



# Zeolite-Clinoptilolite conditioning for improved heavy metals ions removal: A preliminary assessment

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## ABSTRACT

The emerging problem of nickel allergy is increasingly widespread due to the increase in nickel content in everyday foods. The physicochemical structure of the zeolites makes it possible to adsorb nickel ions in solution. The properties of molecular sieves, together with those of a size and a chemical composition compatible with the human gastrointestinal tract, are present in a particular zeolite called clinoptilolite. In this work, a type of natural clinoptilolite was characterized before and after being subjected to two different conditioning processes with NaCl to increase its adsorption efficiency and specificity against nickel. The three forms of clinoptilolite, natural, conditioned, and biconditioned, were compared based on analysis of absolute density, X-ray diffraction pattern, granulometry, porosity, chemical composition, and grain morphology. Finally, nickel ion removal tests were performed in an aqueous solution that simulates the conditions of the gastrointestinal tract. The Ni<sup>2+</sup> removal efficiency of natural clinoptilolite is 73.2%, while after conditioning it reaches 96.6%. Double conditioning with Na does not generate a considerable increase in removal efficiency which remains at 96.8%.

## 1. Introduction

In such a vastly scientifically investigated field, zeolites, used for decades as molecular sieves [1,2], components for agricultural land [3], components for the treatment of polluted waters [4], catalysts of chemical processes [5], food supplements for livestock [6], and aluminosilicate precursors of geopolymer binders [7], still manage to find a space in research thanks to the advancement of technology and the emergence of new areas of application. Zeolites are crystalline hydrated aluminosilicates connected by a 3D anionic structure of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra linked together by the sharing of oxygen atoms. Tetrahedra are combined to form simple geometric structures (rings containing 3 to 6 tetrahedra) or more complex polyhedron structures, such as rings with multiple tetrahedra, chains, cages, and layers. The partial isomorphic substitution of Si<sup>4+</sup> with Al<sup>3+</sup> in the tetrahedral structure produces localized negative charge balanced by alkaline and alkaline-earth cations, mainly Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>. These cations are loosely bound and can be exchanged with other cations, making zeolites effective ion exchange materials [8]. The Cation Exchange Capacity (CEC) is directly influenced by the Si/Al ratio, as each aluminum atom present in the structure of the mineral corresponds to a negative charge located on its

surface [9]. Exchangeable hydrated cations are found on the external surface and inside the cavities and channels that characterize the aluminosilicate structure. Pores and channels are also occupied by water molecules which can be replaced by other adsorbates or reversibly removed. The general composition of the zeolites is expressed by the formula M<sub>m/z</sub>[mAlO<sub>2</sub>·nSiO<sub>2</sub>]·qH<sub>2</sub>O [10], where M represents the exchangeable cation with charge + z, and [mAlO<sub>2</sub>·nSiO<sub>2</sub>] means the crystalline anionic structure. The structure of zeolite is characterized by the presence of pores and channels that penetrate uniformly in the entire volume of the mineral, responsible for the high internal surface and the adsorption capacity toward various inorganic, organic, polar, and non-polar molecules. In this study, the adsorbing capacity of the zeolite towards the nickel ion Ni<sup>2+</sup> will be investigated.

Nickel is a widely diffused transition metal in water and soil deriving from natural sources or anthropogenic activities. The presence of this metal in environments dedicated to fruit and vegetable cultivation, naturally nickel fixers, determines non-negligible concentrations of this element in foods such as cocoa, dark chocolate, dried fruit, cereals, soy, tomatoes, etc. [11]. Furthermore, its widespread use in the metal and electronics industry makes human exposure to nickel practically inevitable [12]. In the past decades, several studies [13–15] have

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demonstrated the toxicity of this metal, and, in thousands of clinical cases and targeted tests, it has been possible to find a sensitivity to nickel in more than 5% of the population. Nickel allergy manifests with various symptoms and is mainly due to contact (allergic contact dermatitis, ACD) [16] or ingestion through food and water (systemic nickel allergy syndrome, SNAS) [15,17]. In both cases, desensitization therapy is used, which proceeds through a dosed and ever-increasing intake of the allergen to accustom the immune system to tolerate it over the years [18, 19]. For a treatment that leads to complete patient recovery, daily detoxifying nutraceutical use must be accompanied by a well-calibrated low-nickel diet for the specific case [19,20]. The methodologies and guidelines of this type of therapy are widely reported in the literature, unlike the techniques for reducing the nickel load in the acute phases of allergic reactions.

In this work, the experimental analysis of the specific removal conditions of the zeolite over nickel ion in an aqueous solution is aimed at studying this phenomenon in carefully designed environments for the simulation of the conditions present within the human gastrointestinal tract. Obtaining a natural nutraceutical supplement would make an innovative contribution to the problem of intolerance to nickel and the reduction of the effects on subjects suffering from this disorder. The results of this research are potentially applicable to an *in vivo* experimental campaign that would provide unpublished data in the literature on the reduction of the effects due to intolerance to nickel and SNAS. Among the studies reported in the literature, it was useful to consider the range of nickel concentration (0.5–3 mg/L) in the gastrointestinal tract of patients suffering from symptoms [21], for which it is necessary to intervene with metal detoxification. For this purpose, the use of natural Na<sup>+</sup> modified clinoptilolite as a food supplement is the potentially cheaper and safer solution with a lower global impact on the environment than current solutions. However, the adsorption process can be very selective or involve multiple types of sorbates [10,22]. In both cases, the exchange activity must be adequate for application purposes. The wide diversity of this mineral in nature, in terms of the chemical structure and atomic composition, determines the need for accurate characterization for the choice of specific applications for maximum effectiveness. In addition to the choice of the type of zeolite suitable for the specific application, physical or chemical treatment processes are often required to increase their efficiency [23]. In these terms, the role of the conditioning process is fundamental, as it determines the presence, in the pores and on the surface of the mineral, of species that, once desorbed, are not harmful to the system in which they are released and are highly selective in adsorption of nickel ions in aqueous solution. For the nutraceutical purposes of adsorbent over the nickel ion in the gastrointestinal tract, it is suggested the use of Na-Clinoptilolite [22], inserted in 2020 by the Food and Drug Administration (FDA) in the substances classified as "safe for human consumption" and declared "non-toxic" from the International Agency for Research on Cancer (IARC). This particular form of clinoptilolite is poorly available in nature as the volcanic processes from which it originates involve many metals and organic compounds that can contaminate the mineral. The presence of heavy metals makes natural zeolite unsuitable for nutraceutical use, as the desorption of these metals in the human body can cause short-term and long-term diseases. The clinoptilolite intended for this application, therefore, undergoes some purification treatments after the extraction process of the crystalline phase. Following these treatments, the micronized clinoptilolite is modified by mixing with NaNO<sub>3</sub> or NaCl solution [24]. During the modification process, complete cationic exchange occurs in favor of Na<sup>+</sup> with the formation of Na-Clinoptilolite. The function of sodium cations is twofold: on the one hand, they are harmless in the body once desorbed and on the other, they make the mineral more attractive and selective towards the nickel ion. The characteristics of the modified form of natural clinoptilolite with Na<sup>+</sup> are exploited in many specific application areas, such as CO<sub>2</sub> capture [24,25], wastewater treatment [26], and the medical field, thanks to its antibiotic activity [27,28].

From quantitative analyses of the amorphous phase (QPA) carried out with the Rietveld method by Davarpanah et al. on clinoptilolite and its form modified with Na<sup>+</sup>, it appears that both show the same phases with very similar bulk compositions: mainly clinoptilolite, kaolinite and illite as clay minerals and an amorphous fraction [25]. This demonstrated that the mineralogical composition of the sample is not affected by the modification process. The chemical composition, however, undergoes variations following cation exchange with Na<sup>+</sup>, present in negligible quantities in natural clinoptilolite. The analyses on the atomic percentage composition carried out by Dosa et al. on natural clinoptilolite show that the cations present in greater quantities are potassium, calcium, and iron (72.5% Si, 14.9% Al, 7.3% K, 3.7% Ca, 1.6% Fe from EDX, and 79.1% Si, 11.1% Al, 3.9% K, 3.8% Ca, 2.1% Fe from XRF analyses) [26]. The modification process with sodium, therefore, is also suitable in the nutraceutical field, where product standards are very high due to the many possible contraindications.

This work aims to evaluate the Ni<sup>2+</sup> removal efficiency of natural and conditioned clinoptilolite over nickel in an aqueous solution at 37.5 °C and pH 4.5 (average conditions in the gastrointestinal tract [29]), considering an initial nickel ion concentration of 2.0 mg/l, which constitutes the tolerance limit of most persons with nickel allergy [30], and a residence time of the zeolite in a treatment of 3 h, corresponding to the average digestion time of a meal.

## 2. Material and methods

### 2.1. Materials

The characterization and evaluation of the adsorption capacity towards the Ni<sup>2+</sup> ion in an aqueous solution were evaluated for three different types of zeolites:

- Natural Clinoptilolite.
- Clinoptilolite conditioned with Na.
- Clinoptilolite biconditioned with Na.

The natural zeolite used is a commercial Zecla superfine clinoptilolite (Atena Bio S. r.l, Treviso, Italy). As stated in the data sheet, the ivory-colored powder is 100% zeolite of which 94.5% is activated clinoptilolite. The product is supplied after a sequence of washes in an acid solution of distilled water to remove the impurities naturally present. Subsequently, the zeolite is micronized to increase the specific surface and therefore the adsorption efficiency. Although not explicitly reported in the datasheet, the most recognized micronization process included in best practices is the Jet Mill [31]. This grinding system provokes particle-to-particle impacts without heat generation and avoids particle contamination by metals and lubricating media. Jet Mill is a sanitary FDA-accepted design, in line with GMP practices and in accordance with all pharmaceutical specifications worldwide.

### 2.2. Conditioning

The conditioning procedure of the natural clinoptilolite [23] was carried out through the preparation of a 2 M NaCl (EMPROVE® bio Ph. Eur., Merck KGaA, Germany) solution with a volume of 600 ml using double distilled water. The solution was magnetically mixed with a stirrer at 200 rpm for a few minutes until the salt was completely dissolved. Subsequently, 60.0 g of natural clinoptilolite was added to the solution, which was left under stirring for 24 h, at room temperature, with a magnetic stirrer at 160 rpm covered with parafilm. The suspension obtained was filtered using a 2 L vacuum flask to collect the permeate. The suspension was poured into a Buchner funnel with a diameter of 100 mm in which a disc of Whatman filter paper (Whatman® plc, UK) with a diameter of 90 mm and 80 µm pores was housed. When the solution was poured, the vacuum was made with a Laboport N86 KT<sup>18</sup> KNF diaphragm pump (KNF®, Italy). The filtrate was tested

for pH with a Hanna Instruments HI12302 pH meter (Hanna Instruments®, USA) with Bluetooth technology. For the second wash, the cake was covered with a centimeter of double distilled water and the vacuum pump activated, finally, the deposit obtained was dried in an oven at 110 °C for 2 h and ground by hand in a ceramic mortar. After the second washing, the pH of the filtrates obtained was measured. The pH measurement as an indicator of the washing to be carried out is essential for the application of conditioned zeolites as a molecular sieve. The zeolites conditioned with NaCl could host in the pores of the structure traces of metal ions exchanged with sodium, but which have not completely counter-diffused to end up in solution, as well as chlorine ions precipitated on the surface or in the pores of the zeolite itself. These substances could reduce the adsorption efficiency of zeolites by inhibiting some active sites or obstructing otherwise accessible pores. Furthermore, these substances could be undesirably released into the solution to be sieved. Biconditioned clinoptilolite was obtained from conditioned clinoptilolite by mixing it for 24 h, at room temperature, in a 2.0 M NaCl solution prepared as for the first conditioning process. The suspension obtained was then filtered, dried, and ground with the same methods seen above. The pH-values of the filtrates of the washes for both conditioning were also detected.

### 2.3. Ni<sup>2+</sup> removal test

For the Ni<sup>2+</sup> removal tests, 2.0 mg/l nickel concentration solutions were prepared using the TraceCERT standard solution (TraceCERT®, Merck KGaA, Germany) at a nickel concentration equal to 1000 mg/l. The desired solutions were obtained by dilution with double distilled water. Three 100 ml solutions at a nickel concentration of 2.0 mg/l were placed in separate beakers and their pH was measured. In the first, 1.00 g of natural zeolite was suspended, in the second 1.00 g of conditioned zeolite, and the third 1.00 g of biconditioned zeolite. In all suspensions, the liquid-to-solid ratio is 100 ml/g-dry, and the pH is 4.5. The suspensions were left under stirring at 100 rpm on a magnetic plate heated to 37.5 °C for 3 h and subsequently filtered with a vacuum filter system to separate the zeolite from the solution. The filtrates were analyzed with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) PerkinElmer Avio 220 Max (PerkinElmer Inc.®, USA). The Ni<sup>2+</sup> removal tests were repeated five times and the results of the ICP analyzes were averaged for each type of clinoptilolite. The results thus obtained were used to calculate the removal capacity ( $q_e$ ) of clinoptilolites with respect to the nickel ion according to the following formula:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and final concentrations of Nickel in the solution,  $V$  is the volume of the solution and  $M$  is the mass of clinoptilolite added to the solution.

### 2.4. Characterization

The three types of clinoptilolite used for this study were characterized with the same techniques for a homogeneous comparison of their physical and chemical properties. The particle size distribution of the powders was analyzed using the Malvern particle sizer 3600 E Type laser granulometer (Malvern Panalytical®, Malvern, UK) operating in a range ranging from hundreds of nanometers to millimeters. These measurements provide three datasets for each sample type to define the average equivalent diameter of the zeolite grains, approximating them to a sphere. For the morphological characterization of the powders, the scanning electron microscope (SEM) Tescan Mira3 (Tescan®, Czech Republic) was used, which obtains images with a view field of 277 μm, 69.2 μm, and 39.5 μm operating at a working distance of 15 mm and a voltage of 15 kV. This analysis was coupled to the Energy Dispersive X-ray spectroscopy (EDS), using an Octane Elect EDS system (Edax®,

USA), to obtain information on the atomic composition of selected sample areas using dedicated software. The samples analyzed by this instrument require a pre-treatment that makes them conductive in order not to create light distortions in the detected images. This operation involves coating the dry sample with conductive material. For this purpose, Edwards Sputter Coater S150B (Edwards®, Sweden) was used for the deposition of a gold film on the sample. Porosity analyzes were performed by physisorption with Micromeritics 3Flex Surface Characterization (Micromeritics Instrument Corporation, USA) analyzer. This technique is applied to calculate the surface area with the BET method, the porous volume, and the distribution of the pore size of porous materials using the BJH method. A complete analysis of the crystalline structure of the powders was carried out by X-ray crystallography (XRD) with the PANalytical X'Pert Pro (Malvern Panalytical®, UK) diffractometer with Cu Kα ( $\lambda = 0.15418$  nm) incident radiation. This instrument produces the diffraction pattern at different angles of incidence of the beam, which was processed thanks to the X'Pert High Score software to determine all the crystalline phases present in the analyzed sample. The density tests were carried out through gravimetric measurements with a water pycnometer and He-pycnometer Micromeritics AccuPyc II 1340 (Micromeritics®, USA) after drying at 110 °C for 2 h to remove the relative moisture present in the powders.

## 3. Results and discussion

The three forms of zeolite analyzed in this study all come in the form of ivory-colored powder. In the conditioning process, pH measurements were made for the filtrates from the washes. From the measurements carried out for conditioned clinoptilolite, reported in Table 1, it was noted that after the first wash, the pH of the filtrate was weakly acidic (average pH 6.41), and after the second wash approached neutrality (average pH 6.67). The trend towards neutrality as the number of washes increases (average ΔpH 0.30) is matched by an ever-decreasing tendency on the part of the zeolite to release ions in the solution. For the biconditioned clinoptilolite, only one wash was performed for the first conditioning and two washes for the second conditioning. The values of the measurements carried out are shown in Table 2 and show the same trend seen above. The pH of the filtrates tends to be neutral as the number of washes increases, in fact, concerning the second conditioning, the average ΔpH (0.23) is very similar to that of conditioned clinoptilolite.

### 3.1. Ni<sup>2+</sup> removal tests

The Ni<sup>2+</sup> removal tests were carried out at an initial concentration of nickel in an aqueous solution of 2.0 mg/l, at a temperature of 37.5 °C, a pH of 4.5, and contact time of 3 h for the three types of clinoptilolite examined. From the results of the IPC analysis on the filtrates of the suspensions, it is possible to determine the final concentration of nickel in the solution. The nickel average concentrations in the solutions treated with natural, conditioned, and biconditioned clinoptilolite are respectively  $0.54 \pm 0.04$ ,  $0.07 \pm 0.02$ , and  $0.06 \pm 0.02$  mg/l. The nickel average removal efficiencies with the different treatments are therefore  $73 \pm 2\%$ ,  $96 \pm 1.5\%$ , and  $97 \pm 1\%$  respectively. Under these conditions the three forms of clinoptilolite show removal capacity ( $q_e$ ) to Ni<sup>2+</sup> of  $0.146 \pm 0.004$  mg Ni<sup>2+</sup>/g natural clinoptilolite,  $0.193 \pm 0.002$  mg Ni<sup>2+</sup>/g conditioned clinoptilolite and,  $0.194 \pm 0.002$  mg Ni<sup>2+</sup>/g

**Table 1**

Measurements of the pH carried out on the filtrates of the washing of the conditioned zeolite.

Wash\Sample	I	II	III	IV	V	Average pH
First wash	6.36	6.43	6.52	6.40	6.41	6.42
Second wash	6.82	6.65	6.70	6.70	6.73	6.72
ΔpH	0.46	0.22	0.18	0.30	0.32	<b>0.30</b>

**Table 2**  
Measurements of the pH carried out on the filtrates of the washing of the biconditioned zeolite.

Wash\Sample	I	II	III	IV	V	VI	VII	VIII	Average pH
First wash-conditioning 1	6.46	6.43	6.44	6.41	–	–	–	–	6.44
First wash-conditioning 2	–	–	–	–	6.49	6.53	6.46	6.52	6.50
Second wash-conditioning 2	–	–	–	–	6.74	6.85	6.62	6.69	6.73
ΔpH	–	–	–	–	0.25	0.32	0.16	0.17	0.23

biconditioned clinoptilolite. The results obtained are in line with those reported in the literature for natural and conditioned clinoptilolite [10, 23]. Fig. 1 shows the error bars referring to the variance of the tests carried out and the error of the instrument. It is evident that natural clinoptilolite put in contact with a nickel solution is able, under the conditions defined above, to stably exchange Ni<sup>2+</sup> ions, which are separated from the solution in the filtering operation.

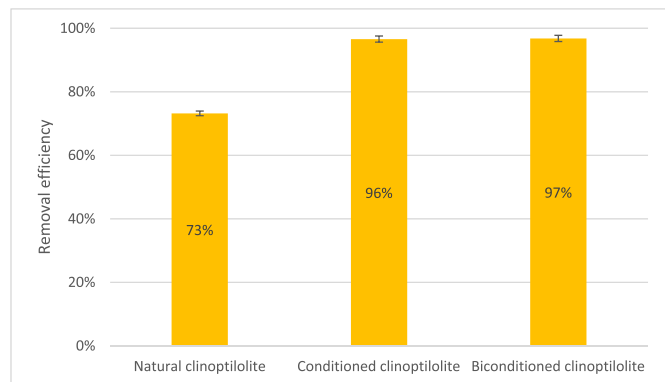
The adsorption process of exchangeable nickel cations in solution was examined by Argun [32] in thermodynamic and kinetic terms in a previous study. Fig. 2 shows the ion-exchange isotherm at 313 K of the clinoptilolite on Ni<sup>2+</sup> ions in conditions approximating those considered in this study. From the fitting of the data, it was found the best correspondence with the linearized Langmuir model expressed by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{bK} + \frac{C_e}{b} \quad (2)$$

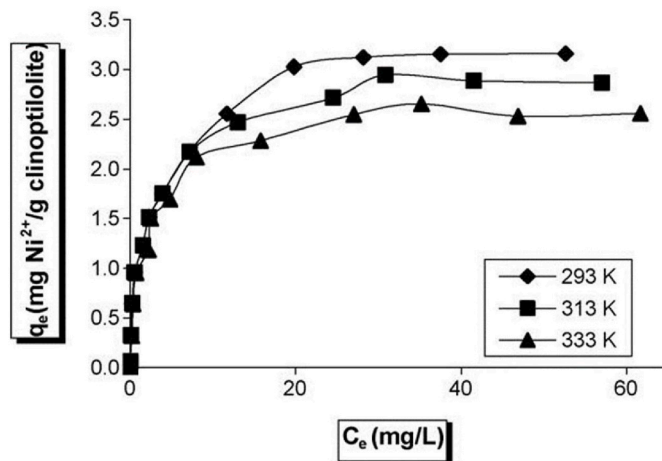
where *b* and *K* were calculated to be 2.97 mg/g and 0.194 l/mg respectively for a dosage of 15 g l<sup>-1</sup> of clinoptilolite at an agitation speed of 250 rpm, contact time of 180 min and pH 7. Under these conditions, Fig. 3 shows the correlation coefficients (R<sup>2</sup>) related to the linearization of the Lungmuir isotherm.

In order to define the ion exchange kinetics of Ni<sup>2+</sup>, pseudo-first-order and pseudo-second-order kinetic models were examined in the same study. From the comparison between the calculated and experimental ion exchange capacities, it was defined that the process follows a pseudo-second-order kinetic model. The second order kinetic constant is found to be 0.75 g mg<sup>-1</sup> min<sup>-1</sup> at a temperature of 313 K.

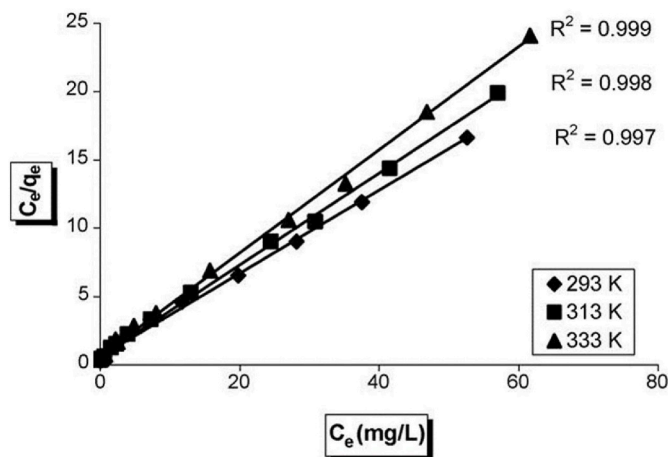
The conditioning of clinoptilolite makes sodium available for ion exchange, which, thanks to its low selectivity, leaves the site on the surface of the mineral to the Ni<sup>2+</sup> ion even at very low concentrations. The removal efficiencies evaluated show that the excellent result obtained for conditioned clinoptilolite did not improve much in the case of double conditioning. This result is limited to the operating conditions of the adsorption process, in which the nickel concentration initially present in the solution is 2.0 mg/l. For very low concentrations of ions in solution, the removal process is kinetically very limited by the low concentration difference (driving force) with respect to the pores of the mineral. The second conditioning process is therefore useless for the



**Fig. 1.** Nickel removal efficiencies from solutions treated with natural, conditioned and biconditioned clinoptilolite.



**Fig. 2.** Ion-exchange isotherms for clinoptilolite using different Ni concentrations ranging from 0.1 to 100 mg Ni(II) L<sup>-1</sup>. The clinoptilolite concentration was 15 g L<sup>-1</sup>, and the contact time was 180 min at pH 7 [32].



**Fig. 3.** The linearized Langmuir isotherm for ion-exchange of Ni<sup>2+</sup> by clinoptilolite. The clinoptilolite concentration was 15 g L<sup>-1</sup>, and the contact time was 180 min at pH 7 [32].

purposes of this research, and uneconomical as it needs double matter and energy compared to single conditioning. For this reason, biconditioned clinoptilolite was not subjected to granulometric and porosimetry characterization. The proposed conditioning process, therefore, is optimal for the adsorption of nickel in solution under the conditions seen. The characterization tests presented in this work are sufficient to demonstrate the conditioning efficacy and the ion exchange capacity of clinoptilolite against the nickel ion.

### 3.2. Characterization

The particle size analysis produced the distribution curves in Fig. 4, in which the same trend is evident for natural and conditioned

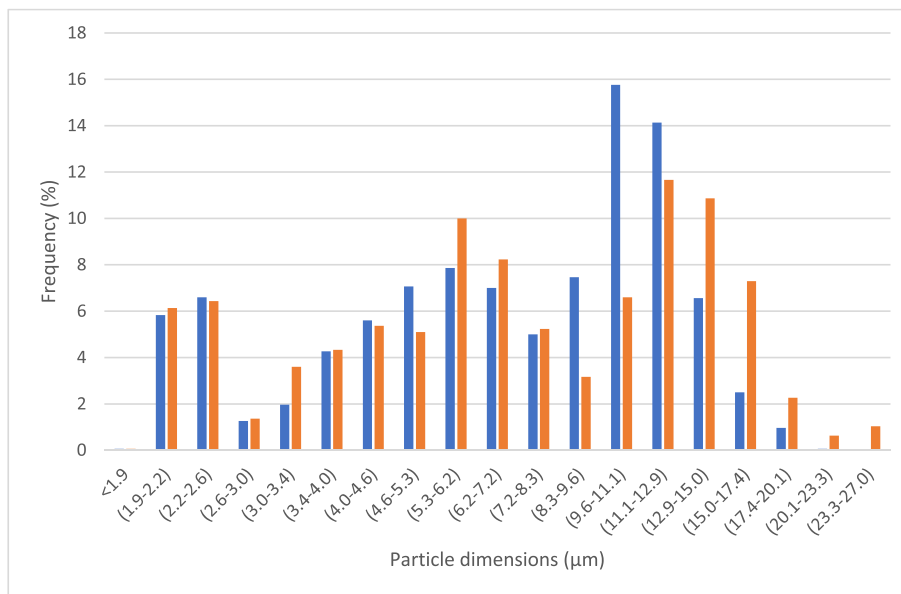


Fig. 4. Particle size distribution diagram of natural clinoptilolite (blue), and conditioned clinoptilolite (orange). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

clinoptilolite characterized by a peak around 2 μm, a second close to 6 μm, and a last one around 12 μm.

The morphology of the particles of the three different types of considered zeolite was investigated with SEM at three different magnification values. From the images detected at 2.5k X magnification (Fig. 5 a, 5. b, 5. c), it is evident, in natural clinoptilolite, the presence of a greater fraction of fine particles compared to the case of the two conditioned clinoptilolites. This effect may be due to the accumulation of sodium on the outer surface of the particles which are slightly larger

after conditioning. At magnification values of 10k X (Fig. 5d, 5e, 5f), the accumulation of sodium on the surface of the conditioned and biconditioned clinoptilolite particles is evident from the morphology of the single grains on which it is possible to notice compact agglomerates covering the entire surface of the single particles.

On the surface of three particles, among those observed at magnification 17.5k X, three areas (2.5x3 microns) were selected to carry out EDX analysis. The results, reported in Fig. 6 and Table 3, show that calcium, potassium, and magnesium are present in natural clinoptilolite

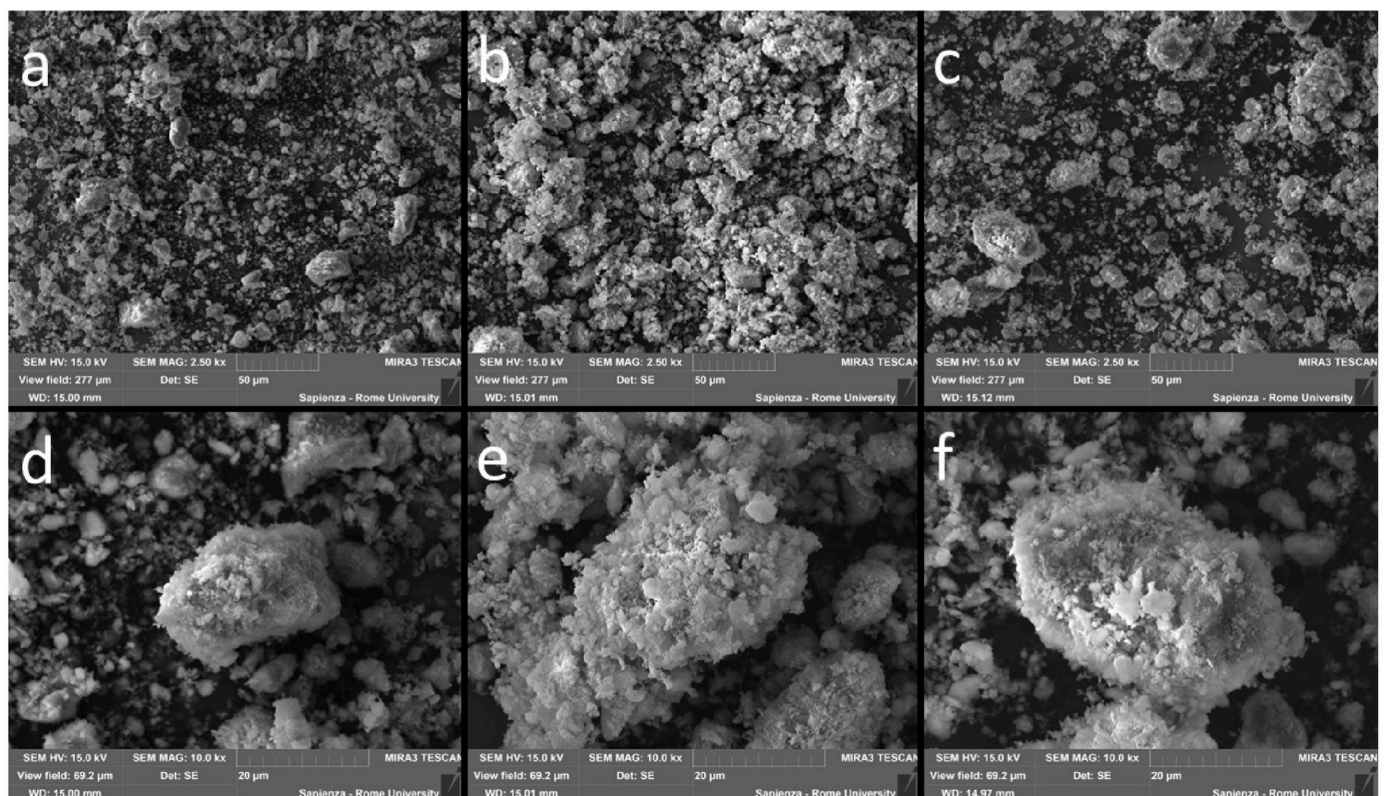


Fig. 5. SEM images of samples of natural clinoptilolite (a, d), conditioned clinoptilolite (b, e), and biconditioned clinoptilolite (c, f) at two different view field values.

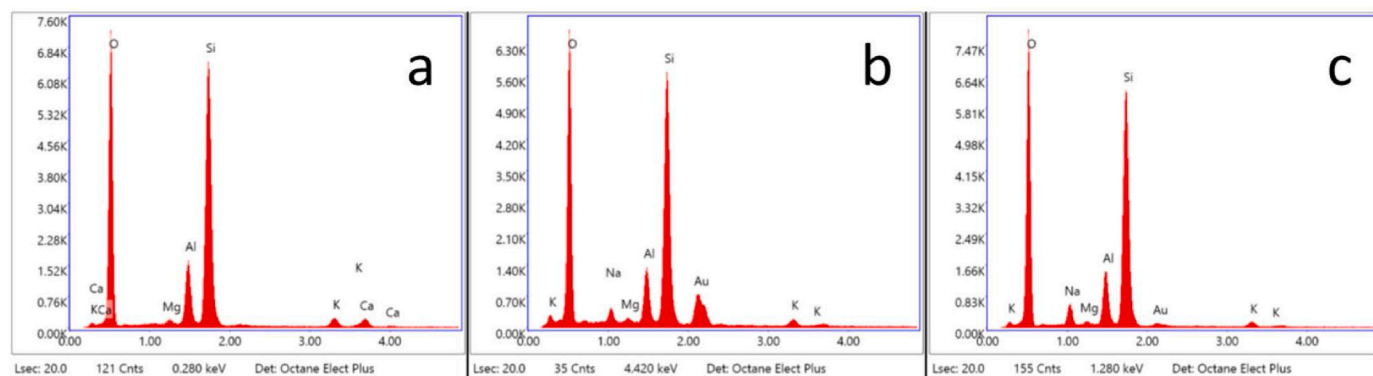


Fig. 6. EDX spectra for the elemental analysis of: a) natural clinoptilolite; b) conditioned clinoptilolite; c) biconditioned clinoptilolite.

Table 3

Elemental composition in atomic percentage of natural clinoptilolite, conditioned clinoptilolite, and biconditioned clinoptilolite particles carried out by EDX analysis.

Elements	Natural	Conditionated	Biconditionated
Si	74.4	76.9	75.8
Al	15.9	15.2	15.4
K	4.4	4.3	4.1
Mg	1.0	0.8	0.6
Ca	4.3	–	–
Na	–	2.8	4.1

as cations that balance the negative charge of the anionic structure composed of oxygen, silicon, and aluminum. Considering that the EDX analysis provides inaccurate data, especially for light elements such as oxygen, the results have been remodulated considering only aluminum, silicon, and the exchange metals. In conditioned clinoptilolite, calcium is absent, and 2.8% sodium is present in the atomic percentage. Biconditioned clinoptilolite has an atomic percentage of sodium (4.1%) comparable to the atomic percentage of calcium present in natural clinoptilolite (4.3%). Following the replacement of an almost equimolar amount of  $\text{Ca}^{2+}$  with  $\text{Na}^+$ , an excess of negative charge is created on the surface of the conditioned clinoptilolites. The charge can be balanced by  $\text{H}^+$  ions released by the water during the conditioning process. This confirms that the conditioning process produced the desired ion exchange between calcium and sodium and that the double conditioning increases the amount of sodium chemically bonded to the zeolite structure. Finally, these results confirm the characteristics Si/Al ratios for clinoptilolite (4.7 for natural clinoptilolite, 5.0 for conditioned clinoptilolite and 4.9 for biconditioned clinoptilolite).

From the physisorption tests performed, it was found that the isothermal adsorption curves of the three types of clinoptilolite analyzed belong to the IV class IUPAC, which is related to mesoporous materials. Using the BET method, surface area values of  $29.1 \text{ m}^2/\text{g}$  for natural clinoptilolite and  $30.3 \text{ m}^2/\text{g}$  for conditioned clinoptilolite were calculated. From the adsorption isotherms, it was possible to obtain a BJH analysis for the two types of clinoptilolite analyzed. In both cases, the pore size distribution curves show a peak between 15 and 20 nm (characteristic of mesoporous materials) and another peak in an interval close to 4 nm, which also guarantees the presence of a microporous structure of the particles. The values of the pore's surface area and the volume of the pores are comparable in the two cases as the conditioning process of the zeolite does not modify its anionic structure, which defines the porosity of the mineral. The results of the BET and BJH analysis are in accordance with those of the literature [33–35].

Confirming the chemical stability of the crystal structure of clinoptilolite in the conditioning process, the diffraction pattern of natural, conditioned, and biconditioned clinoptilolite was obtained. The pattern

obtained were treated through the software with which the characteristic intensity peaks were also identified and compared with the pure clinoptilolite pattern found in the literature. The matching between the literature data and the XRD analyses carried out confirms that for the natural zeolite and the two conditioned ones, the prevailing crystalline structure is that of clinoptilolite, with a monoclinic structure and chemical formula  $[\text{Na}_{1.84}\text{K}_{1.76}\text{Mg}_{0.2}\text{Ca}_{1.24}(\text{H}_2\text{O})_{21.36}][\text{Si}_{29.84}\text{Al}_{6.16}\text{O}_{72}]$  [36]. The obtained pattern, shown in Fig. 7, shows the angles corresponding to the intensity peaks. The three patterns are characterized by peaks practically coinciding with those reported in the literature for pure clinoptilolite [36].

In light of the results of the chemical composition and XRD analyses, it is evident that none of the three zeolite species analyzed corresponds stoichiometrically to pure clinoptilolite. EDS analyses reveal that sodium is not present among the cations of natural clinoptilolite, while calcium is present in higher atomic concentrations. The coincidence of the two patterns, therefore, suggests that it is Ca-Clinoptilolite, generally a product of the modification process of clinoptilolite with  $\text{Ca}(\text{NO}_3)_2$ . Similarly, the results obtained allow us to identify the two conditioned forms as Na-Clinoptilolite due to the prevalent presence of sodium, the absence of calcium and the correspondence of the physisorption and textural properties seen above. The chemical analysis finally confirmed that the deposit, highlighted in the micrographs, of the conditioned forms is due to accumulations of sodium, perfectly dissociated from the chlorine, which is not among the elements detected by the EDS analyses.

The density measurements performed by water pycnometer were repeated five times for each type of clinoptilolite. The results of the absolute density calculations ( $2.2 \pm 0.055 \text{ g/cm}^3$  natural clinoptilolite,  $2.19 \pm 0.017 \text{ g/cm}^3$  conditioned clinoptilolite,  $2.150 \pm 0.004 \text{ g/cm}^3$  biconditioned clinoptilolite) show that the ion exchange between the sodium of the conditioning and the metal species present on the surface of the natural clinoptilolite is occurred thus lowering the average of absolute density of the clinoptilolite after any conditioning process. The tests with a helium pycnometer confirmed the trend of the results obtained ( $2.238 \pm 0.0024 \text{ g/cm}^3$  natural clinoptilolite,  $2.227 \pm 0.0011 \text{ g/cm}^3$  conditioned clinoptilolite,  $2.188 \pm 0.0005 \text{ g/cm}^3$  biconditioned clinoptilolite) resulting in higher average values given the greater permeability of the helium with respect to the water in the pores. These results are in fact more reliable and consistent with the literature data [33,34]. In light of the results of the characterization, it is possible to hypothesize that the substitution between calcium and sodium, which took place in the first conditioning, decreased the mass of the conditioned clinoptilolite. At the same time, the apparent volume of the mineral has also decreased since the  $\text{Ca}^{2+}$  ions are sterically bulkier than the  $\text{Na}^+$  ions and can obscure part of the pores. In the calculation of the densities, in these two cases, similar values are obtained as mass and apparent volume decrease, balancing, following conditioning. In the second conditioning process, there is an accumulation of sodium with an increase in the volume of the mineral. The increase in atomic percentage

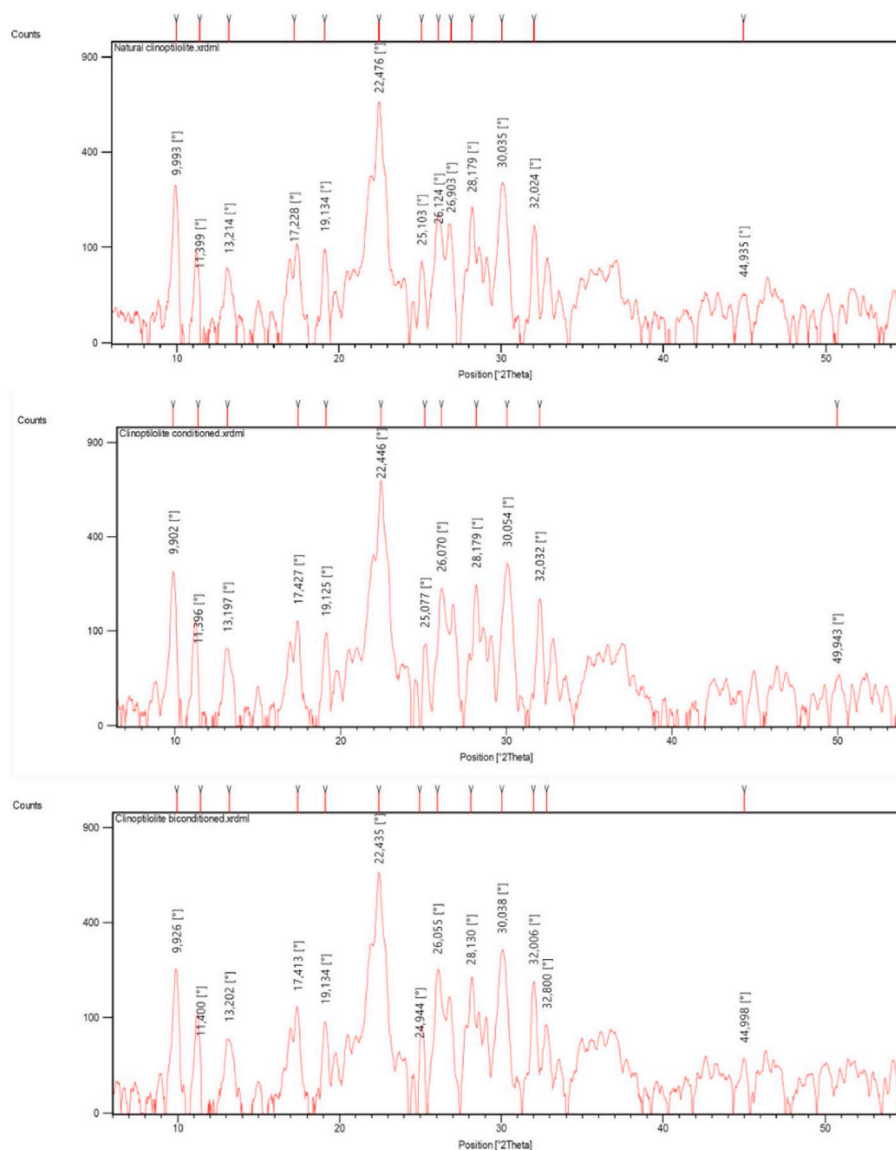


Fig. 7. XRD pattern of natural clinoptilolite, conditioned clinoptilolite and biconditioned clinoptilolite samples. The values of the angles corresponding to the intensity peaks are indicated in the respective graphs.

of Na in the biconditioned clinoptilolite causes a reduction in the average atomic weight with a corresponding significant decrease in density.

#### 4. Conclusion

Clinoptilolite in micronized powder form could be suitable as a nutraceutical for reducing the load of heavy metals from the gastrointestinal tract. Regarding nickel allergy, the ion exchange capacity of clinoptilolite against the  $\text{Ni}^{2+}$  ion has been confirmed through in vitro adsorption tests. Nickel solutions simulate conditions in the gastrointestinal tract (pH 4.5, 37.5 °C) with an initial concentration of 2.0 mg/l and residence time of 3 h. The studied zeolites are natural clinoptilolite, conditioned with sodium, and doubly conditioned with sodium. The crystalline structure of clinoptilolite is unchanged following the conditioning process, which is confirmed as a suitable treatment for the use of zeolite in the nutraceutical field. The chemical composition, after conditioning, varies in the presence of sodium, substituted for the calcium initially present in natural clinoptilolite. The latter has a similar density than conditioned clinoptilolite. In the second conditioning, more sodium was adsorbed without releasing other ions, and the oversaturation of

biconditioned clinoptilolite is demonstrated by a lower absolute density value than in the case of conditioned clinoptilolite. The morphology of the particles shows an accumulation of sodium on the surface of the two conditioned clinoptilolites. The images confirm the lower specific surface value for natural clinoptilolite, which therefore has a slightly smaller average particle size than the conditioned ones. The conditioning does not modify the porosity of the mineral as the surface area values are similar for the three clinoptilolites studied. The adsorption tests on the  $\text{Ni}^{2+}$  ion have shown that the conditioning process improves the removal efficiency from  $73 \pm 2\%$  of natural clinoptilolite to  $96 \pm 1.5\%$  of conditioned clinoptilolite. The second conditioning, on the other hand, is irrelevant in nickel removal as the removal efficiency of biconditioned clinoptilolite ( $97 \pm 1\%$ ) does not vary with respect to single conditioning. The excellent removal efficiency shown by Na-conditioned clinoptilolite and its compatibility as a nutraceutical supplement foresee, as the future development of this work, the tuning of an experimental in vivo campaign of clinoptilolite administration for the reduction of nickel load from allergy sufferers and the consequent reduction of associated symptoms. Negative effects on human health are also found due to the ingestion of other heavy metals such as Hg, Pb and Cd for which clinoptilolite is an adsorbent. The removal phenomena and

the characterization of the powder will be developed in a similar way by considering the metals individually and competitively. Finally, the characterization of zeolite powders defines the chemical and physical parameters of clinoptilolite with the prospect of designing an efficient and eco-sustainable synthesis process to avoid the depletion of natural resources and the natural variability of the mineral.

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## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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