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Effect of Acid Treatment on the Physicochemical Characteristics and Sorption Capacity of a Natural Zeolite

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Abstract

Mining is a very important industry for the development of emerging economies; however, it generates a large number of environmental externalities such as acid mine drainages; these have acid pH values and high heavy metal content. Although there are several methods for the elimination of metals in different solutions, they require a large economic investment. Recently, the use of adsorbent materials for the removal of heavy metals in acid drains such as agricultural by-products and natural zeolites has been developed as a cheaper alternative. In spite of the environmental benefits of using natural zeolites as adsorbent, one of the disadvantages is dealumination, which to a great extent could depend on the geological origin of the mineral that shapes some of its characteristics. This study characterized chemical and physical properties of natural and modified zeolites using various techniques, such as X-ray diffraction (XRD), N2 adsorption- desorption, inductively coupled plasma − optical emission spectroscopy (ICP-OES), and SEM-EDS to determine the effect of an acid treatment on the physical and chemical characteristics of a natural zeolite, correlating these with their sorption capacity. When giving acid treatment to a zeolite there are no significant changes in the crystal structure, the Si/Al ratio indicates a dealumination of the structure but with minimal changes, the surface area and density of the micropores increased considerably. A significant increase in the capacity of copper adsorption was registered. According to XRD, no significant changes occur to the structures.

Keywords: Dealumination; aluminosilicates; AMD; acid treatment; metal removal.
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1. INTRODUCTION

Acid mine drainage (AMD) is a challenging environmental problem created by numerous mining operations (Kaur et al., 2018). AMD poses severe pollution problems to current and future generations, due to low pH, high concentrations of potentially toxic dissolved metals, metalloids, and sulphates. Given the toxic characteristics of AMD, the surrounding ecosystems are always at risk; several accidents caused by AMD have been reported. Therefore, it is necessary to develop more suitable methods of management to treat water bodies that have been contaminated (Kaur et al., 2018; Kefeni et al., 2017). Heavy metals are extremely toxic, non-biodegradable, and tend to bioaccumulation, causing various human diseases and environmental pollution (Ayari et al., 2007; Hesnawi et al., 2017; Kalin et al., 2006; Sprynskyy et al., 2006). The use of low cost adsorbents to remove heavy metals or recover valuable metals from an aqueous solution is one of the most recent developments in environmental and remediation technologies (Kim et al., 2015; Park et al., 2016), due to their ability to bind heavy metals. Zeolites are minerals of hydrated aluminosilicates that can be used as adsorbent material. The zeolite structure consists of a three-dimensional lattice of tetrahedra of SiO_4^+ and AlO_4^+ (Abdel Salam et al., 2011; Hesnawi et al., 2017; Wang et al., 2016b). Industrial acid drainages have very acidic pH values, which can affect the adsorption capacity of a zeolite by modifying the exchange sites of the zeolite surface. The pH of the solution affects both aqueous chemistry and surface bindings of the adsorbent (Demiral and Güngör, 2016). Zeolites are acid catalysts, which are widely used in the petrochemical and refining industry (Silaghi et al., 2014), and they are also used as a neutralizing agent of acid drainages. Zeolite dealumination is useful for reducing the concentration of the acid sites, improving thermal stability, and modifying the structure of the pores (González et al., 2011); this can be achieved by means of an acid treatment and this can have advantages in later uses. Their adsorption properties are modified using techniques that change their surface (Paul et al., 2017). A rearrangement in the pore structure and size influences the accessibility to the aluminum atoms in the lattice (González et al., 2011). Viswanadham and Kumar (2006) treated zeolite (mordenite) with nitric acid, which increased the volume of the micropores and the surface area, improving the adsorption characteristics of this zeolite. The treatment with nitric acid caused the dealumination of the mordenite and the magnitude of the dealumination was directly related to acid concentration

(Viswanadham and Kumar, 2006). Acid treatment on zeolite caused partial ruptures of the Al-O-Al and Al-O-Si bonds; these ruptures provoked a decrease in Si/Al ratios. On the other hand, the Al-O- and Si-O- dealuminated bonds are possible ion exchange sites; these sites can be widely distributed in the zeolite due to rupture of the silica and aluminum tetrahedra, producing proton exchange sites, for example: Al-O-H and Si-O-H (Paul et al., 2017). Aluminum that remains in the solution after dealumination by acid could be easily incorporated to the zeolite structure by adjusting the pH value of the solution (Oumi et al., 2002); this shows that this process is reversible to some degree (Oumi et al., 2003). A previous study was carried out to determine the effect of acid and alkaline treatments on the hydrophilicity/ hydrophobicity of a natural zeolite by characterizing the zeolites before and after the treatments; however, these treatments were not correlated with the adsorption properties of zeolites (Wang et al., 2019). Knowing the changes to zeolite characteristics and properties is very important if they are to be used for heavy metal removal.

Mining is one of the main economic activities in Chihuahua, Mexico. AMD production due to this activity is a major environmental concern in this region and in other countries (Kefeni et al., 2017; Moodley et al., 2018; Park et al., 2018; Ryu et al., 2019). In Northern Mexico there are important zeolite deposits, however, no studies have been carried out about their heavy metal adsorption capacity or about the effect of an extremely acidic solution on their physicochemical characteristics. Relatively little research has been done concerning the dealumination of the structure of a natural zeolite by means of an intense acid treatment, but there are still fewer investigations that correlate these treatments with a modification in their capacity of adsorption and ion exchange, the latter being crucial if treated zeolites are intended to be used as adsorbent material. Most studies on dealumination of zeolites have focused on the effect on pore structure, and most studies have used artificial zeolites (Wang et al., 2019). No studies include a systematic comparison of the effect of a concentrated acid treatment on the heavy metal adsorption capacity of zeolites from Northern Mexico. It is well known that surface structure and pore size can be modified by an acid treatment. The effect of an acid treatment on a mineral depends on the mineralogical and chemical composition, amount of exchangeable ions, duration and temperature of the treatment, nature and concentration of the reagent, among others (Bel'chinskaya et al., 2016). In order to know objectively the effect of an intense acid treatment on a particular mineral, the specific material must be subject to experimentation. The objective of the present work is determining the possible disturbance to physicochemical characteristics that may influence on the sorption capacity of zeolites subjected to an acid treatment.

2. MATERIALS AND METHODS.

2.1 Preparation of the adsorbent material

Zeolitic materials were extracted from a deposit located in Aldama City, Chihuahua, Mexico. The material was crushed and sieved passing through screen No. 10 mesh. The material was treated with sulphuric acid 50%, (H_2SO_4) for 24 hours without stirring at 200 C. The material, labeled as Treated Zeolite (TZ) was washed with distilled water and dried in an oven at 1060 C. The unmodified material labeled as Natural Zeolite (NZ) was stored for characterization.

2.2 Reagents

All the reagents used were reactive grade. Copper solutions were prepared from a certified standard of 1000 µg mL-1 in 2% HNO_3 (High-Purity Trademark, catalogue no. 100014-1), from which the necessary dilutions were made to adjust the desired concentrations. Deionized water was used for all tests and solutions.

2.3 Characterization of samples

The X-ray diffraction (XRD) patterns were collected on a Bruker model D8 Advance Lynxeye detector X-ray diffractometer (Cu Kα, 40 kV, 40 mA) for 2θ values from 50 to 1000 with a step size of 0.0330.

Surface morphologies of the NZ and TZ were examined using a scanning electron microscope (SEM) equipped with an energy dispersive spectrophotometer (EDS) (Hitachi Scanning Electron Microscope SU 3500).

The surface area of the NZ and TZ were measured by BET theory (Brunauer–Emmett–Teller nitrogen adsorption technique) using a Brunauer, Emmett and Teller Surface Area Analysis instrument. Nitrogen sorption at 770 K was carried out in a Quantachrome Autosorb Automated Gas Sorption System instrument. Before the measurements the samples were degassed at 5230 K for 12 h.

Elemental Composition of the zeolites was determined by two analytic methods: Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) on Thermo Scientific iCap 6500 DUO (USA) and semiquantitative Dispersive Energy Detector analysis (EDS) on Hitachi Scanning Electron Microscope SU 3500, with the operating conditions at 60 Pa, 15Kv, 100x.

2.4 Adsorption tests

To a volume of 100 mL of solution with a concentration of 50 mg L-1 of Cu^{2+}, 3 g of zeolite was added. The samples were shaken in polypropylene bottles with a screw cap with a capacity of 250 mL; the tests were performed at a constant speed of 160 rpm in a Shaking incubator SI-600 (JEIO TECH). It was stirred for 24 hours to ensure that equilibrium was reached. The tests were carried out in a pH range from 4.77 to 4.96, the pH values were adjusted with 2 M, 0.5 M and 0.01 M NaOH; and with 50% H2SO4 as necessary. The pH values at which the test was performed were determined according to a graph of chemical species of copper versus its pH value (Puigdomenech, 2000). The test was carried out at pH values where the predominant species was in its dissolved form (Figure 1). The pH measurements were carried out by means of a HACH Pocket Pro + Multi 2 potentiometer. When the agitation was over it was filtered with Whatman No. 2 paper and the metal was quantified by means of ICP-OES (Thermo Scientific iCap 6500 DUO (USA)).

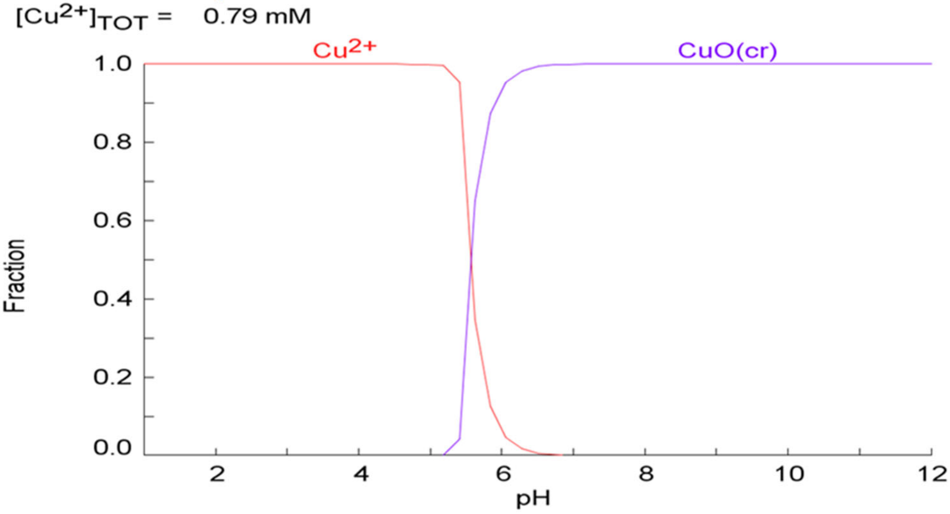

Figure 1. Fraction of Cu^{2+} versus pH at concentration 50 mg L-1 (Puigdomenech, 2000)

The percentage of sorption was calculated with the following expression:

$$\%Sorption = \frac{Ci - Cf}{Ci} * 100 \quad (1)$$

$$qe = \frac{Ci - Cf}{m} * V \quad (2)$$

Where, Ci and Cf are the initial and final concentrations respectively (mg L-1), qe is the capacity of adsorption of the metal (adsorbate) by the zeolitic material (mg g-1), m is the mass of the zeolitic material (g) and V is the volume of the metal ion solution (L) (Abdel Salam et al., 2011; Ghasemi et al., 2016; Gupta et al., 2012; Kim et al., 2015; Li et al., 2015; Lin et al., 2011; Malamis and Katsou, 2013; Park et al., 2010; Shukla et al., 2009).

3. RESULTS AND DISCUSSION

3.1 Mineralogical Composition

Using the X-ray diffraction (XRD) patterns, it was determined the presence of Clinoptilolite-Ca (Heulandite) (Ca3.16Si36O72 (H2O)21.80), Stellerite (Ca2Al4Si14O36 ·14H2O), Quarz (SiO2), Calcite (CaCO2), Anortite (CaAl2Si2O8) and other trace compounds. The XRD pattern of natural zeolite (Figure 2) has been compared with the diffraction pattern for Clinoptilolite (Reference code: 01-070-1859) and Stellite (Reference code: 00-025-0124), taken from the International Center for Diffraction Data databases. This material contained ~85% clinoptilolite.

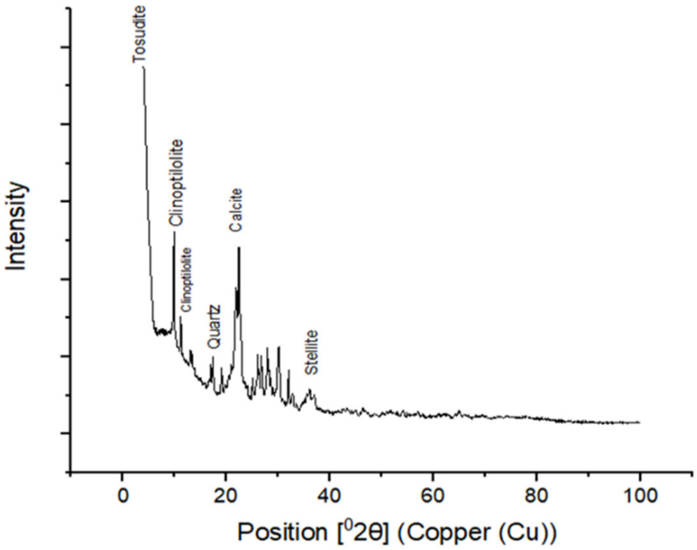

Figure 2. XRD Pattern of Natural zeolite (Cu Kα, 40 kV, 40 mA).

3.2 Surface Area and Pore Size Determination

In order to know the characteristics of the pores of a solid material, the technique of physical adsorption of a gas has been commonly used. With this technique are obtained the surface area, pore volumes, and pore size distribution. These data are obtained by quantifying the amount of gas adsorbed by the material (Ates, 2018; Groen et al., 2003; Oumi et al., 2002). The technique used universally involves the adsorption of N2 at 770 K and at pressures below atmospheric, this allows an understanding of the physical characteristics of the material, such as porosity and surface area. This method provides information about the pore size distribution in the micro, meso and macro range (approximately 0.5-200 nm). Barret, Joyner and Halenda (BJH) in 1951, developed a pore size model, currently considered the classical model of adsorption, which is based on the Kelvin equation. This method calculates the distribution of the surface of the pores in the range of the mesopores and part of the macropores. To calculate the distribution of micropores, the Horvath-Kawazoe (HK) model was used. This model is suitable for pore geometries in the form of slits (carbons) and cylindrical pores (zeolites) (Groen et al., 2003). In order to discriminate between micro- and mesoporosity, the t-plot method was used (Verboekend et al., 2012). The mesoporous size distribution was obtained using the model of Barrett − Joyner − Halenda (BJH) (Groen et al., 2003; Viswanadham and Kumar, 2006). To calculate the volume of the mesopores, the following equation was used:

$$V_{meso} = V_{TotalPore} - V_{Micro} \tag{3}$$

Where: VTotal Pore is Total Pore Volume (cm3 g-1), Vmicro is t-Method Micro Pore Volume (cm3 g-1) and Vmeso is Meso pore volume (cm3 g-1) (Matias et al., 2009).

For the calculation of Meso Surface, the following equation was used:

$$S_{meso} = S_{ext.} - S_{micro} \tag{4}$$

Where: Sext. is t-Method External Surface (m^2 g-1), Smicro is t-Method Micro Pore Surface (m^2 g-1) and Smeso is Meso Surface (m^2 g^{-1}). For the calculation of the % change in the surface area, pore volume and size, the following expression was used:

$$\%Change = \left[\frac{(M_{TZ} - M_{NZ})}{M_{TZ}} \right] * 100 \tag{5}$$

Where: M_{TZ} and M_{NZ} are the measurements made to TZ and NZ, respectively. The results are shown in the Table 1. Five samples of each zeolite were analysed, a one-way analysis of the variance (ANOVA) was made, the results are presented in Table 2. In statistical analysis p-values < 0.05 indicate the differences between the means are statistically significant with 95% of confidence level. As shown in table 2, only one parameter did not show significance, the average pore diameter value obtained by the method BJH presented statistically equal values; that is, an acid treatment had no effect on this parameter. For all remaining parameters, significance was observed; with this it is affirmed that acid treatment on a natural zeolite modifies the surface area and pore size.

Under the general classification presented by the International Union of Pure and Applied Chemistry (IUPAC) with respect to the pore size of a material, it is established that materials whose pore size is in the range of 2-50 nm are mesoporous; the average pore diameters of NZ and TZ were within this range, so it could be established that both materials are mesoporous; thus it is interpreted that no change occurred to average pore diameter. Pore diameter measured by the SF model was within the classification of inter-nanopore (1-10 nm) for both zeolites. Pore diameter measured by the BJH model, and pore width measured by the HK model were classified as inter-nanopore. In general, in this experiment, the pore size decreased due to the acid treatment;

Surface Area	Natural	Treatment	%Change
Multipoint BET ($m^2 g^1$)	23.2	60.1	61.4
Langmuir Surface Area ($m^2 g^{-1}$)	35.3	85.5	58.7
BJH Method ($m^2 g^{-1}$)	19.5	41.2	52.6
t-Method External Surface ($m^2 g^{-1}$)	17.2	36.3	52.6
t-Method Micro Pore Surface ($m^2 g^{-1}$)	6.2	27.9	77.8
Meso Surface ($m^2 g^{-1}$)	11.02	8.39	-31.3
Pore Volume			
Total Pore Volume ($cm^3 g^{-1}$)	0.108	0.133	18.6
BJH Method ($cm^3 g^{-1}$)	0.106	0.129	18.0
HK Method ($cm^3 g^{-1}$)	0.010	0.024	58.6
t-Method Micro Pore Volume ($cm^3 g^{-1}$)	0.0028	0.0101	72.3
Meso Volume ($cm^3 g^{-1}$)	0.106	0.123	13.6
Pore Size			
Average Pore Diameter (nm)	19.15	9.05	-111.4
BJH Method Diameter (nm)	1.36	1.36	-0.6
HK Method Pore Width (nm)	1.39	1.35	-2.6
SF Method Pore Diameter (nm)	2.61	2.54	-2.8

Table 1. NZ and TZ Pore Properties

Parameter	F-value	P-value
Surface Area		
Multipoint BET	233.5	3.3E-07
Langmuir Surface Area	186.4	8.0E-07
BJH Method	196.7	6.5E-07
t-Method External Surface	103.9	7.4E-06
t-Method Micro Pore Surface	329.2	8.7E-08
Meso Surface	11.3	9.9E-03
Pore Volume		
Total Pore Volume	19.5	0.00223
BJH Method	20.9	0.00182
HK Method	250.7	2.5E-07
t-Method Micro Pore Volume	283.5	1.6E-07
Meso Volume	10.5	0.012
Pore Size		
Average Pore Diameter	152.8	1.7E-06
BJH Method Diameter	3.8	0.08831
HK Method Pore Width	189.9	7.4E-07
SF Method Pore Diameter	83.7	1.6E-05

Table 2. One-way analysis of the variance (ANOVA)

this should not be interpreted as diminishing pore size in the bulk, but rather as favouring the formation of new micropores. When comparing with the findings of Mays (2007), the average pore diameter for NZ was in the super-nanopore range (between 10 and 100 nm), while TZ the average pore was positioned in the range of the inter-nanopore (pore size between 1 and 10 nm). According to the above, the reduction factor of pore size expressed previously was confirmed; secondary porosity or micropores were formed. Pore diameter measured by the BJH method, and pore width measured by the HK method were situated in the inter-nanopore range. According to the previous classification, those zeolites can be classified as nanoporous material (Mays, 2007).

Each zeolite has different characteristics, such as the size and shape of its pores and channels, depending on its geological origin and chemical composition. Their unique characteristics increase the possibility of them being used in very varied conditions; therefore, the modifications experienced under certain treatments (acid, alkaline or thermal) will result in a new material with particular characteristics (Ates, 2019; Wang et al., 2016a).

The surface area experienced a perceptible increase after acid treatment. Depending on the model used for this quantification, the results show a variation to a greater or lesser extent, but in all cases the increase in surface area was evident. This behaviour is consistent with the results of another study, where a zeolite that was put in contact with phosphoric acid increased surface area (Kussainova et al., 2019).

In this study it was observed that as the amount of micropores increased, the amount of meso-pores decreased; this does not mean that the meso pores ceased to be present, but that their internal surface was transformed into micropores, quantifying this as an increase in the surface area of the micropores. In previous studies it was observed that the dealumination of the zeolites led to an increase in the secondary porosity and not in the main channels (Nagano et al., 1999), which is reflected in the increase of micropores, as observed in this study.

The area of the meso-pores had a small decrease but at the same time an increase was observed in the area of the micropores; therefore, an increase in the total surface area is quantified.

Based on the above, it may be concluded that surface area of TZ increased significantly after acid treatment, by an increase in micropores.

3.3 Element Analysis

Table 3 shows the analysis of the chemical composition of the zeolites.

Wt.%	ICP-OES		Scanning Electron Microscope (EDS)	
	Sample		Sample	
Composition	Natural	Treatment	Natural	Treatment
Si (%)	35.08	35.76	31.96	37.66
Al (%)	5.71	5.06	5.52	5.38
Ca (%)	1.71	1.07	1.86	1.26
Fe (%)	0.73	0.72	0.98	1.12
K (%)	1.45	1.02	2.02	1.44
Mg (%)	0.52	0.44	0.60	0.50
Mn (%)	0.02	0.03	N. D	N. D
Na (%)	0.39	0.19	0.48	0.22
Ti (%)	0.09	0.09	0.15	0.18
Ratio Si/Al	6.14	7.06	5.78	7.00

Table 3. Chemical Composition of the zeolites

When comparing the results obtained by means of ICP-OES and EDS, it can be observed that the numerical values for all the elements were very similar; with these results both analytical methods were validated. The same behaviour was present in both analytical methods: as the quantity of Al decreased, Si increased, which is congruent with dealumination of the structure of the zeolite, but this dealumination was low, 12.11% on average, taking into account that the material was subjected to an intense acid treatment. With acid treatment, the surface area of the porous zeolite increased, and its pre-existing native cations were replaced by protons during the transition to an H-form zeolite (Gibb et al., 2018), this was corroborated when a loss of sodium, potassium and calcium was observed.

The dealumination of the zeolites is induced by an acid treatment, in which protons attack and weaken Al–O bonds causing structural emptiness. The vacancy enlarges the zeolite pore aperture, increasing the surface area and adsorption ability. Acid treatment could be used as a simple and economical method to increase the adsorption capacity of natural zeolites, and hence improve the feasibility of zeolite as an adsorbent material (Wang et al., 2012).

3.4 X-ray Diffraction Patterns

The X-ray diffraction patterns (Figure 3) show that the NZ and TZ samples are virtually identical, determining that the acid treatment had no significant changes in the crystalline structure of the samples, which is congruent with several previous studies (Matias et al., 2009; Paul et al., 2017; Wang et al., 2016b). Clinoptilolite (zeolite) presents a high stability to acids allowing modifications but without destroying the mineral framework; the changes presented will depend on the content of the cations, the amount and type of impurities and the conditions of the process (Xu et al., 2014). This evidenced there were no significant changes in XRD patterns of NZ and TZ.

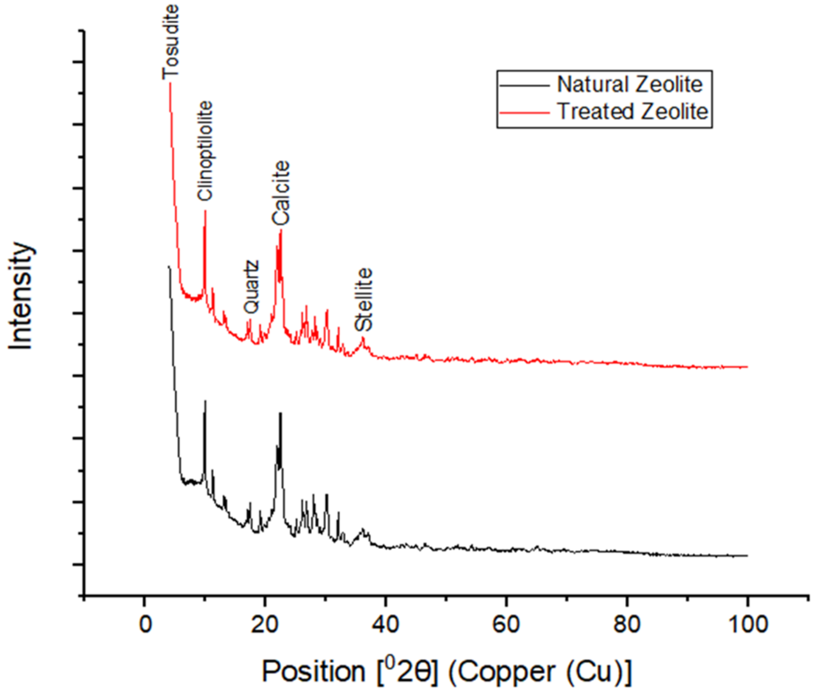

Figure 3. NZ and TZ x-ray diffraction patterns

3.5 Surface morphologies

Using Hitachi Scanning Electron Microscope SU 3500, with the following working conditions: vacuum 60 Pa, Accelerating Voltage 15KV, magnification 30x, photomicrographs of zeolites were obtained, in order to determine whether surface morphologies had undergone an obvious change. Figure 4 shows the TZ surface and Figure 5 shows the NZ surface. The photomicrograph shows that the physical structure did not undergo a significant change, and no modification could be observed. Photomicrographs were taken from random granules from the samples used, the surface structure was observed unchanged in the NZ and TZ samples, and at first glance no change in the surface of the materials was observed. This is consistent with the observations of x-ray diffraction patterns.

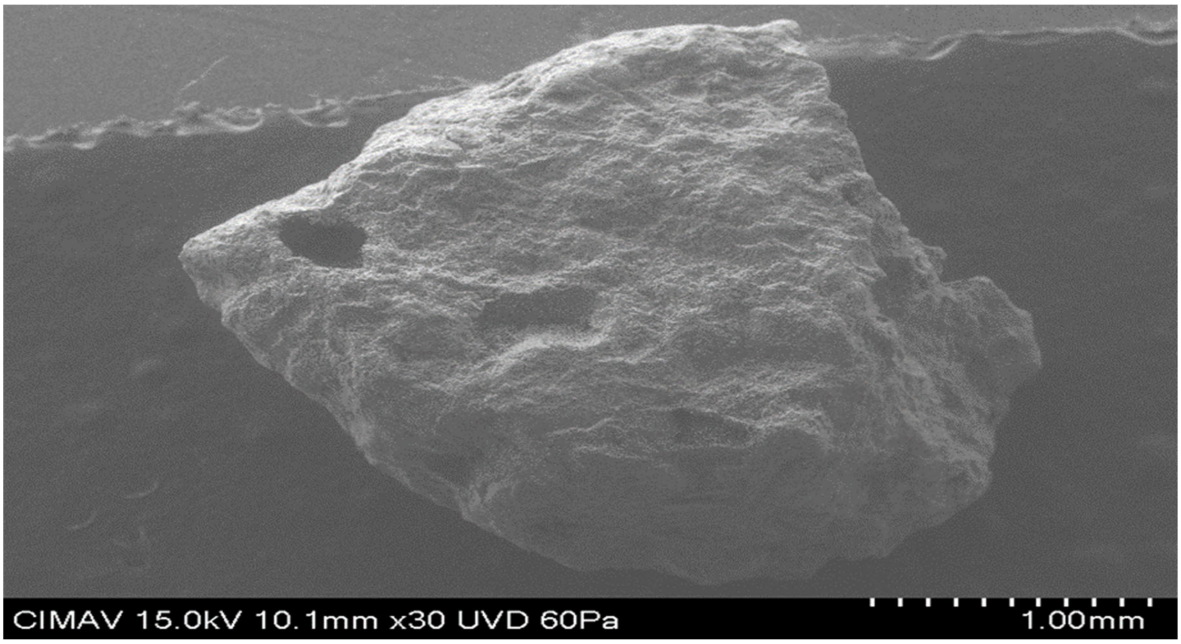

Figure 4. Photomicrograph of Treated Zeolite

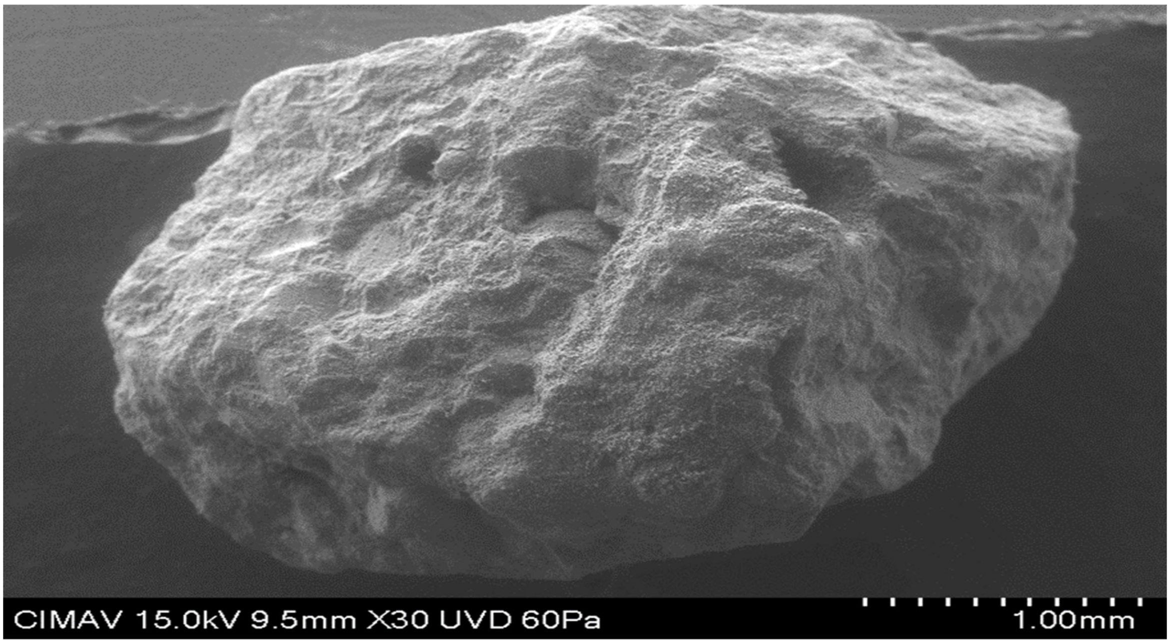

Figure 5. Photomicrograph of Natural Zeolite

From the same granules, magnifications were made to the macropores observed on the surface (Figures 6 and 7).

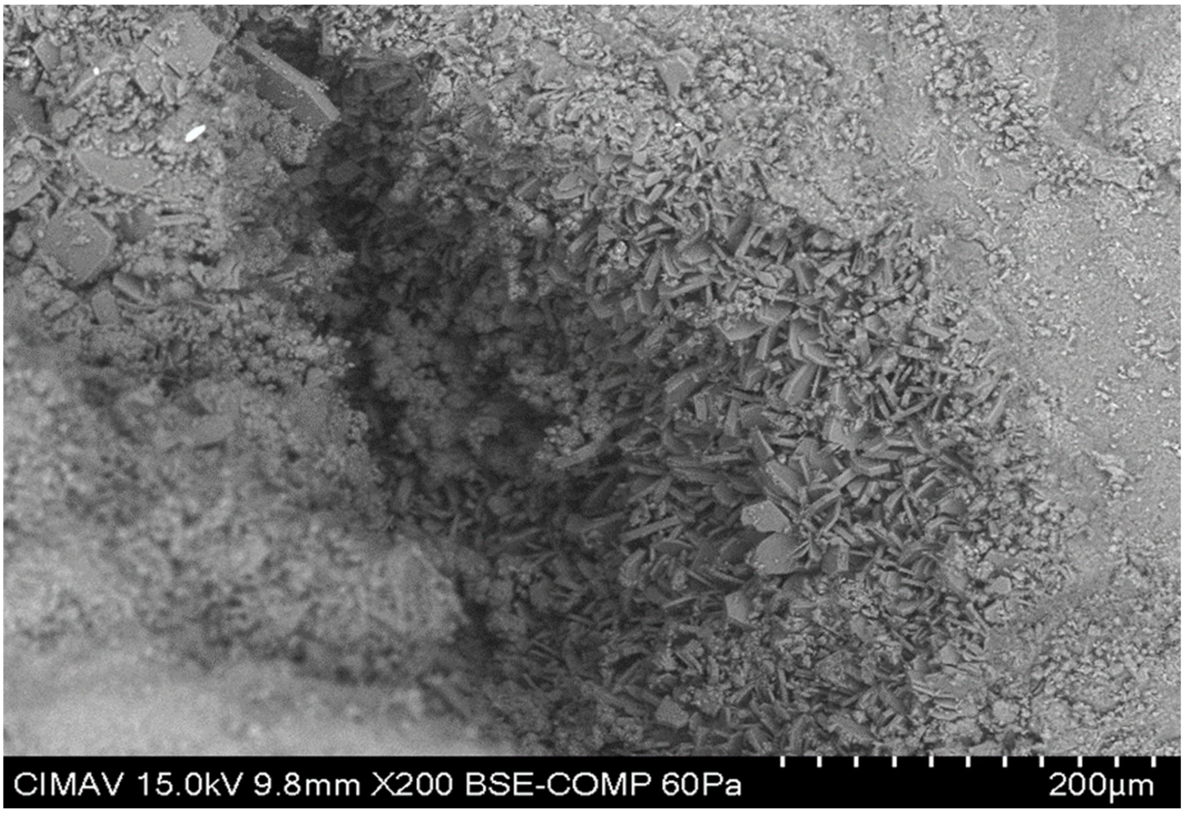

Figure 6. Magnification of a pore in Natural Zeolite

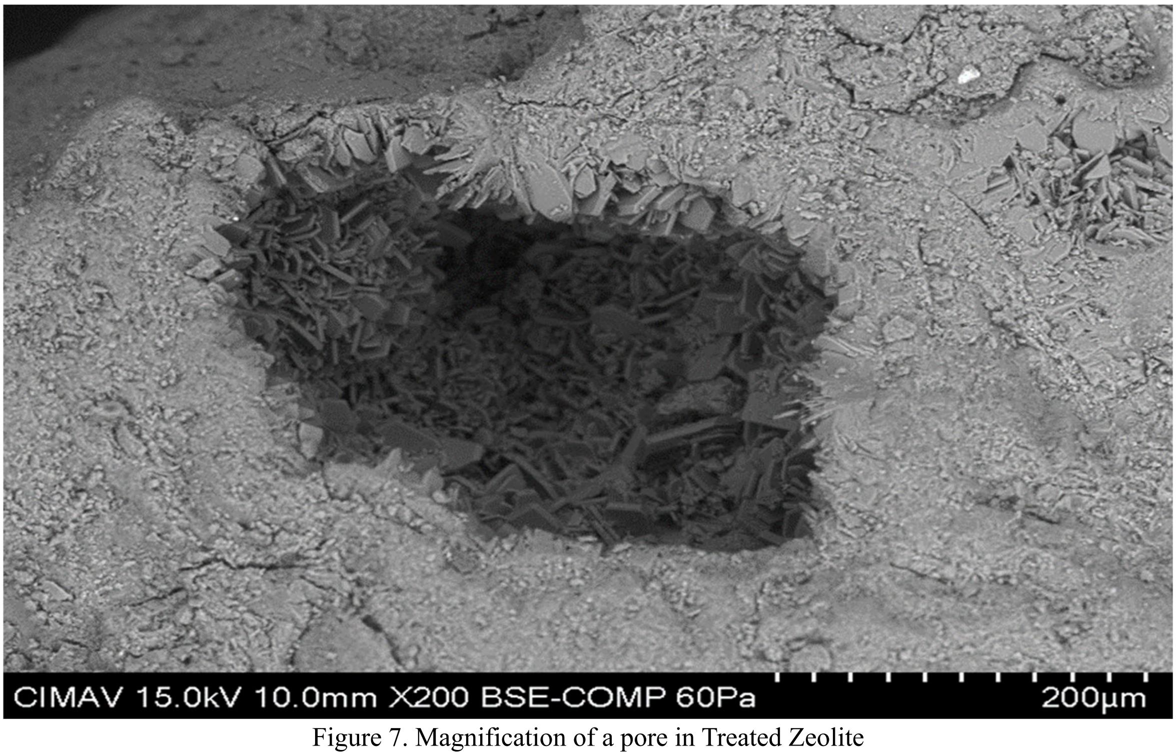

Figure 7. Magnification of a pore in Treated Zeolite

A detailed study of the structures in a zeolite granule was obtained with the use of electron microscopy techniques, joining the meso- and nano- scales. In this case, it is important to consider that as the resolution increases, the visual field decreases invariably, which requires a careful evaluation of the measurements of the images so that they are representative (Mitchell et al., 2015, 2012).

When the pores magnifications were compared, it was observed that obstructions in TZ were cleared, while in the NZ the macropore was saturated with materials, this being consistent with the findings of a previous study, where it was determined that more than half of the pores of a zeolite were blocked and that by an acid treatment this blockade was effectively eliminated, which helped the sorbent to be in contact with the exchange sites (Kuehne et al., 1998). Acid treatment is particularly useful; it removes pore-blocking impurities, increases the surface area and porosity, and replaces sorbed cations with H+ ions (conversion to a near- homoionic H-form zeolite) (Gibb et al., 2017). It can be seen that the size of the cavities on the TZ surface are larger than in the NZ, which is similar to the findings of other experiments (Kussainova et al., 2019).

3.6 Amount of Cu(II) Sorbed for g of Zeolite and % Removal

By treating the zeolitic material with a strong acid, the adsorption capacity of material was significantly improved. Table 4 shows the analytical results. One-way ANOVA analysis of % removal and qe between TZ and NZ was performed. An $\alpha = 0.05$ was used. The mean % removal for TZ was 45.11 with a $\sigma2$ of 10.24, while the mean for NZ was 18.55 with a $\sigma2$ of 14.41 (P-value = 0.00075); with this it may be concluded that there were significant differences between the means. With respect to the adsorption capacity, the mean for NZ was 0.315 with a $\sigma2$ of 0.003, the average for TZ was 0.766 with a $\sigma2$ of 0.004 (P-value = 0.0008), and the P-value indicates that the means present significant differences. The TZ adsorbed little less than 50% of the copper fed, while a NZ removed only 19% on average, showing a significant increase. Partial dealumination of a zeolite increases the pore volume, improving the thermal stability and making aluminosilicates improve their adsorption capacity (Xu et al., 2014), this behaviour was observed in this study, since copper removal increased when the zeolite was treated with an acid.

In a previous study it was concluded that treating a zeolite with an acid increased pore formation, which increased the uptake of heterocyclic compounds and their hydroisomeration activity (van Donk et al., 2001). It is pertinent to compare this fact with the metal removal observed in this study. A dealumination of the zeolite network generates secondary micropores that facilitate the connection between adjacent channels, increasing the microporosity of the material (Nesterenko et al., 2004; Viswanadham and Kumar, 2006). Essential characteristics, such as the activity and hydroisomeric selectivity of a zeolite, are strongly influenced by an acid treatment. This modifies the structure of the zeolite, making the exchange sites more accessible (Tromp et al., 2000), with which the adsorbates will be more easily in contact with the exchange sites, increasing removal. In the zeolite structure certain sites are occupied by cations such as Ca2+, Na+, Mg2+ among others. Upon contact with an acid solution, these cations are replaced by H+; this substitution generates exchange sites that may be occupied by other cations, thereby improving the zeolite exchange capacity (Kussainova et al., 2019).

Sample	mass (g)	Ci (mg L-1)	Cf (mg L-1)	% Removal	qe (mg Cu2+ g-1 Zeolite)
TZ1/rep. 1	3.0014	50.80	29.76	41.42	0.701
TZ/rep. 2	3.0024	51.06	27.14	46.85	0.797
TZ/rep. 3	3.0002	51.10	27.05	47.06	0.802
NZ2/rep.1	3.0008	50.80	42.23	16.87	0.286
NZ/rep.2	3.0002	51.06	42.95	15.88	0.270
NZ/rep.3	3.0013	51.10	39.40	22.90	0.390

Table 4. Amount of Cu(II) Sorbed for Mass of Zeolites and % Removal

4. CONCLUSIONS

The surface area of a zeolite increases when performing an acid treatment.

With an acid treatment, the zeolitic material experienced dealumination in its structure, but this is minimal, considering the extreme nature of the treatment used.

The crystallographic structure of the zeolites remains practically unaltered even after an extreme acid treatment.

A decrease in the aluminium content of zeolites increased their copper adsorption capacity as a result of increasing ion exchange capacity of zeolites.

The capacity of adsorption of copper by means of a zeolite improves when an acid treatment is carried out.

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