simulated soil experiments we used a more little cell, whose dimensions are length 12 cm, width 4.5 cm and height 13 cm.

The electrokinetic cell used in the experiments is shown in Fig. 1.

A home-built slice of fine nylon net, filled of specific zeolites is the cationic confining slice (about 1 cm thin) In the aqueous studies, each electrochemical process is performed with 2L of freshly distilled water solution of Cu^{2+} , containing 15 g/L of free Cu^{2+} ions. We used two different cop-

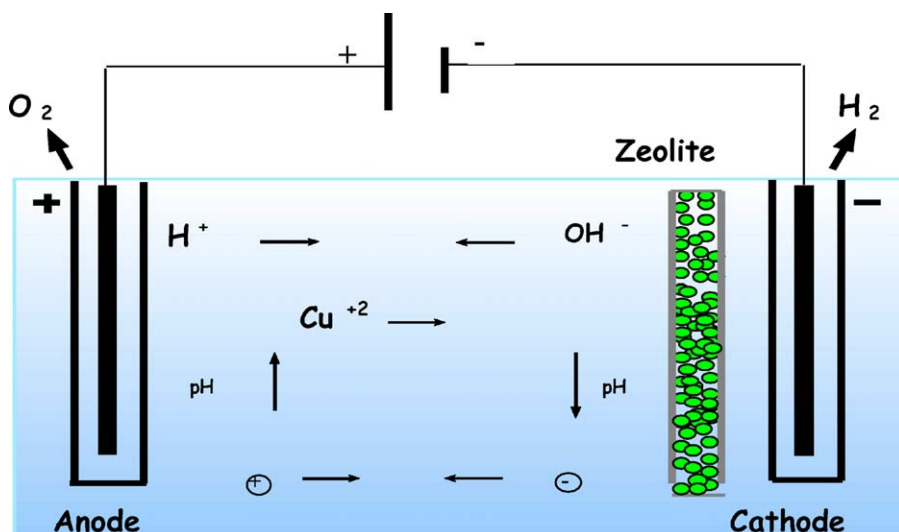


Fig. 1. Electrokinetic cell: a schematic picture of ions electric field migration toward the electrodes and the zeolite-slice to trap the Cu^{2+} ions.

Table 1
Cation exchange capacities (CEC) of different zeolites for the 0.24 M CuSO₄ solution at different times

Zeolite	HNO ₃	Cu ²⁺ present in the solution at the beginning (mg)	Time (h)	Cu ²⁺ present in zeolite (mg)	mg Cu/g zeolite (mg/g)	% Cu measured in zeolite (%)	mg Cu ²⁺ in solution (mg)	mg Cu ²⁺ /ml solution (mg/mL)	% Cu ²⁺ in solution (%)	Total % balance (%)
13x		3784.8	7	889.6	133.6	23.5	2900.0	11.6	76.6	100.1
13x		3764.4	24	786.0	119.1	20.9	2295.0	9.2	61.0	81.8
13x	pH 1	3779.5	7	425.6	63.9	11.3	3300.0	13.2	87.3	98.6
5A		3779.5	7	857.4	128.7	22.7	2840.0	11.4	75.1	97.8
5A		3779.5	24	795.6	119.5	21.1	3410.0	13.6	90.2	111.3
5A	pH 1	3780.0	7	206.6	31.0	5.5	3690.0	14.8	97.6	103.1
CBV100		3779.5	24	514.8	77.3	13.6	3270.0	13.1	86.5	100.1

For each exchange experiment: (1) The zeolite weight is 6.6 g. (2) The volume of CuSO₄ solution is 250 ml. (3) 15 g of CuSO₄·5H₂O (MW 249.7) is solved in 250 ml of deionized water. (4) The solution's molarity is 0.24 M. The CEC for each zeolite depends on the framework geometry, the SiO₂/Al₂O₃ ratio and the pore dimensions.

per salts as CuSO₄·5H₂O, and Cu(NO₃)₂·3H₂O, obtained by Aldrich.

In the aqueous experiments the slice contains ca. 50 g of zeolites and is located in front of the cathode.

We investigated different electrochemical time: 140, 280 min, till a maximum of 420 min to follow the progress of the cation exchange efficiency.

The electrodes are supplied by a dc of 12.5 V, positioning them at 15 cm of distance.

Starting with a well-known concentration of copper in water, the progress of the electrochemical process is followed by measuring at steps-time the Cu²⁺ concentration in solution and inside the zeolites by atomic absorption spectrometry.

The soil's electrokinetic experiments were performed for three different clays: sand, kaolinite and montmorillonite. In the clays experiments, we wetted the clays with the solutions of Cu²⁺ and by an accurate mixing, we made sure of the homogeneous distribution inside the clays.

In the clays experiences we operated at the electrode's distance of 8 cm, supplying the system with the right voltages to have currents of 1.0 and 0.2 A.

The volume of Cu(NO₃)₂ solution added to soils, is calculated from time to time, considering the used clays weight. The amount of Cu²⁺ present in the clays, at the beginning of the experiment, is guaranteed of ca. 5 mg of cations for each grams of sand.

3. Results and discussion

3.1. Cation exchange capacity (CEC) of zeolites

In the Table 1 are reported the experimental data for the exchange proofs, employing three different zeolites, at different time of cationic exchange with the same salt, i.e. CuSO₄, at the same molar concentration.

In the Table 2 are reported the results of exchange experiences, using as source of cations Cu²⁺ the salt Cu(NO₃)₂, the 13X zeolite, and measured at different time of exchange.

In the Table 3 are reported the exchange data for two different zeolites, using as source of cations Cu²⁺ the salt Cu(NO₃)₂ with a molar concentration less than before, equal to 0.1 M. In the Table 1 and the Table 2, are described the amount of copper ions (mg) present for gram of zeolite and the copper remaining in solution. In the last column are reported the total of percent data of the copper exchanged in the zeolite and the copper residual in solution. Note of these values are quite similar to 100%, meaning there is a good balance between the distribution of Cu²⁺ ions in the solution and those captured by zeolites. Moreover the amount of Cu²⁺ ions present into zeolites varies between the value as 133 mg of Cu²⁺ for gram of the zeolite 13X when is used CuSO₄ salt and a bit lower value like ca 123 mg of Cu²⁺ for gram of the zeolite 13X with the solution of Cu(NO₃)₂. The exchange experiments reported in the Table 3 show a linear trend

Table 2
Cation exchange capacities (CEC) of 13X zeolite for the 0.24 M Cu(NO₃)₂ solution at the different times

Proof no.	Zeolite	HNO ₃	Cu ²⁺ present in the solution at the beginning (mg)	Time (h)	Cu ²⁺ present in zeolite (mg)	mg Cu ²⁺ /g zeolite (mg/g)	% Cu recovered in zeolite (%)	mg Cu ²⁺ in solution (mg)	mgCu/ml solution (mg/ml)	% in solution (%)	Total % balance (%)
1a	13x		379.2	3	70.2	105.6	18.5	345.0	13.8	91.0	109.5
1b	13x		3791.9	7	817.7	122.8	21.6	3020.0	12.1	79.6	101.2
1c	13x		3927.3	24	799.7	120.8	20.4	2730.0	10.9	69.5	89.9
1d	13x	pH 1	3927.3	7	299.8	45.3	7.6	3640.0	14.6	92.7	100.3

For the experiments 1b, 1c, 1d: (1) The zeolite weight is 6.6 g. (2) The volume of Cu(NO₃)₂ solution is 250 ml. (3) 14.5 g of Cu(NO₃)₂·3H₂O (MW 232.6) is solved in 250 ml of deionized water. (4) The solution's molarity is 0.24 M. For the experiment 1a the zeolite weight is 0.66 g and the volume of Cu(NO₃)₂ solution is 25 ml, the solution's molarity is 0.24 M.

Table 3
Cation exchange capacities (CEC) of 13X and CBV100 zeolites for the 0.10 M Cu(NO₃)₂ solution at the different times

Proof no.	Zeolite	Cu ²⁺ present in the solution at the beginning (mg)	Time (h)	Cu ²⁺ present in zeolite (mg)	mg Cu ²⁺ /g Zeolite (mg/g)	% Cu ²⁺ recovered in zeolite (%)
1a	13x	944.7	2	36.2	54.4	3.8
1b	13x	944.7	3	40.6	61.1	4.3
1c	13x	944.7	4	49.0	73.7	5.2
1d	13x	944.7	8	56.0	84.1	5.9
1e	13x	944.7	24	66.3	99.6	7.0
2a	CBV100	944.7	2	28.4	42.7	3.0
2b	CBV100	944.7	3	35.5	53.3	3.8
2c	CBV100	944.7	4	35.2	53.0	3.7
2d	CBV100	944.7	8	27.7	41.7	2.9
2e	CBV100	944.7	24	38.9	58.4	4.1

For all the experiments. (1) The zeolite weight is 0.665 g. (2) The volume of Cu(NO₃)₂ solution is 150 ml. (3) 3.5 g of Cu(NO₃)₂·3H₂O (MW 232.6) is solved in 150 ml of deionized water. (4) The solution's molarity is 0.10 M.

of ionic capture in the time. The exchange process is slower than these obtained at high molarity, but show a gradual and progressive trend. The percent value of copper exchanged, for 13X and CBV-100 zeolites, varies between the 65% and 60% ca of the theoretical value. The theoretical values are calculated and reported in the Table 4.

3.1.1. Relationship between the CEC and the zeolite structure

The crystalline structure of 13X zeolite, corresponds at the mineral faujasite, and is formed by almost spherical supercages (12-ring structure) with a crystallographic aperture of 7.4 Å and an effective diameter of 9 Å, interconnected with sodalite cages through six-membered rings to form hexagonal prisms. The aperture of six-membered rings of sodalite cages is 2.2 Å, and the effective diameter is 2.5–2.6 Å. [7]. The unit cell contains 8 sodalite cages, 8 supercages and 16 hexagonal prisms. Since adjacent rings are always shared, the total number of tetrahedra in the framework is 192/unit cell. The maximum number of Al is 96/u.c., because adjacent tetrahedra are not allowed (Loewenstein's rule.) [8]. The zeolite 13X used by us, is characterized by a SiO₂/Al₂O₃ ratio = 2.46, and corresponding a unit cell formula like Na₈₆[(AlO₂)₈₆(SiO₂)₁₀₆]·220H₂O. This formula allows to calculate the theoretical exchange's number for each unit cell and the theoretical weight of cations present in a fixed amount, 1 g, of zeolites. We are calculate these value, described in the Table 4, considering that the copper ions is bivalent, so the number of cations necessary to compensate the negative charge associated at AlO₂ units, is the half than univalent cations. In the Graph 1 are

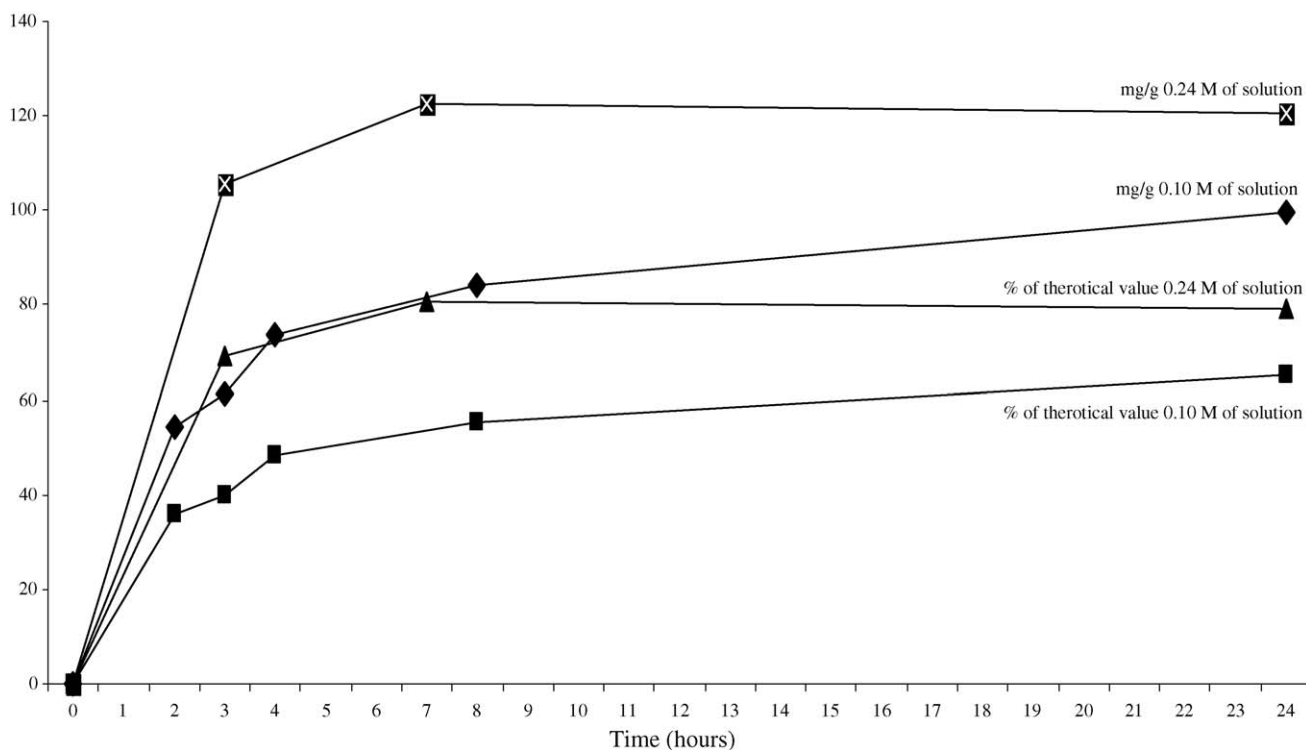
reported the curves for the experimental exchange values of the zeolite 13X expressed as mg of copper ions present in 1 g of zeolites, compared with the percent ratio between the experimental values and the theoretical weight of copper ions present for gram of zeolites. We observe that, the curve trends are the same for the two different starting molar concentration of salt. The weight (mg of Cu²⁺ present in each gram of zeolite) of copper captured by zeolite framework, for the solution 0.1 M is lower than the 0.24 M solution, at the same exchange time corresponding at a slower process. To obtain the same amount of copper ions present in the zeolite framework longer exchange times are necessary. The percent ratio curve shows that for 0.24 M solution, after 7 h of exchange, we reach the 80% of theoretical copper amount and this value does not vary in the following time suggesting an achieved equilibrium.

The zeolite CBV-100 too, used in the exchange experiments, has the structure of the mineral faujasite and differs from 13X in the composition. This zeolite is characterized by a ratio SiO₂/Al₂O₃ = 5.11. This means that the unit cell formula is Na₅₄[(AlO₂)₅₄(SiO₂)₁₃₈]·230H₂O. In order to increase the CEC of the zeolite, is necessary that the ratio SiO₂/Al₂O₃ becomes low, so the major number of Al atoms, responsible of the isomorphic substitution, allows to accommodate in the framework a higher number of cations. The zeolite CBV-100 differs by the 13X, due to the higher ratio of SiO₂/Al₂O₃ but not for the crystallographic structure, so the theoretical CEC results lower. The zeolite 5A is a three-dimensional system characterized by circular eight-ring structure as main channels with diameter of about 5 Å and a unit cell formula like Na₁₂[(AlO₂)₁₂(SiO₂)₁₂]·27H₂O.

Table 4
Theoretical number of exchanges, calculated for a bivalent cations, considering the unit cell formula for each zeolite

Zeolite	Unit cell formula	MW calculated	Unit cell weight (g)	Cell's number in 1 g zeolite	Number of Cu ²⁺ ions exchanged	Gram-atom Cu	Cu ²⁺ mg in 1 g of zeolite
5A	Na ₁₂ [(AlO ₂) ₁₂ (SiO ₂) ₁₂]·27H ₂ O	2238	3.72 × 10 ⁻²¹	2.69 × 10 ⁺²⁰	1.61 × 10 ⁺²¹	0.002681	168.90
CBV-100	Na ₅₄ [(AlO ₂) ₅₄ (SiO ₂) ₁₃₈]·230H ₂ O	17400	2.89 × 10 ⁻²⁰	3.46 × 10 ⁺¹⁹	9.35 × 10 ⁺²⁰	0.001552	97.76
13X	Na ₈₆ [(AlO ₂) ₈₆ (SiO ₂) ₁₀₆]·220H ₂ O	17796	2.95 × 10 ⁻²⁰	3.38 × 10 ⁺¹⁹	1.46 × 10 ⁺²¹	0.002416	152.23

The theoretical weight of Cu²⁺ ions (expressed as mg) present for one gram of the zeolites.



Graph 1. Curve trend for the percentage values and the mg/g values for experimental CEC of 13X conducted with $\text{Cu}(\text{NO}_3)_2$.

Calculating the ratio, expressed as percent ratio, between the experimental CEC value obtained with the theoretical CEC calculated (Table 4), we can conclude that:

- the amount percent of copper exchanged, for 13X and CBV-100 zeolites, is always 80% ca. of the theoretical value;
- for the 5A zeolite the amount percent is a bit smaller like 76% of the theoretical value;
- the real weight of copper ions present in the framework (expressed as mg of Cu^{2+} per gram of zeolite) depends on the geometry, the cavity dimensions, the structural properties of the zeolites, and on the cation's positions in the framework;
- longer time of exchange does not increase the amount of copper present in the zeolites. At the longer time the copper amount exchanged in the zeolite shows a little decreasing. This behaviour is explainable as the competitive action of other cations present in the solution (H^+ or Na^+) and as a reached equilibrium inside the zeolite cages.

3.1.2. Relationship between the zeolite's structure and the ion's competition

In the aqueous experiments, the Cu^{2+} ions are present in hydrated form. Considering that the ionic radius of the bare ions Cu^{2+} is 0.69 Å, it is responsible for the tightly bound hydration shell. The hydrated Cu^{2+} radius is described as 4.2 Å. [9]. The 13X zeolite has a variety of cation positions, but it is hypothesized [10] that the hydrated transition metal ions are unable to migrate through the hexagonal prisms, thereby generating an ion sieving effect that greatly prefers hydronium ions to exchange into the small cages.

The amount percent of copper exchanged in the 5A zeolite like at 76% of the theoretical value is explainable considering that the hydronium ions is tightly favourite compared with the larger hydrates Cu^{2+} ion into the small cages of 5A zeolite.

3.1.3. pH effect

The pH trend, in the CEC measurement, for the salt solutions are described in the Graph 2 and in the Graph 3.

These different pH values are correlated to the salt acid hydrolysis reactions.

The higher H^+ concentration for the $\text{Cu}(\text{NO}_3)_2$ solution, at the starting time of exchange proof, explains the lower CEC at the shorter time (7 h).

For the CuSO_4 solutions, the competitive effect between H^+ and Cu^{2+} is a bit more remarkable at longer exchange time (24 h) (Tables 1 and 2).

3.2. Zeolite's CEC in the electrokinetic process in aqueous conditions

To investigate if the zeolite's CEC allows to use these porous materials to capture the cations also during the electrokinetic process, first of all, we followed, the process during the time, for aqueous solution of different salts as source of Cu^{2+} , using the devise reported in the Fig. 1.

The results of the electrokinetic process, relevant to the copper polluted solution, are presented in the Table 5. We want to underline that in all these aqueous experiments we register a progressive pH change. During the process the pH bent to become equal to 1. Knowing that in liquid electrolyte, with

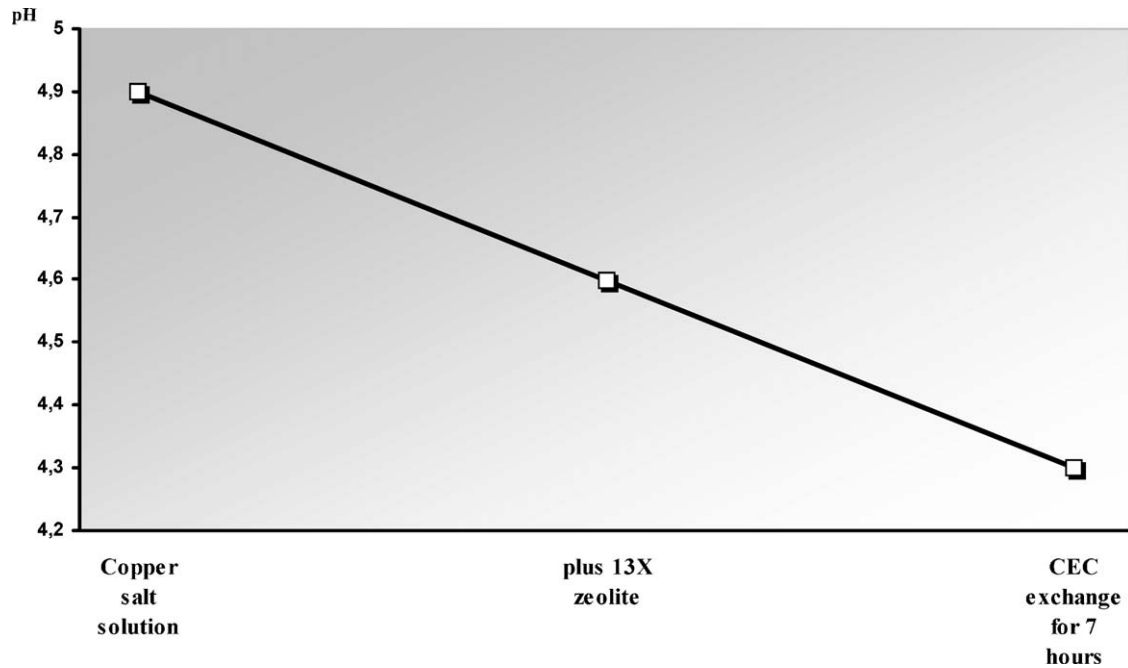
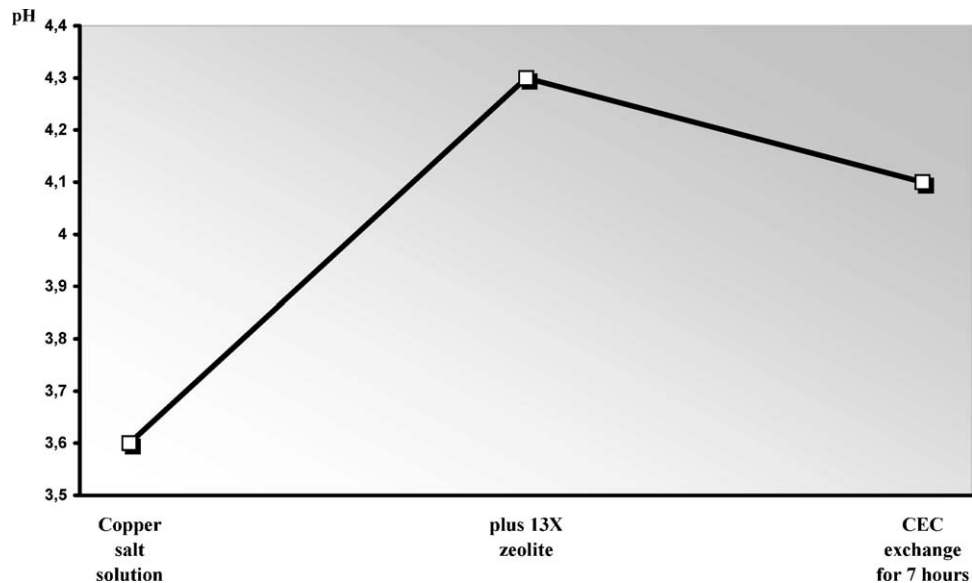
Graph 2. pH trend for CuSO₄·5H₂O solution in the CEC measurement for 13X zeolite.

Table 5
Electrokinetic process for aqueous solution of different salts as source of Cu²⁺ ions

Zeolite	Salt	Cu ²⁺ weight (g)	Time (min)	Cu ²⁺ in zeolite (g)	mg Cu ²⁺ /g zeolite (mg/g)	% Cu ²⁺ in zeolite (%)	Cu ²⁺ in solution (g)	% in solution (%)	Total % balance (%)
13X	Cu(NO ₃) ₂	31.7	140	2.1	39.6	6.6	20.1	63.4	70.0
13X	Cu(NO ₃) ₂	31.7	280	3.9	74.8	12.4	15.3	48.3	60.7
13X	Cu(NO ₃) ₂	31.7	420	3.8	71.7	11.9	10.4	32.8	44.8
13X	CuSO ₄	30.0	140	3.4	64.7	11.3	20.3	67.6	79.0
13X	CuSO ₄	30.0	280	4.7	90.4	15.8	24.7	82.3	98.1
13X	CuSO ₄	30.0	420	4.9	94.2	16.5	13.3	44.5	61.0

The zeolite weight used for the experiments is 52.56 g. The salt weight for the electrokinetic proof with Cu(NO₃)₂ is 115.9 g, the solution's volume is 2000 ml, the molarity is 0.249. The salt weight for the electrokinetic experience with CuSO₄ is 117.8 g, the solution's volume is 2000 ml, the molarity is 0.236.

Graph 3. pH trend for Cu(NO₃)₂·3H₂O solution in the CEC measurement for 13X zeolite.

sufficient mixing, the electroic process of water could not produce a net pH changes, because the generation of protons at the anode and of hydroxyl ions at the cathode are in balance, it is necessary to find a plausible reason to explain our experimental pH changes. When the copper salts are dissolved in water, the complete salt dissociation takes place. So in solution there are Cu^{2+} ions. Besides the water electrolysis produces at the cathode the hydroxyl ions. We presume that the reaction between the hydroxyl ions and the Cu^{2+} ions present, in the same local place, takes place forming $\text{Cu}(\text{OH})_2$. The copper hydroxide substracts, even more, the hydroxyl anions, so the pH balance is not more existing. Proceeding the electrokinetic process, the pH becomes so on more lower. This process is independent from the electric field flow of copper ions versus the cathode. The copper ions are responsible of $\text{Cu}(\text{OH})_2$ precipitation, both motionless and moving. The water electrolysis process, instead, is responsible by formation of hydroxyl ions. To support this explanation, we underline that in the exchange aqueous experiences, the pH doesn't change in this strong way and never reaches value like one.

The comparison of the Cu^{2+} ions amount captured in the 13X zeolite slice during the electrokinetic process, with the copper amount present in the cation exchange procedure 0.24 M, we observe, in the electrokinetic process, (Table 5) an efficiency very near to the maximum value of the aqueous CEC (Table 2) even considering the competitive H^+ effect.

The time steps of the electrochemical process show the following capture of metallic ions. During the first time-step, using CuSO_4 salt, the Cu^{2+} captured in the 13X zeolite increases by 40%. In the following time-step, the Cu^{2+} amount captured in the 13X zeolite, is still increasing to being close to the cation exchange capacity measured in classical conditions. As underline before, in our electrokinetic process, along the time, the solution's pH comes to 1 and the electric field promotes the migration of the Cu^{2+} ions and simultaneously an acid front which moves from the anode to the cathode. To understand as the competitive H^+ ions could influence the zeolite's CEC, we decided to repeat the cation exchange experiments in solution 0.24 M of copper salts, where we forced the pH at very low value, adding a solution of HNO_3 until pH 1.

In the Table 1 is shown the dramatic effect induced by H^+ ions competitive with Cu^{2+} ions in the 13X and 5A zeolite's cavities. The cation exchange capacity, in the 13X, drastically decreases about 52% using CuSO_4 salt, till to 64% using $\text{Cu}(\text{NO}_3)_2$ salt. (Table 2).

In the electrokinetic process, instead, the amount of Cu^{2+} ions captured in the zeolite framework, at the electrokinetic pH 1, is well greater than CEC at the same low pH; the 13X zeolite adsorption is 94.2 mg Cu^{2+} /g zeolite, using CuSO_4 salt, compared with the low 64.0 mg Cu^{2+} /g zeolite in CEC at pH 1.

This means that in the electrokinetic process the zeolites capture the Cu^{2+} ions with a high efficiency, despite of the high concentration of H^+ . The dynamic condition of the electrokinetic process and the ion mobility induced by the electric field, allow to have a high capture efficiency of metallic ions in the zeolite-slice. The noise generated by H^+ is exceed in the electrokinetic process.

Comparing the minimum value of CEC at pH 1 (i.e. 64.0 mg Cu^{2+} /g zeolite for CuSO_4 and 45.4 mg Cu^{2+} /g zeolite for $\text{Cu}(\text{NO}_3)_2$) with the relevant amount of Cu^{2+} captured in the electrokinetic process, working at the same low pH 1, it is remarkable that the electric field induces an increase of Cu^{2+} adsorbed in the 13X zeolite of the same amount in the both salts, like 30 mg Cu^{2+} /g zeolite.

CEC at pH 1 + electric field effect (constant value)

= electrokinetic Cu^{2+} capture capacity.

If as source of copper ion is used $\text{Cu}(\text{NO}_3)_2$, in the electrokinetic process, the first time-step increases about of 90% the amount of copper captured in the 13X zeolite. The further time does not rise this amount, being quite constant.

In the literature [6] it is described that the anion effect becomes significant when the ion exchange is carried out at concentrations 0.5 M or higher. The reason is due to the anions–cations association and their exclusion from the zeolite channels because of the repulsion exerted by the negative charges of the pore apertures. We used copper salts concentration 0.24 M, so less than the critical value. In fact in the ion exchange process (Tables 1 and 2) the amount of copper ion present in the 13X zeolite is quite similar, unrelated to the salt nature.

However the electrokinetic process shows a little “anion effect”; the amount of Cu^{2+} captured in the 13X zeolite is a bit lower if $\text{Cu}(\text{NO}_3)_2$ salt is used as source of copper ions. It is true that after 7 h of electrokinetic process, the Cu^{2+} percent captured in the zeolite's framework is inferior at the copper in the solution, but we observe a linear and progressive trend of capture. Even if admitted that 7 h is a too little time respect to the classic field electrokinetic processes, the linear and progressive increase of copper exchanged in the zeolite's framework shows that these materials keep on to exchange progressively.

3.3. Zeolite's CEC in electrokinetic process with different clays

Once examined the CEC behaviour of 13X zeolite as Cu^{2+} exchanger for aqueous solutions in the electrokinetic process, we investigated the process using different typologies of clays, in the laboratory experiments. The clays and their adequate mixture [11] allow to well reproduce the properties of low permeability soils. The clays choosed are: the sand, the kaolinite and the montmorillonite. In the Tables 6–8 are reported the results of the electrokinetic processes for these different clays.

With the sand, we have conducted different proofs as evidenced in the Table 6. It's worth of note: when the sand is wet with low volume of $\text{Cu}(\text{NO}_3)_2$ solution as 150 ml, the amount of Cu^{2+} exchanged in the zeolite does not have a linear trend progressive with the time. The higher amount corresponds at the middle time. During the following time the Cu^{2+} ions presents in the zeolite decrease. In our laboratory experiments, we could explain the behaviour with a drying process evidenced

Table 6
Electrokinetic process using sand as soil phase, conducted with zeolite 13X and $\text{Cu}(\text{NO}_3)_2$ 0.24 M solution used to get soil wet

Zeolite weight (g)	Sand weight (g)	Volume used (ml)	Cu^{2+} present in the sand at the beginning (g)	Time (min)	Cu^{2+} present in zeolite (mg)	mg Cu^{2+} /g zeolite (mg/g)	% Cu^{2+} in zeolite (%)
1.0 A							
3.127	450	150	2.28	140	184.0	58.84	8.06
3.127	450	150	2.28	280	210.2	67.22	9.21
3.127	450	150	2.28	420	166.9	53.37	7.32
1.0 A							
7.367	772	250	3.81	140	142.1	19.29	3.73
7.367	772	250	3.81	280	284.3	38.59	7.46
7.367	772	250	3.81	420	348.1	47.25	9.14
0.2 A							
7.36	1000	280	4.26	140	187.3	25.45	4.39
7.36	1000	280	4.26	280	149.2	20.27	3.50
7.36	1000	280	4.26	420	255.3	34.69	5.99
0.2 A							
3.134	450	150	2.28	140	162.4	51.82	7.12
3.134	450	150	2.28	280	193.0	61.58	8.46
3.134	450	150	2.28	420	152.2	48.56	6.67

We prepared a solution of $\text{Cu}(\text{NO}_3)_2$ 0.24 M and for each electrokinetic experiment, and depending on the sand weight, we used a suitable solution's volume to get the sand wet.

Table 7
Electrokinetic process using kaolinite, conducted with zeolite 13X and $\text{Cu}(\text{NO}_3)_2$ 0.24 M solution used to get soil wet

Zeolite weight (g)	Kaolinite weight (g)	Volume used (ml)	Cu^{2+} present in the kaolinite at the beginning (g)	Time (min)	Cu^{2+} present in Zeolite (mg)	mg Cu^{2+} /g zeolite (mg/g)	% Cu^{2+} in zeolite (%)
0.2 A							
3.128	423	345	5.26	140	100.3	32.07	1.91
3.128	423	345	5.26	280	176.2	56.33	3.35
3.128	423	345	5.26	420	193.07	61.72	3.67

We prepared a solution 0.24 M of $\text{Cu}(\text{NO}_3)_2$ (29.0 g dissolved in 500 ml) and used the suitable volume to get the kaolinite wet.

by a voltage varying (a decrease) as the clays becomes dry. Our experiment were conducted with a power generator able to fix the current and to reads the resultant voltage or viceversa. The progressive drying of the sand involves the conducibil-

ity's decrease, explainable with the slower ion's electric flow.

This behaviour is confirmed by the experiences carried out at major volume of solution, reported in the Table 6.

Table 8
Electrokinetic process using montmorillonite, conducted with zeolite 13X and $\text{Cu}(\text{NO}_3)_2$ solution used to get soil wet

Zeolite weight (g)	Salt weight (g)	Montmorillonite weight (g)	Volume used (ml)	Cu^{2+} present in the clays at the beginning (g)	Time (min)	Cu^{2+} present in Zeolite (mg)	mg Cu^{2+} /g zeo (mg/g)	% Cu^{2+} in zeolite (%)
1.0 A								
3.128	23.13	396	305	4.64	140	29.2	9.33	0.63
3.128	23.13	396	305	4.64	280	31.77	10.15	0.68
3.128	23.13	396	305	4.64	420	31.07	9.93	0.67
0.2 A								
3.13	10.41	360	300	2.74	120	21.04	6.72	0.77
3.13	10.41	360	300	2.74	240	20.97	6.70	0.77
3.13	10.41	360	300	2.74	360	15.66	5.00	0.57
3.13	10.41	360	300	2.74	420	21.55	6.88	0.79

For the experiment carried out at 1.0 A, the molarity of the $\text{Cu}(\text{NO}_3)_2$ solution used to get soil wet is 0.24 M. (23.13 g salt dissolved in 400 ml). For the experiment carried out at 0.2 A the molarity of the $\text{Cu}(\text{NO}_3)_2$ solution used is 0.14 M. (10.41 g salt dissolved in 300 ml). This different amount of Cu^{2+} present at the beginning of the electrokinetic process doesn't change, essentially the CEC behaviour of zeolite. The high surface charge density and then the high buffering capacity of montmorillonite influences drastically the ion's movements by electric field.

The bigger volume of water warrants a linear and progressive in the time capture of Cu^{2+} ions in the zeolite. The amount of Cu^{2+} ions captured by the zeolite 13X during the same time of the electrokinetic process is different between the aqueous conditions and the clays experiments. In fact in free solution the trapped Cu^{2+} ions is a bit more. Considering that the CEC of 13X zeolite is the same, the reason of this behaviour, is due to greater resistance to the ion mobility offered by the wet clays; so the ion's migration is slower than in aqueous solution. The effective ionic mobility of a specific ion in a porous medium [1] is a function of soil porosity and tortuosity factor.

In the experiment conducted with the kaolinite (Table 7), the zeolite 13X captures the Cu^{2+} ions progressively along the time, increasing the trapped amount in following times. For the sand, (Table 6) the time necessary to capture the relative maximum amount of the Cu^{2+} ions is lower than to the kaolinite. The different times, required by the sand and the kaolinite, to adsorb about 60–70 mg of Cu^{2+} ions per gram of 13X zeolite, is explainable with the different ion migration rates within the clays.

These clays have different surface charge densities [3,11] increasing in the following order: sand < kaolinite < illite < montmorillonite.

The surface charge density is the total electric charge per unit surface area. A higher surface charge density means a higher cation exchange capacity. A specific ion is tightly hold back in a clay with major CEC, so the ion mobility rate is lower in kaolinite clay than in sand. In both electrokinetic clays processes, the cathode presents a very clear surface. No trace of metallic copper is present on the cathode. This means that zeolite 13X captures the slow migrating Cu^{2+} ions completely.

The competitive effect of H^+ ions on 13X zeolite CEC is still present in simulated soil electrokinetic processes. Even if the effective ion mobility of H^+ , in wet clays soils is about seven times greater than metallic cations, the zeolite-slice adsorbs all the slow-soil migrating Cu^{2+} ions.

The montmorillonite clay presents an peculiar behaviour (Table 8). During the electromigrating process the amount of copper ions trapped in the zeolite is poor and doesn't change in the time. This time the 13X zeolite is not able to trap the migrating Cu^{2+} ions with comparable capacity of the previous two clays. Our plausible explanation of this behaviour is based on two determinant factors: first of all, the montmorillonite is a clay with high surface charge density and shows a high buffering capacity. The transport of the hydrogen ion in this clay is hardly retarded, so the ions generated by water electrolysis remain confined near the respective electrode where they are formed. The Cu^{2+} ions are strongly adsorbed into the clays, and due to the high buffering capacity of this clay the Cu^{2+} ions move toward the cathode, by electric field, very slowly. Near to the cathode a very high concentration of hydroxyl ions is present. The Pourbaix diagram for the copper and the relevant stable species, as free ions or as copper oxides in the aqueous equilibrium, suggests that in very high basic condition the copper is stable as oxide and subsequently as copper hydroxide.

Neither the copper oxide nor any other plausible intermediate species, present in basic equilibrium, cannot be captured and trapped in the framework zeolite cavities.

The ion exchange of zeolite and then the possibility of introduce in the zeolite cavities metallic ions or alkaline metals is based on the availability of metal as cations. Only in this case, the cations can be coordinated within the zeolite frameworks, and occupy specific cavities by their coordination with the framework oxygen positions. Therefore the copper oxide or any other neutral intermediate species present at very basic pH conditions, are not trapped in the 13X zeolite slice. The copper oxide could precipitate in the montmorillonite soil or could be reduced on the surface electrode.

4. Conclusions

The zeolite's CEC measured in solution, where the ion's mobility is spontaneous and free, suggest the opportunity to introduce in the reticular framework the metallic cations.

The experimental values come to an agreement with the theoretical calculations obtained by the specific unit cell formula of each zeolite. The real weight of copper ions present in the framework depends on the geometry, the cavity dimensions, the structural properties of the zeolites, and on the cation positions in the framework.

In the electrokinetic system where the ion's mobility is induced by the electric field, we could distinguish different trend depending on the resistance of the medium and therefore the effective ionic mobility. In the aqueous electrokinetic process the dynamic condition and the ion mobility induced by the electric field, allow to have a high capture efficiency of metallic ions in the zeolite-slice. The zeolites capture the Cu^{2+} ions with a high efficiency, despite of experimental high concentration of H^+ . The noise generated by H^+ is exceed in the electrokinetic process.

In the electrokinetic process conducted with the clays, the zeolite CEC is hardly bind to the resistance offered by the clays. The effective ionic mobility of an ion is a function of soil porosity and tortuosity factor. Moreover, the surface charge density of the clays means an high buffering capacity. A specific ion is tightly hold back in a clay with major CEC.

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