Use of natural and treated zeolite for soften drinking water in the municipality of Carmen

Uso de zeolita natural y tratada para ablandar el agua potable del municipio del Carmen

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The main contribution of this research lies in the evaluation of clinoptilolite zeolite, both in its natural and modified form, as a sustainable and economic solution for the softening of drinking water in the municipality of El Carmen. This study not only structurally characterizes the properties of the zeolite using advanced techniques such as XRD and IR, but also delves into its chemical behavior by determining the point zero charge (PZC) and evaluating adsorption isotherms. In addition, the effects of pH on the adsorption process were identified. These results contribute to the development of alternative materials for water treatment, reducing the dependence on conventional technologies of higher cost and energy consumption, and promote the use of local resources with low environmental impact. The relationship between pH and adsorption: pH control is essential to avoid precipitate formation and maximize the effectiveness of the material in practical applications. The structural stability of the treated zeolite: This ensures its viability for long-term implementation in water treatment systems. The flexibility and scalability of the method: The results allow extrapolating this approach to other global contexts where water hardness represents a problem, promoting the application of economical and environmentally friendly solutions. Structural analyses confirmed that the chemical modification does not significantly affect zeolite stability, but does increase its ion exchange capacity. However, it was identified that pH plays a crucial role in the adsorption process, since under basic conditions it can promote the precipitation of hardness ions, which affects the accuracy of the measurements. This work highlights the importance of optimizing the experimental conditions, in particular pH control, to improve the efficiency of the process.

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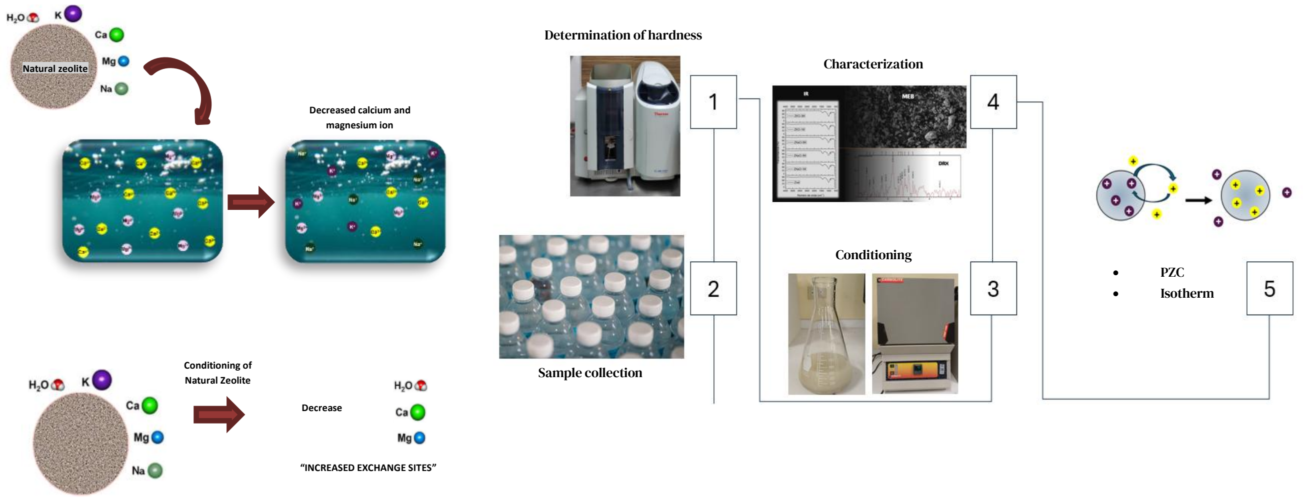
Abstract

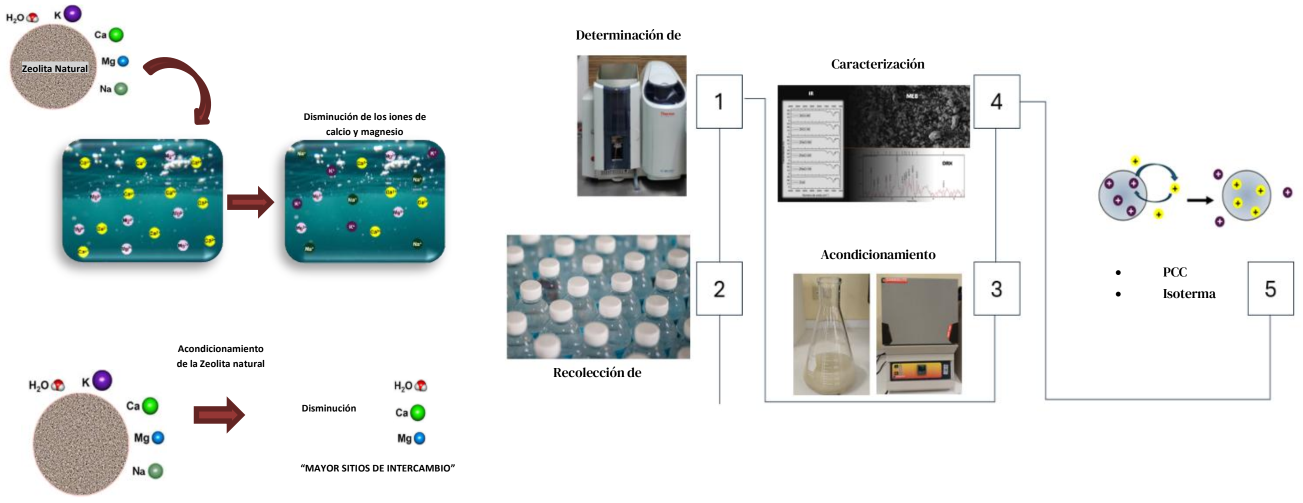
This study addresses the use of Clinoptilolite-type zeolite, natural and modified with sodium chloride (1M, 3M y 5M) and potassium chloride (1 M y 3 M), to reduce water hardness by adsorbing calcium and magnesium ions. Clinoptilolite is structurally characterized by X-ray diffraction (XRD) and infrared spectroscopy (FTIR) to evaluate changes in its structure and functional groups after modification, and its point of zero charge (PZC) is determined to understand the effect of pH on adsorption. Adsorption experiments, performed under controlled conditions, show that modified zeolite increases its efficiency compared to natural zeolite, although it is observed that pH can induce precipitation of hardness ions, affecting the accuracy of the measurements.



Hardness, Ion exchange, Zeolite

Resumen

Este estudio aborda el uso de zeolita tipo Clinoptilolita, natural y modificada con cloruro de sodio (1 M, 3 M y 5 M) y cloruro de potasio (1 M y 3 M), para reducir la dureza del agua mediante la adsorción de iones de calcio y magnesio. La Clinoptilolita se caracteriza estructuralmente mediante difracción de rayos X (DRX) y espectroscopía infrarroja (FTIR) para evaluar cambios en su estructura y grupos funcionales tras la modificación, y se determina su punto cero de carga (PZC) para entender el efecto del pH en la adsorción. Los experimentos de adsorción, realizados en condiciones controladas, muestran que la zeolita modificada incrementa su eficacia en comparación con la zeolita natural, aunque se observa que el pH puede inducir la precipitación de los iones de dureza, afectando la precisión de las mediciones.



Dureza, intercambio iónico, zeolita

Introduction

Water hardness is a widely studied phenomenon of significant relevance, as it affects both the efficiency of distribution systems and the lifetime of household appliances and other water-dependent equipment. Hardness is mainly due to high concentrations of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, which react with cleaning agents, forming insoluble compounds that reduce their effectiveness, and the accumulation of scale that affects water conveyance systems. In the Municipality of Carmen, Mexico, where water hardness levels represent a challenge for residents, there is an urgent need to implement affordable and sustainable solutions to improve drinking water quality.

There are several techniques for water softening, including the use of membrane technologies and reverse osmosis, which are the most common, but have certain limitations such as high energy consumption and high operational costs. In the face of these limitations, the use of natural and treated zeolites emerges as a promising alternative due to their ion exchange capacity, low cost and availability in various regions. Zeolites are porous minerals with a crystalline structure that allows the adsorption and exchange of specific ions; in the context of this project, their ability to remove calcium and magnesium, responsible for water hardness, is investigated.

This study focuses on Clinoptilolite zeolite, a type of natural zeolite, whose effectiveness is analysed after a modification process with sodium and potassium. These elements are selected because of their ability to increase the zeolite's affinity for calcium and magnesium ions, thus improving its ion exchange capacity compared to untreated zeolite. In addition to evaluating the efficiency of treated zeolite in water softening, this study investigates the structural stability of the material during the adsorption process, an essential feature for its possible implementation in domestic filtration systems.

Methodology

Water sample collection

Water samples were collected at various locations in the Municipality of Carmen, Campeche, and nearby areas, including Chicbul, Checubul, Sabancuy, Isla Aguada, Frontera, Hecelchakán and Mérida. In each of these localities, samples were taken from representative water bodies, while in the case of the Municipality of Carmen, samples were taken directly from the household drinking water intake at the point of domestic supply.

The samples were collected in polystyrene bottles of approximately 1 L, previously cleaned and rinsed to avoid external contamination. They were then transported to the laboratory under appropriate conditions. The pH of each sample was measured and the concentration of calcium and magnesium was calculated by flame atomic absorption spectrophotometry using a Thermo Scientific ^{iCETM} 3000 spectrophotometer. For the determination of calcium, acetylene gas was used, and for magnesium, nitrous oxide, using ultra-dry air as an auxiliary gas in both cases.

Conditioning of Clinoptilolite-type natural zeolite

Clinoptilolite-type natural zeolite was initially washed with 500 mL of deionised water, immersing 100 g of the material. It was left in agitation at 190 rpm for 30 minutes. This procedure was repeated three times, followed by additional rinses with deionised water until the rinse water was clear. The zeolite was allowed to dry at room temperature and subsequently heat treated at 250 °C for two hours.

Subsequently, the washed zeolite was conditioned in sodium chloride (NaCl) solutions at 1 M, 3 M and 5 M concentrations, and in potassium chloride (KCl) solutions at 1 M and 3 M concentrations. For the NaCl treatment, 50 g of zeolite were immersed in 500 mL of the solution and left in constant agitation at 190 rpm for 3 hours; this procedure was repeated twice for each concentration. In the case of the KCl treatment, 50 g of zeolite were immersed in 500 mL of the solution for 2 hours with agitation at 190 rpm, repeating the procedure three times for each concentration.

Once the treatments with NaCl and KCl at different concentrations were completed, the zeolite was rinsed with deionised water, then filtered and dried at room temperature. Finally, the conditioned zeolite was sieved using a #10 sieve to ensure uniform particle size.

Characterisation

The crystalline structure of the natural and conditioned zeolite was analysed by X-ray diffraction (XRD) using a GNR APD 2000 PRO diffractometer. The analysis was performed with Cu-Kα radiation (1.5406 Å) in a 2θ range from 10° to 60° and a step size of 0.02°.

Characterisation of the zeolite functional groups was performed by Fourier Transform Infrared Spectroscopy (FTIR) in the range of 4000 to 500 cm-^{1}. The spectra were obtained in terms of % transmittance, allowing the identification of the characteristic vibrational modes of the functional groups present in the zeolite structure.

Determination of the point zero charge (PZC)

The point zero charge (PZC) of natural and conditioned zeolite is calculated using the pH derivative method. For this purpose, a series of 0.01 M calcium chloride ($CaCl_2$) solutions were prepared with pH adjusted to values of 2, 4, 6, 8, 8, 10 and 12, using HCl or NaOH as required. To each 50 ml of the pH-adjusted solution, 0.1 ± 0.0005 g of zeolite was added.

The suspensions were allowed to stand for 24 hours to reach equilibrium. Subsequently, they were filtered to obtain only the resulting solution, and the final pH of each solution was measured using a Hanna Instruments edge® pH meter, which allows accurate pH and temperature measurement with automatic temperature compensation (ATC).

To determine the PZC, the final pH is plotted against the initial pH of each solution. The zero loading point was identified at the pH value where the curve shows that the initial pH and final pH are equal, indicating the absence of net loading on the zeolite surface.

Evaluation of adsorption isotherms

The adsorption capacity of zeolite for calcium and magnesium ions was evaluated by means of adsorption isotherms. For this purpose, solutions of calcium and magnesium ions were prepared at different concentrations (10, 20, 50, 100, 250, 500, 500, 700, 800, 900 and 1000 ppm). In each adjusted solution, 0.1 ± 0.0005 g of natural or conditioned zeolite was dispersed and left in contact for 24 hours under constant stirring at 190 rpm to ensure adsorption equilibrium.

, the samples were centrifuged for 3 minutes at 1680 RCF to separate the zeolite from the solution. The final concentration of ions in the solution was determined by flame atomic absorption spectrophotometry using a Thermo Scientific iCE 3000 spectrophotometer. The data obtained allowed the evaluation of the adsorption capacity of the zeolite as a function of the initial concentration of ions in solution.

Results

X-ray diffraction (XRD)

The structural characterisation of the natural zeolite and its modified versions was performed by X-ray diffraction (XRD) as shown in figure 1, evaluating the effects of treatment with sodium chloride (NaCl) at 1 M, 3 M and 5 M concentrations, and with potassium chloride (KCl) at 1 M and 3 M concentrations on the crystalline structure of the Clinoptilolite type zeolite. The XRD pattern of the natural zeolite shows characteristic peaks of Clinoptilolite at 2θ at approximately 22.5°, 27.5° and 32.2°, indicating a well-defined crystal structure. Samples treated with NaCl at different concentrations maintain the main peaks of natural zeolite, although a gradual decrease in the intensity of these peaks is observed with increasing NaCl concentration. This effect suggests a progressive ion exchange that slightly affects the crystallinity without significantly altering the structure of the clinoptilolite. On the other hand, samples treated with KCl at 1 M and 3 M also retain the main peaks, with a slight decrease in intensity that becomes more pronounced at higher concentrations. The reduction in the intensity of the peaks in these samples may be related to the larger size of the K^+ ion in comparison to Na^+.

Box 1

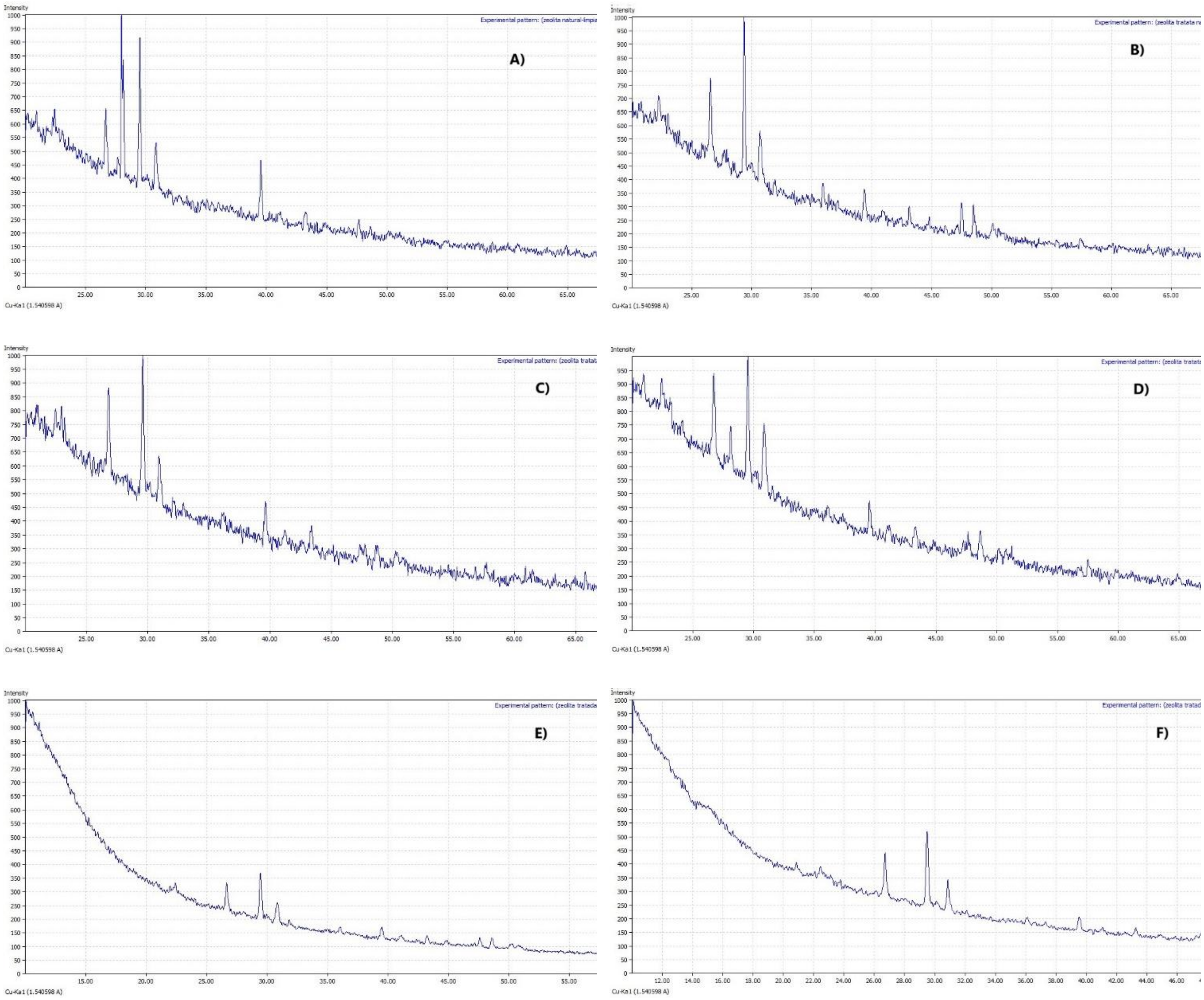


Figure 1

XRD patterns corresponding to Clinoptilolite type zeolite: A) clean natural zeolite, B) zeolite treated with 1M NaCl, C) zeolite treated with 3M NaCl, D) zeolite treated with 5M NaCl, E) zeolite treated with 1M KCl, F) zeolite treated with 3M KCl.

Source: [*Own elaboration*]

In conclusion, XRD patterns indicate that the structure of Clinoptilolite in zeolite remains stable after NaCl and KCl treatments, although a slight decrease in crystallinity is observed with increasing cation concentration. These results demonstrate the ability of clinoptilolite to withstand ion exchange modifications without losing its basic crystalline structure, which supports its use in water treatment applications.

Infrared (IR) spectroscopy

Infrared (IR) spectra of both natural and modified Clinoptilolite zeolite samples were obtained to evaluate structural changes and the presence of key functional groups. In the range 4000-3000 cm-^{1}, a broad band is observed in all samples, corresponding to the stretching vibrations of the -OH groups, which is characteristic of the presence of water in the zeolitic structure, an inherent feature of zeolitic materials due to their hydrated structure. The bands around 1650 cm-^{1} are associated with the bending vibrations of adsorbed water, evidencing the ability of clinoptilolite to retain water even after modifications.

In the case of the NaCl and KCl treated samples, slight variations in the band intensities will be observed in the 1000-450 cm-^{1} range, especially in the peaks around 1020 cm-^{1}, which correspond to the asymmetric stretching vibrations of the Si-O and Al-O bonds in the Clinoptilolite structure. This suggests that, although the basic crystal structure of the zeolite is maintained, the ion exchange process generates slight modifications in the chemical environment of the Si-O-Al groups due to cation substitution at the exchange sites.

The bands between 600 and 450 cm-¹, related to the bending vibrations of SiO_4 and AlO_4 tetrahedra, show subtle changes in the treated samples, which could indicate modifications in the cation exchange sites due to the introduction of Na^+ and K^+ ions. According to previous studies, these changes in the intensities of the IR bands may be associated with an increased affinity of the modified clinoptilolite for the adsorption of certain metal ions, due to alterations in the electric field generated by the exchanged cations (Hao et al., 2018; Mamba, 2010).

Box 2

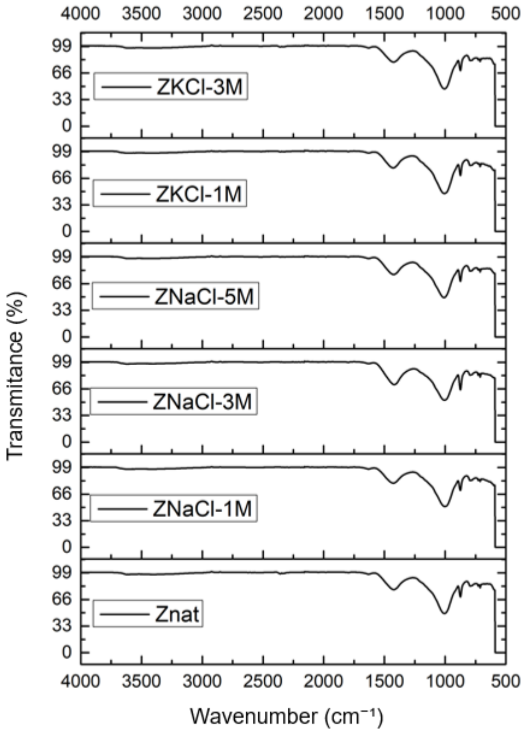


Figure 2

FTIR spectra of zeolite type Clinoptilolite, natural and treated with NaCl (1M, 3M and 5M) and KCl (1 and 3M).)

Source [Prepared by the author]

These results confirm the structural stability of clinoptilolite after treatment with NaCl and KCl and suggest that these modifications may optimise its ion exchange capacity for water treatment applications by increasing the accessibility of active sites without compromising the integrity of the zeolitic structure.

Point of zero charge (PZC)

The determination of the point zero charge (PZC) was performed for natural and modified zeolite with sodium chloride (NaCl) and potassium chloride (KCl) at different concentrations. Figure 3 shows the results of initial pH vs. final pH for each sample, which allows the PZC of each sample to be identified. The PZC of the natural zeolite is found at pH 7.8, indicating that at this pH the net surface charge of the zeolite is neutral, an important characteristic for its ion exchange efficiency. In the case of zeolite modified with sodium chloride at a concentration of 1 M, the PZC decreases slightly to 7.4, suggesting that this modification may enhance the zeolite's ability to attract positive ions, such as calcium and magnesium, in a slightly lower pH range. This behaviour is consistent with the idea that ion exchange with Na^+ can adjust the surface charge of zeolite, making it more receptive to specific cations in solution. By increasing the sodium chloride concentration to 3 M, the PZC increases slightly to 7.6. This change suggests that the higher NaCl concentration can partially compensate for the decrease in PZC observed at lower concentration, maintaining the effectiveness of the material for ion exchange applications. On the other hand, the zeolite modified with potassium chloride at a concentration of 1 M shows a PZC of 7.8, a value similar to that of the natural zeolite, indicating that modification with K^+ does not significantly alter the surface charge of the zeolite compared to the natural zeolite.

Box 3

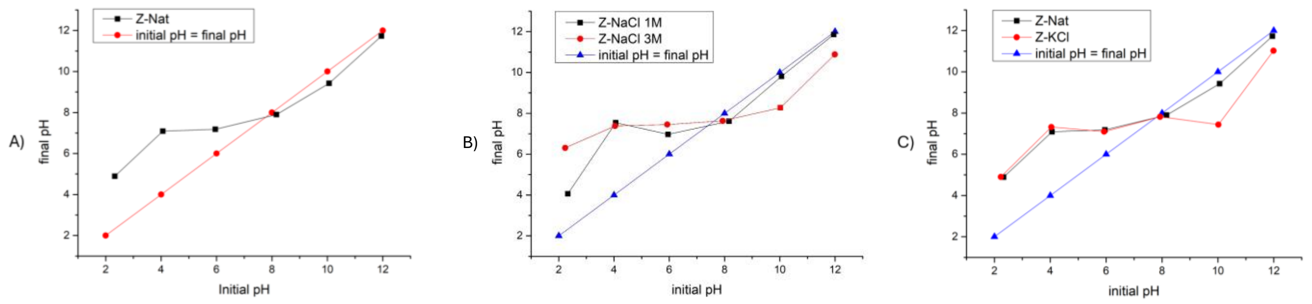


Figure 3

pHpzc of Clinoptilolite type zeolite: A) clean natural zeolite, B) zeolite treated with NaCl at 1M and 3M, C) zeolite treated with KCl at 1M and 3M compared to clean natural zeolite

Source [Own elaboration]

Evaluation of adsorption isotherms

Calcium and magnesium adsorption isotherms on natural zeolite show inconsistent results in terms of concentration variation between initial (Ci) and final (Cf) values after 24 hours of contact. At some concentrations, the final concentration of calcium and magnesium ions in solution is higher than the initial concentration, which is not an expected behaviour in an adsorption process. Additionally, it is observed that the initial concentrations of the solutions decrease after the waiting period, suggesting that the concentration values of the prepared solutions were altered during the adsorption time. This phenomenon could be related to the interaction of the zeolite with the solution, which could have caused an ionic exchange releasing calcium and magnesium from the zeolite matrix into the solution (Kordala & Wyszkowski, 2024). Alternatively, the high pH may have favoured processes of partial dissolution of impurities present in the zeolite or the formation of colloidal species that did not completely precipitate, thus contributing to an increase in the concentrations of these ions detected by atomic absorption spectroscopy (Kordala & Wyszkowski, 2024).

Box 4

Table 1

Isotherm of magnesium for natural zeolite		
Concentration (ppm)	**Ci (mg/L)**	**Cf (mg/L)**
10	0.73	4.54
20	5.78	5.46
50	12.025	13.05
100	45.5	44.1
250	56.3	68.7
500	157.5	177.5
700	120.4	100.8
800	598.4	446
900	568.4	546
1000	714	433

Source *[Own elaboration]*

Box 5

Table 2

Isotherm de calcium para zeolita natural		
Concentration (ppm)	**Ci (mg/L)**	**Cf (mg/L)**
10	5.19	4.22
20	12.79	16.36
50	26.32	30.05
100	59.94	74.66
250	126	163.5
500	284.2	344.9
700	405	376.8
800	500.2	512.3
900	567.1	579
1000	681.5	752

Source [Own elaboration

Calcium and magnesium concentrations in the collected water samples show relatively low hardness values (Table 3). This low concentration could be related to the influence of pH in the samples, as they present pH values around 7 and 8, which could be promoting the sedimentation of calcium and magnesium ions in the form of precipitates, thus reducing the measurable concentrations of these ions in the water (Neal & Stanger, 1984; Yan et al., 2020). This phenomenon suggests that the atomic absorption equipment is not capturing the total hardness of the samples due to the sedimentation of the hardness ions under basic pH conditions (Neal & Stanger, 1984; Yan et al., 2020).

Box 6

Table 3

Calcium and magnesium concentration in water samples

Place	Conc. De Ca (mg/L)	Conc. De Mg (mg/L)
Champotón	39.15	26.1
Chekubul	15.18	13.02
Aguada Island	14.16	4.71
Merida City	16.5	7.65
Frontera	31.53	22.29
Hecelchakán	35.94	18.42

Source [Own elaboration]

Conclusions

In this study, the adsorption capacity of Clinoptilolite zeolite, both in its natural and modified form, was evaluated for the removal of calcium and magnesium ions under specific concentration and pH conditions. The results indicate that natural and modified zeolite with sodium chloride and potassium chloride show a tendency to reduce the concentration of these ions in solution, although with some inconsistencies attributed to the effect of pH on the adsorption process. The relationship between the point zero charge (PZC) of the zeolite and the pH of the solution was decisive: when the pH of the solution exceeds the PZC of the zeolite (approximately pH 7.8), the surface of the zeolite acquires a negative charge that favours the adsorption of the hardness ions. However, at higher pH, precipitation of the ions in the form of insoluble compounds becomes a relevant factor, affecting the accuracy of concentration measurements by atomic absorption spectroscopy.

The sedimentation of calcium and magnesium ions, both in the solutions prepared for the isotherms and in the water samples collected, represents a challenge for obtaining reliable hardness measurements. These results suggest that pH control is a critical factor in future studies of hardness ion adsorption on zeolites. Adjusting the pH of solutions or implementing complementary techniques to quantify total hardness in the presence of precipitates could improve the accuracy and reliability of measurements. In conclusion, although clinoptilolite presents considerable potential for the treatment of hardness in water, the results of this study highlight the need to optimise the experimental conditions, especially with regard to pH control and knowledge of the zeolite PZC, to ensure effective adsorption and accurate measurement of hardness ions in solution. Future studies should focus on optimising these variables and evaluating the zeolite's efficacy under varying environmental conditions in order to maximise its applicability in water treatment systems.

Declarations

Conflict of interest

The authors declare that they have no conflicts of interest. They have no financial interests or personal relationships that could have influenced this book.

Authors' contribution

Gutiérrez-Laffon, Yazmin Michelle: Drafting, data analysis, figure development
Anguebes-Franseschi, Francisco: General revision
Abatal, Mohamed: Editorial revision, review of results and proofreading.
Aguilar-Ucán, Claudia Alejandra: General revision.

Availability of data and materials

The information contained in this document is not available, as data are still being worked on.

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Abbreviations

DRX	X-ray diffraction
FTIR	Infrared spectroscopy
PZC	Zero point charge
RCF	Relative centrifugal force

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Background

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