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# Sorption processes and XRD analysis of a natural zeolite exchanged with $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ cations

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## Abstract

In this study the $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ adsorption capacity of a natural zeolite was evaluated in batch tests at a constant pH of 5.5 by polluting this mineral with solutions containing increasing concentrations of the three cations to obtain adsorption isotherms. In addition X-ray powder diffraction (XRD) was used to investigate the changes of zeolite structure caused by the exchange with cations of different ionic radius. The zeolite adsorption capacity for the three cations was $Zn > Pb > Cd$. Moreover a sequential extraction procedure [$H_2O$, 0.05 M $Ca(NO_3)_2$ and 0.02 M EDTA] was applied to zeolite samples used in the adsorption experiments to determine the chemical form of the cations bound to the sorbent. Using this approach it was shown that low concentrations of $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ were present as water-soluble and exchangeable fractions (<25% of the Me adsorbed), while EDTA extracted most of the adsorbed cations from the zeolite (>27% of the Me adsorbed).

The XRD pattern of zeolite, analysed according to the Rietveld method, showed that the main mineralogical phase involved in the adsorption process was clinoptilolite. Besides structure information showed that the incorporation of $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$, into the zeolite frameworks changed slightly but appreciably the lattice parameters. XRD analysis also showed the occurrence of some isomorphic substitution phenomena where the $Al^{3+}$ ions of the clinoptilolite framework were replaced by exchanged $Pb^{2+}$ cations in the course of the ion exchange reaction. This mechanism was instead less evident in the patterns of the samples doped with $Cd^{2+}$ and $Zn^{2+}$ cations.
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## 1. Introduction

Zeolites form a large family of aluminosilicates which have been studied by mineralogists for more than 200 years [1]. Zeolites are microporous crystalline solids with well-defined structure, consisting of a three-dimensional network of $SiO_4$ and $AlO_4$ tetrahedra linked together by common oxygen atoms [1,2]. The isomorphic substitution of $Si^{4+}$ by $Al^{3+}$ causes a negative charge density in the zeolite lattice [3,4]. This charge is neutralized by introducing exchanged cations in the structural sites of the zeolite (sodium, calcium and potassium ions) [5]. The mobile non-framework cations are located in cavities in the channel walls and coordinated with the water molecules within the channel [6].

For their chemical, physical and structural characteristics, zeolites are suitable for a number of applications in various fields such as adsorption of cations, separation, ion exchange and catalysis [7–10].

Among these the zeolites capacity to reduce the heavy metals solubility through chemical immobilization is of particular interest [11]. The process is based either on an ionic exchange between heavy metals and cations, such as sodium and potassium [12,13], or on the precipitation of metal hydroxides over the zeolite external surfaces [14,15]. The ion exchange process in zeolites is influenced by several factors such as concentration and nature of cations and anions, pH value and crystal structure of the zeolite [16]. However any natural zeolite can show very different features that depend on the environmental conditions (pH, quantity and type of ions) in which they crystallized. These latter can deeply influence the structural features of zeolite and in particular those related to pore dimensions and adsorption capacity. Hence the suitability of a zeolite to be used as heavy

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metals sorbent depends largely on its own properties. In this context the identification of the main phases of the zeolite, bearing the active sites involved in the metal fixation process, appears crucial in order to elucidate the nature of the interaction mechanisms between the heavy metal and the sorbent. The stronger is the interaction Me–zeolite the more effective is the chemical immobilization during time.

Despite the great interest of the scientific community in zeolite ion exchange, only few reports exist on the structural changes occurring in the sorbent after the exchange with heavy metals. At this regard the X-ray diffraction (XRD) technique can provide substantial information. The recent advances of the powder X-ray diffraction technique, in terms of instrumentation and numerical analysis, make it possible to distinguish and evaluate quantitatively the phase contributions even in comparatively complex natural systems. This approach can provide not only a quantitative estimation of the zeolite phases but also some useful information on the sorbent structure and microstructure such as lattice parameters, average crystallite size and microstrain.

In this study a natural zeolite coming from a layer in the north of Sardinia has been artificially polluted with single aqueous solutions containing increasing concentrations of $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ cations to obtain adsorption isotherms. Besides, the changes in the sorbent structure caused by the exchange with cations of different ionic radius were investigated by X-ray powder diffraction.

## 2. Materials and methods

### 2.1. Sample description

The natural zeolite used in the experimental tests came from a layer situated in Bonorva (near Sassari, North Sardinia, Italy). The zeolite, ground and sieved to <0.02 mm, was washed with distilled water to remove the soluble salts possibly present prior to conditioning and capacity measurements. The zeolite samples were activated by two washings with 25 mL of 0.05 M HCl followed by a washing in distilled water, before to be artificially contaminated. All the determinations (chemical and mineralogical analysis) were performed both on the natural and on the activated zeolite.

The pH and electric conductivity (EC) values were determined in 1:25 ratio of sorbent/distilled water [17]. The method used for the cation exchange capacity (CEC) determination of zeolite is a batch procedure in which zeolite was treated with a 0.1-M triethanolamine buffered at pH 8.2 $BaCl_2$ solution followed by a re-exchange with a 0.1-M $MgSO_4$ aqueous solution. The zeolite samples were saturated with $Ba^{2+}$ cations; particularly, zeolite samples of 1.0 g were treated with 25 mL of $BaCl_2$ solution. The zeolitic/cationic solution was intensely shaken for 2 h. Two other identical washings were carried out and, after the ion exchange process, the zeolites were washed with distilled water. The solid and liquid phases were separated by centrifuging and filtering. The adsorbed $Ba^{2+}$ was re-exchanged by saturating the zeolite samples five times with a 0.1-M $MgSO_4$ solution. Shaking time was 2 h. After each step the suspension is centrifuged and the clear supernatant is decanted into a 250-mL volumetric flask. All filtrates are combined. In these solutions $Ba^{2+}$ is analysed using a Beckam D.C. plasma atomic emission spectrometer, and this represents CEC of zeolite samples. All analyses were performed in triplicate [17].

The specific surface area was determined by applying the BET model to the $N_2$ adsorption results obtained from a Sorptomatic Carlo Erba (Milan, Italy). The samples were also pre-treated by outgassing at $40\,^{\circ}C$ combined with vacuum at $10^{-9}$ bar for 12 h. The error in the determination of SBET was $\pm 3\,m^2\,g^{-1}$.

### 2.2. Adsorption and release of lead, cadmium and zinc from zeolite

The $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ adsorption capacity of a natural zeolite was evaluated by polluting the sorbent with solutions containing increasing concentrations of the three cations to obtain adsorption isotherms. The cations used in the adsorption tests have been selected on the basis of their presence and abundance in the mining region of SW Sardinia.

Activated zeolite samples of 1.0 g were treated with 25 mL of cationic solutions which concentration varied between $4 \times 10^{-3}$ and 0.1 M (which correspond to 0.1 and 2.5 mmol 25 $mL^{-1}$, respectively) of $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$, derived from their nitrate salts. The adsorption tests were carried out at controlled temperature and pH. A buffer solution of acetic acid–sodium acetate was used to maintain a constant pH (5.5) for the $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$–zeolite samples at each point of the isotherms (12 points on the whole were obtained). The sorbent/cation mixtures were intensely shaken for 24 h, which was proved beforehand to be sufficient for reaching equilibrium. The solid and liquid phases were separated by centrifuging and filtering.

A sequential extraction procedure was applied to all zeolite samples used in the adsorption experiments to analyze the chemical form of the cations bound to the sorbent. To extract the soluble phase, each sample was treated with 25 mL of distilled water (pH 6.5) and shaken for 2 h at room temperature. It was then treated with 25 mL of 0.05 M $Ca(NO_3)_2$ to extract the exchangeable phase, and with 25 mL of 0.02 M EDTA to extract the cations tightly bound to sorbent and not readily bioavailable or leachable [18]. After each step of the extraction process the samples were centrifuged and filtered to separate the liquid and solid phases. After the third washing, the residual fraction of cations was determined by drying the solid phase overnight at $105\,^{\circ}C$ and digesting it with $HNO_3$ and HCl (ratio 1/3) in a Microwave Milestone MLS 1200. The heavy metal concentrations were analysed using a Beckam D.C. plasma atomic emission spectrometer. All the data reported are the mean of three replicates.

### 2.3. Powder X-ray diffraction analysis (XRD)

Before analyses all the samples were dried at $65\,^{\circ}C$ for 8 h. The patterns were recorded for zeolite samples not polluted with metals and for the samples exchanged with cations to evaluate mineralogical and structural changes.

Table 1
Properties of the natural and activated zeolite used in the study

|  | Natural zeolite | Activated zeolite |
|---|---|---|
| Chemical parameters |  |  |
| pH | 8.1 | 7.6 |
| Electric conductivity (mS cm$^{-1}$) | 1.15 | 8.05 |
| $S_{BET}$ (m$^2$ g$^{-1}$) | 27.0 | 31.0 |
| CEC (mmol$_{(+)}$ g$^{-1}$) | 1.50 | 1.48 |
| Mineralogical phases (wt%) |  |  |
| Clinoptilolite [(Na,K,Ca)$_2$-3Al$_3$(Al,Si)$_2$Si$_{13}$O$_{36}$(OH)·9H$_2$O] | 63.0 | 63.0 |
| Anorthite [CaAl$_2$Si$_2$O$_8$] | 25.0 | 25.0 |
| Quartz [SiO$_2$] | 7.0 | 8.0 |
| Biotite [K(Mg, Fe$^{2+}$)$_3$[AlSiO$_3$O$_{10}$(OH,F)$_2$]] | 5.0 | 4.0 |

XRD analysis was carried out with a Rigaku D/MAX diffractometer (Cu Kα). The X-ray generator worked at a power of 40 kV and 40 mA, the goniometer was equipped with a graphite monochromator in the diffracted beam. The patterns were collected in the angular range from 10° to 80° with 0.05° of step size. The powder patterns were analysed according to the Rietveld method [19], using the programme MAUD [20] running on a personal computer. Crystalline phases were identified using the database of the International Centre for Diffraction Data for Inorganic Substances (Inorganic Crystal Structure Database).

## 3. Results and discussion

### 3.1. Characteristics of the sorbent

Table 1 shows the properties of the natural and activated zeolite used in the study. The pH and electric conductivity of the activated zeolite were 7.6 and 8.05 mS cm$^{-1}$, respectively. The CEC of the activated zeolite slightly decreased after the acid pre-treatment (1.48 mmol g$^{-1}$). The specific areas of natural and activated zeolite were 27 and 31 m$^2$ g$^{-1}$; these values were not very high for good sorbents. However XRD analysis showed that the activated zeolite mainly consisted of clinoptilolite (63 wt%), the main mineralogical phase involved in the adsorption processes, which has a specific area higher than the natural zeolite used (about 70–151 m$^2$ g$^{-1}$) [21–23]. Minor quantities of anorthite (25 wt%), quartz (8 wt%) and biotite (4 wt%) were also retrieved.

### 3.2. Zeolite adsorption isotherms

The total amount of cations in the polluting solutions (2.5 mmol, 25 mL$^{-1}$) was sufficient to satisfy the CEC of the zeolite (1.48 mmol g$^{-1}$). For all the cations tested the adsorption in the zeolite was lower with respect to CEC. However the total cation exchange capacity is not necessarily indicative of the sorption capacity of a particular zeolite [24]. In fact the effectiveness of the zeolite as sorbent agent is determined by the specific crystal structure and by the distribution and accessibility of the exchange sites for cations [25].

The isotherm analyses showed different adsorption behaviour for Pb$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$. Metal adsorption increased in the following order: Zn > Pb > Cd (Fig. 1). The isotherms of three

cations were regular, positive, and concave to the concentration axis (Fig. 1). Particularly Zn$^{2+}$, Pb$^{2+}$ and Cd$^{2+}$ adsorption was higher when the metal concentration in solution was lower (Me$_{ads}$/Me$_{added}$ ratio higher than 0.9, 0.8 and 0.6 for Zn$^{2+}$, Pb$^{2+}$ and Cd$^{2+}$, respectively at the first eight points of the isotherm). Then the ratio metal adsorbed/metal added decreased as the concentration of cations in solution increased, but total adsorption increased, until a plateau was reached (1.36 mmol g$^{-1}$) (Fig. 1). This was due to the increased occupation of active surface sites of the sorbent when the concentrations of metal increased in the aqueous solutions [26]. Since the solution pH at equilibrium in the adsorption experiments was 5.5, hydroxide precipitation of Cd and Zn can be excluded, while it is possible that a low precipitation of Pb-hydroxide occurred [27].

The selectivity of ion exchangers is an equilibrium parameter and may have several physicochemical causes. The zeolite may be more selective for certain cations while it is less selective for others. This can depend on the size and charge of the cation and on the possible presence of different chemical species, i.e. Me$^{2+}$ and MeOH$^+$ [24]. It should be noted that the results of our previous investigations, in which the same zeolite polluted with multicomponent solutions of Pb$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$ has been used, are conflicting with the results from this study [28]. The cations sorbed from multicomponent solutions were significantly lower than those sorbed from the single solutions, and this was in agreement with the results reported by other authors [16]. It may be concluded that in the multicomponent solution the competitive effect of the three cations caused a general decrease of
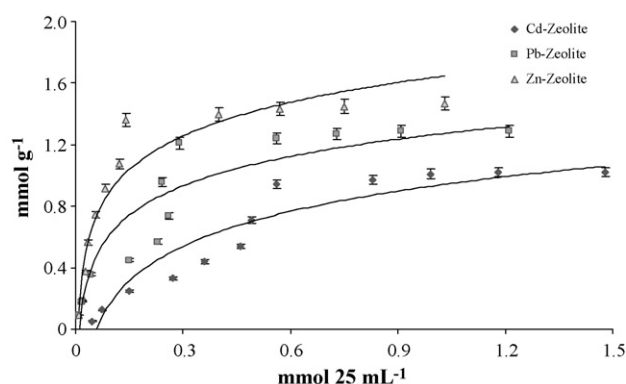


Fig. 1. Pb$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$ adsorption isotherms on zeolite.

the sorption. Moreover the cations sorbed from the multicomponent solutions followed the order: Pb > Cd > Zn. Probably in the multi-element solution the zeolite was less selective for $Zn^{2+}$ because its energy and sphere of hydration is greater than those of $Pb^{2+}$ and $Cd^{2+}$. Therefore during the ion exchange processes, the moving of $Zn^{2+}$ towards the zeolite surface was unfavoured. By contrast in the single-element the zeolite seemed more selective for $Zn^{2+}$. These differences in ion exchange selectivity for cations in the single-element solutions, could be attributed to the higher capacity of $Zn^{2+}$, in absence of competition with $Pb^{2+}$ and $Cd^{2+}$, to interact with the active sites of the zeolite. These results suggested the absence of individual sorption centers of the zeolite for $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$. In fact if the cations interacted only with specific sorption sites, the amounts of $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ sorbed by the zeolite from the single and multicomponent solutions should be the same. Probably the sorption was simply related to the cation nature (charge density and diameter of hydrate ions), and to the facility of access to the active sites.

The adsorption data were fitted into the Langmuir's equation to evaluate which parameters were physically significant

$$\frac{x}{m} = \frac{kbC}{1 + KC}$$

where the Langmuir parameter $b$ refers to maximum adsorption capacity and $K$ is a proportional constant of the adsorption energy [29,30]. The maximum adsorption capacity values of $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$, obtained from the Langmuir's equation, agreed with the experimental results (Table 2). The maximum $Zn^{2+}$ adsorption $b$ was in fact higher than $Pb^{2+}$ and $Cd^{2+}$ (the ratios between the $b$ value for $Zn^{2+}$ and the $b$ values for $Pb^{2+}$ and $Cd^{2+}$ were respectively 1.24 and 1.27).

If it is supposed that for ionic exchange reactions, at least some of the water molecules of hydration must be stripped from the solvated ions [31] then the $Zn^{2+}$, which in the unhydrated form has a large charge density, could draw near to the zeolite surfaces establishing strong bonds. By contrast $Pb^{2+}$ and $Cd^{2+}$, having a great ionic radius and a small charge density, could bind to the zeolite surfaces with weaker bonds. This was supported by the Langmuir's parameter $K$ which showed the highest values for the zeolite exchanged with $Zn^{2+}$ (the ratios between the $K$ for $Zn^{2+}$ and the $K$ for $Pb^{2+}$ and $Cd^{2+}$ were respectively 3.85 and 1.22) (Table 2).

All the samples, after artificial contamination, were treated with solutions of gradually increasing extraction capacity in order to study the different heavy metal–zeolite interaction mechanisms.
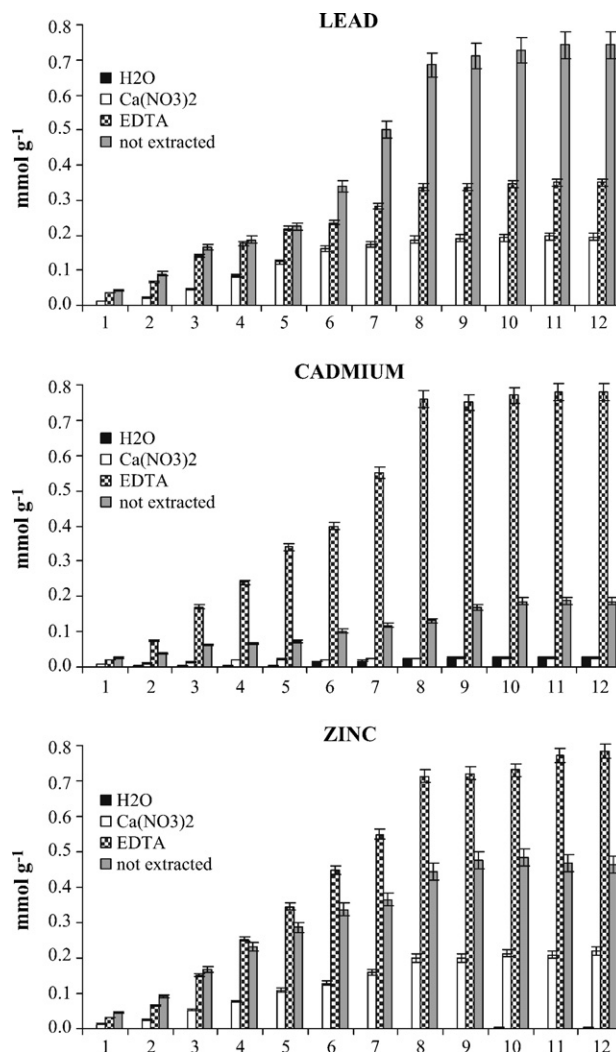


Fig. 2. $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ fractions extracted with $H_2O$, $Ca(NO_3)_2$, EDTA and not extracted from zeolite. *The numbers in the $X$-axis correspond to the isotherm points.

The fractions extracted with $H_2O$, which are associated with the greater environmental hazard being the most soluble and bioavailable fractions, were less than 3.0% of the $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ adsorbed (Fig. 2). The $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ fractions extracted with $Ca(NO_3)_2$, which are associated with the relatively labile exchangeable fractions, slightly increased as the quantity of metal adsorbed increased. However, the metal fractions extracted with $Ca(NO_3)_2$ were always lower than 22.0, 13.0 and 16.0% of the $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ adsorbed, respectively.

The $Cd^{2+}$ and $Zn^{2+}$ fractions extracted with EDTA, which represent the not readily bioavailable fractions [32], increased with the increase of the adsorbed metal and they reached the 80 and 54% of the $Cd^{2+}$ and $Zn^{2+}$ adsorbed, respectively in the last point of the isotherms. The $Pb^{2+}$ fractions extracted with EDTA did not show a similar trend, being always lower with respect to the residual fraction of $Pb^{2+}$ ($Me_{ads}/Me_{extracted}$ EDTA ratio increasing in the isotherm).

The fractions of non-extracted cations would not be expected to be readily released under natural conditions [33]. The residual

Table 2
The Langmuir parameters $b$ and $K$, refer to the $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ adsorption capacity and intensity of zeolite

| Polluting cation | $b$ (mmol g$^{-1}$) | $K$ (L mmol$^{-1}$) | $R^2$ |
|---|---|---|---|
| $Pb^{2+}$ | 1.19 | 0.60 | 0.99 |
| $Cd^{2+}$ | 1.16 | 1.89 | 0.95 |
| $Zn^{2+}$ | 1.47 | 2.31 | 0.99 |

Table 3
Lattice parameters of the monoclinic clinoptilolite in the untreated zeolite and in the zeolite polluted with $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ cations

|  | Untreated zeolite | $Pb^{2+}$ | $Cd^{2+}$ | $Zn^{2+}$ |
|---|---|---|---|---|
| $a$ (Å) | 17.672($\pm$5) | 17.728($\pm$5) | 17.685($\pm$5) | 17.685($\pm$5) |
| $b$ (Å) | 17.940($\pm$5) | 17.983($\pm$5) | 17.917($\pm$5) | 17.951($\pm$5) |
| $c$ (Å) | 7.414($\pm$2) | 7.424($\pm$2) | 7.413($\pm$2) | 7.414($\pm$2) |
| $\beta$ | 116.23($\pm$3) | 116.27($\pm$3) | 116.27($\pm$3) | 116.24($\pm$3) |
| $\langle D \rangle$ (Å) | 1130($\pm$70) | 960($\pm$70) | 940($\pm$70) | 1000($\pm$70) |
| $\sqrt{\langle \varepsilon^2 \rangle} \times 10^{-3}$ | 1.7($\pm$3) | 1.2($\pm$3) | 0.8($\pm$3) | 2.0($\pm$3) |
| $R_{wp}$ | 8.9 | 9.5 | 11.7 | 10.4 |

fractions of $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ were respectively the 57, 18 and 32% of the cations adsorbed (Fig. 2).

The results of the sequential extraction procedure showed that low quantities of $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ were as water-soluble and exchangeable fractions. By contrast it was possible to believe that the main interaction mechanism between the sorbent and $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ was of physical nature; as a consequence of the electrostatic attraction between the negative charge density of the zeolite lattice and the positive charge of the cations. Therefore higher fractions of $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ extracted with $Ca(NO_3)_2$, as a consequence of formation of other sphere bonds, were expected. Instead the highest fraction of cations was extracted with EDTA. Likely, the $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ were adsorbed on zeolite through the formation of specific inner-sphere bonds, or alternatively the cation exchange process was of irreversible type.

These results suggested that a high fraction of $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ sorbed by zeolite was incorporated into the mineral and occupied the internal cages and channels of the zeolite. In this case, once present within the structure, the metals should remain trapped and no more soluble or exchangeable [25]. Then the cation fractions extracted with $H_2O$ and $Ca(NO_3)_2$ probably reflect the amount of metals sorbed at the external surfaces.

### 3.3. XRD analysis of zeolite samples

The quantitative analysis according to the Rietveld method [19] showed that the zeolite used in this study was mainly composed of clinoptilolite mineral (63 wt%) a tecto-alumo-silicate of Na, K and Ca with a monoclinic structure and the following cell parameters: $a = 17.67$ Å, $b = 17.94$ Å, $c = 7.41$ Å, $\beta = 116.23°$ (Table 3). Among the secondary phases the most important was the anorthite (25 wt%) which is a monoclinic Ca-alumo-silicate; traces of biotite and quartz were also present (Table 1).

The curve reported in the lower part of Fig. 3 represents the contribution of just the clinoptilolite phase calculated by the program in the final fit to the experimental data of unpolluted zeolite diffractogram. It can be seen that this contribution is preponderant and appears suitable to account for large part of the experimental data set. Thus, for its structural and chemical characteristics, clinoptilolite represents the phase of higher surface reactivity (Table 1).

Doping this natural zeolite with $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ cations seems to change slightly but significantly the monoclinic structure of clinoptilolite. The lattice parameters, retrieved after the

best fit procedure, do not change significantly and are reported in Table 3. This suggested that the $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ had to be partially or totally dehydrated when they were incorporated in the internal cages and channels of the zeolite [25].

Besides, formation of $Pb^{2+}$-, $Cd^{2+}$- and $Zn^{2+}$-hydroxides was not noticed.

As it concerns addition of $Pb^{2+}$ cations, it can be noticed in the upper pattern of the figure that most intense $(0\,2\,0)$ line profile, around 9.6 in the $2\theta$ degree, is lowered with respect to the not polluted zeolite. Overall, a change of the peak intensities is due to a change of some atomic positions within the unit cell or to an atomic density change [34]. After comparison of atomic coordinates of atoms it may be concluded that the most likely sites subjected to change are Wickoff positions 8$j$, which are commonly occupied by aluminium and silicon cations [35]. Thus, it is possible that $Pb^{2+}$ cations may be replaced for aluminium atoms in the lattice in the course of the ion exchange reaction. The substitution for silicon atoms appears more difficult. This mechanism may also be operative even in samples doped with Cd and Zn. Nevertheless due to the lower number of electrons involved in the exchange, the effects are less evident in the patterns so that conclusions about this point cannot be drawn.
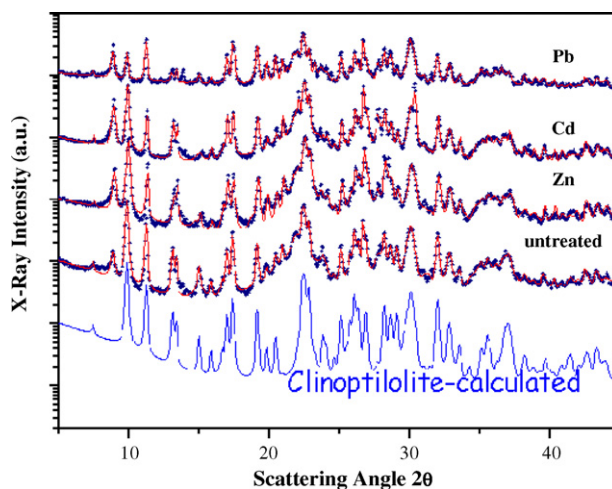


Fig. 3. Data points of experimental X-ray diffraction patterns and full lines after Rietveld refinement for the untreated zeolite sample and zeolite samples doped with $Zn^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ ions. The close match between experiment and calculation testify the fine structure description of the four zeolite systems. The curve at the bottom is the contribution to the simulation of the untreated pattern of only the clinoptilolite phase.

As it concerns the morphological feature of the phases it can be noticed that the X-ray peaks of the zeolite samples exchanged with $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ are broadened per se beyond the instrumental conditions. Generally this broadening is associated to the simultaneous effects from a reduced size of the microcrystals (crystallites) and to an increased amount of lattice disorder (microstrain) [36].

The MAUD programme used at the end of the numerical refinement process suggested that the microcrystallites of clinoptilolite of polluted samples are in average extended between 900 and 1100 Å, while the lattice disorder density is attested at a value of 1–2 defects each 1000 lattice planes considered across to the normal of the crystallographic direction observed (see values reported in Table 3) [20].

## 4. Conclusions

The natural zeolite used in this study was more selective for $Zn^{2+}$ cation. Besides the interaction between this metal, which has a smaller ionic radius, and the active surface of the zeolite was more intensive with respect to $Pb^{2+}$ and $Cd^{2+}$.

The quantities of cations extracted with $H_2O$ and $Ca(NO_3)_2$ from the polluted zeolite samples were lower than the fractions extracted with EDTA. The adsorption process probably did not involve only the superficial sites of the zeolite. In fact the metals could have entered into the cages and channels of the porous structure of this tectosilicates remaining trapped. The adsorption of these cations in their hydrated forms was impossible because according to their sizes they could not diffuse to the clinoptilolite micropores. This was confirmed by XRD analyses which showed that the incorporation of $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$, into the zeolite frameworks changed slightly the lattice parameters.

Besides, XRD analysis suggested the occurrence of some isomorphic substitution phenomena where probably the $Al^{3+}$ ions of the clinoptilolite framework were replaced by exchanged $Pb^{2+}$ cations.

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