

Remediation of the Acid Drainage with Zeolite: Amalgamated Twofold Functions pH Control and Removal Copper, Lead and Zinc

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Abstract:- The generation of acid drainages is one of the environmental problems generated by the mining industry. Acid Mine Drains (AMD) are generated from the oxidation of metal sulphides in the presence of water and by the metal beneficiation processes. One of the objectives of acid water treatment methods is the neutralization of acidity and removal heavy metals. Tests were carried out in batches with the value of pH 2. To 100 mL of the test solution is added 15 g of zeolite with constant stirring. For a time of 195 minutes pH measurements were made every 15 minutes. The test was performed in triplicate. For the validation of all the results, the General Lineal Models (GLM) procedure of SAS® was used, with $\alpha = 0.05$. Adsorption tests were made with a trimetallic solution with different amounts of adsorbent material that was previously used to control the pH of an acid. The objective of this work was to determine the basic design parameters for the scaling of an innovative neutralization technology for an acid mine drain, as well as to determine the effect of the acid treatment on the adsorption properties of the zeolite. The adequacy of the pH values is feasible by means of a zeolite and the removal of metals stand for this is possible after undergoing a strongly acidic solution.

Keywords:- Neutralization; Aluminosilicates; AMD; Acid Treatment; Removal Metals.

I. INTRODUCTION

The nature of mining includes consumption, affectation and possibly serious contamination of our water supply sources (1,2). During the exploitation of certain deposits (coal, metal sulphides, iron, uranium and others) large amounts of sulfur minerals are exposed to weathering that can form acidic drainages (3). For the formation of these will be necessary the existence of sufficient amounts of water, oxygen and simultaneously the catalytic action of bacteria (1,4–6). The most significant alteration in the waters produced by the mining activity is the contamination with heavy metals (such Fe, Al, Mn, Zn, Cu, Pb, among others) and the acidification of the same, this directly affects the water quality and the use of the soil, which has an adverse impact on the resources natural (1,4). These elements in these concentrations are harmful to biological activity, pollute the waterways and also these waters can damage the structure and foundation of buildings (7). There are several methods for adapting the pH values of an acid drainage but require expensive equipment (8). Another type of

treatment does not require equipment but requires large areas of land, as is the case with passive treatments (9). For these treatments, Limestone (CaCO_3) or calcium hydroxide ($\text{Ca}(\text{OH})_2$) is generally used, but these are expensive and may not be found where they will be used (6). In order to replace these compounds, an Aluminosilicate mineral (Natural Zeolite) was used. In order to carry out a neutralization process, the hydrogen ion H^+ must be put in contact with the ion exchange sites that is immersed in the zeolite matrix. The rate of the neutralization and adsorption process can be controlled by mass transfer and/or diffusion. Mass transfer is important in the initial stages of the process. The application of appropriate agitation increases the mobility of the ions in the solution and thereby reduces the resistance to mass transfer (10). Usually, when an AMD is treated, a product was used to adjust the pH values, and for the removal of the heavy metals an adsorbent material is used, in this case we use a zeolite for pH control and in one step later with this material we removed the metals present. The natural zeolites present variations in their purity and composition, making indispensable a detailed study of their physicochemical properties for the determination of their potential application to specific processes. This information is also essential for the determination of possible pretreatments to modify the structure of the zeolites in order to improve their sorption and ion exchange properties (11). The objective of the study was to demonstrate the technical feasibility, by determining the basic design parameters of the pH remediation of an acid drain with a zeolite, and determine the effect of the acid treatment on the adsorption properties of the zeolite.

II. MATERIALS AND METHODS

A. Reagents

All the reagents used for the preparation of the standard solutions were made with reactive grade products. The Cu (II), Lead (II) and Zn (II) standard solution was prepared with Copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), lead nitrate ($\text{Pb}(\text{NO}_3)_2$) and zinc sulfate (ZnSO_4) respectively. Sulphuric acid (H_2SO_4) was used to treat the natural zeolite sample.

B. Obtention of the adsorbent material

For this study, a mineral zeolitic material extracted from a deposit that is located in the vicinity of the city of Aldama, Chihuahua, Mexico ($28^\circ 48'36''\text{N}$, $105^\circ 54'3.0''\text{W}$) was used. The samples were crushed and passed through a metal sieve. The material that went through a No. 10 mesh (U.S. STD. Sieve), with an opening of 2 mm was used for the study.

C. Characterization of the adsorbent material

In order to be certain that, if the acid treatment to which the zeolite was subjected during the neutralization process had an impact on the physicochemical characteristics of these, a study was made of the material used for the neutralization and a material without treatment. The samples were identified as Natural Zeolite (NZ) and Zeolite treated (ZT).

Elemental Composition of the Zeolites were determined by two analytics methods: Inductively coupled plasma optical emission spectroscopy (ICP-OES) on Thermo Scientific iCap 6500 DUO (USA) and semiquantitative dispersive energy detector analysis (EDS) was used to identify the elements contained therein. Used Hitachi Scanning Electron Microscope SU 3500. Surface morphologies of the natural and treated zeolites were examined using a field emission scanning electron microscope (SEM) (Hitachi Scanning Electron Microscope SU 3500).

The surface area of the Zeolites was measured by BET method (Brunauer–Emmett–Teller nitrogen adsorption technique) by using a Quantachrome Autosorb Automated Gas Sorption System instrument. The t-plot method was used to discriminate between micro- and mesoporosity. The mesopore size distribution was obtained by the Barrett–Joyner–Halenda (BJH) model applied to the adsorption branch of the isotherm (12,13).

The powder X-ray diffraction (XRD) data were collected on a Bruker model D8 Advance Lynx eye detector X-ray diffractometer (Cu K α , 40 kV, 40 mA), in the 2 θ range of 4° to 50° with an angular step size of 0.033° and a counting time of 1 s per step.

D. pH control with Zeolite

Neutralization experiments were carried out in batches, at velocity constant of 125 rpm in oscillating shaker. An artificial acid drain prepared with H₂SO₄ was used. The pH values will be adjusted with 0.01 N H₂SO₄ and with the necessary amount until adjusting the desired pH value, for this case it was a value of 2 +/- 0.05. For the tests, 100 mL of artificial acid drainage was used, to which 15 g of the zeolitic material was added. The tests lasted 195 minutes and measurements of the pH values were carried out every 15 minutes with a Hanna HI 2550 device. The experiment was carried out in triplicate. The variable pH was analyzed under a statistical model of analysis of variance using the GLM procedure of the statistical package SAS®, for the comparison of the variance, time was considered as block repetition.

Once the neutralization test was finished, the samples were filtered, the solid phase was separated (Zeolite) and this was dried in an oven at 106 °C, for later use.

E. Adsorption Studies

The adsorbent material subjected to an acid treatment in the previous step of neutralization was used for these tests. Adsorption experiments will be carried out in batches, in triplicate at a constant agitation speed. Zeolite concentrations of 3, 6 and 9 g was added at 100 mL of the solution of known concentration was mixed, for 24 hours to be sure that it reached

equilibrium. The pH values will be adjusted with 0.01 N H₂SO₄ and 0.01N NaOH according to the case and with the necessary amount until the desired pH value was adjusted at range 4.0- 4.2 unit. This value is determined according to a graph pH versus soluble dominant species (14) (**Figure 1**). The initial concentrations for copper, lead and zinc were 100.28, 0.26, and 0.51 milimol (mM) respectively. It was decided to use these concentrations since they were the average concentration of the aforementioned metals found in a previous study conducted to an acid mine drainage. Once the test was finished, the samples were separated on Number 1 Whatman filter paper. The concentration of residual metals was measured by ICP-OES Perkin Elmer OPTIMA 8300. The percentage of adsorption and amount of metals sorption per g of zeolite was calculated with the followings expressions:

$$\% \text{ Adsorption} = \frac{c_i - c_f}{c_i} * 100 \quad (1)$$

$$q_e = \frac{c_i - c_f}{m} * V \quad (2)$$

Where: C_i and C_f are the initial and final concentration of metals respectively (mg L⁻¹), q_e is the sorption capacity of the metals (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) (15–18).

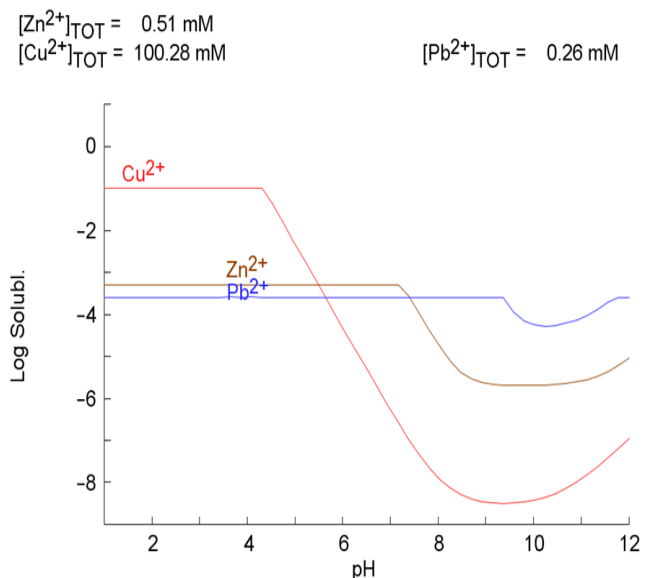


Fig 1. Solubility of copper, lead and zinc versus pH

III. RESULTS AND DISCUSSION

A. Adjust pH with Zeolite

During the first 15 minutes of the test, pH values higher than 6.6 were obtained, which meets the requirements established by the Official Mexican Standard NOM-001-SEMARNAT-1996, which establishes the maximum permissible limits of contaminants in discharges of wastewater in national waters and goods, where section 4.1 establishes the permissible range of hydrogen potential (pH) that is established from 5 to 10 units (19). With these values, the requirements established in the federal code of regulations (CFR) of the

United States of America are met in Title 40, Chapter I, Subchapter N of part 440, which establishes that the of the pH values for the mining industry is from 6.0 to 9.0.

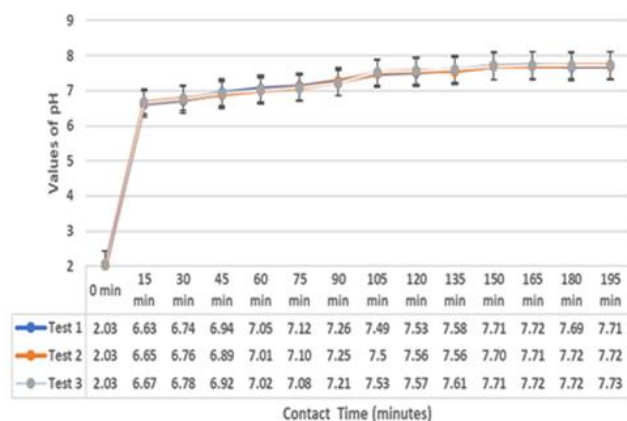


Fig 2 shows the results of the test. To determine the statistical significance of the tests, $\alpha = 0.05$ was used. For the zeolite test, no statistical significance ($P > 0.05$) was observed for the tests.

Source of Variations	Degrees of Freedom	Type I Sum of Squares	Mean Square	F Value	P>F
Test	2	0.0027744	0.00138718	3.11	0.0628
Time	12	5.6175077	0.46812564	1050.76	<0.0001

Table 1 shows the results of statistical analysis of the variance. Test 1, $\mu = 7.32$ and σ^2 of 0.15, Test 2, $\mu = 7.32$ and σ^2 of 0.16 and Test 3, $\mu = 7.33$ and σ^2 of 0.16.

With this it is concluded that the means of the tests from the statistical point of view are equal. According to this test, it is observed that there is statistical significance (P -value < 0.0001) with respect to time, with which it can be affirmed that there are differences between quantified times. It is observed that from the time of 150 minutes the curve becomes asymptotic. A statistical analysis of the variance was performed for the times from 150 to 195 minutes, with $\alpha = 0.05$.

Source of Variations	Degrees of Freedom	Type I Sum of Squares	Mean Square	F Value	P>F
Test	2	0.0003167	0.00015833	1.54	0.2884
Time	3	0.0003333	0.00011111	1.08	0.4256

Table 2 presents the analysis of the variance for retention times of 150 to 195 minutes. No statistical significance (P -value ≥ 0.05) is observed for this period, with which we can conclude that from the time 150 minutes there are no significant changes in the pH values; with the amount of Zeolite that was added and starting from a pH value of 2.0.

There are no significant differences (P -value > 0.05) with respect to the tests (P -value= 0.2884) and also between the contact times (P -value=0.4256). Under the conditions used, the maximum expected value of pH will be 7.72 on average.

B. Effect of acid treatment on the structure of Zeolite

To induce significant changes in the stability and physicochemical characteristics in a zeolite, with which we could modify the catalytic and adsorption capacities, a variation in the Si / Al ratio in the zeolitic framework will suffice. A change in this relation is mainly associated with the isomorphous substitution of aluminum by silicon, either by the use of an external agent or by the extraction of aluminum by means of steam, acids or ligands(20). Zeolites are acid catalysts, which are widely used in the environmental protection and in the field of adsorption (21), another application is sought to be used as a neutralizing agent of acid drainages. In order to reduce the concentration of acidic sites, improve thermal stability and modify the structure of the pores, we can use the dealumination. There are certain factors that influence this, as it could be, the type of structure and especially the methods used for this purpose (22), this can be achieved by means of an acid treatment. The adsorption properties of zeolites are modified using techniques that modify the surface of the same (23). The structure and the size of the pores can be modified rearrange the zeolitic structure and with this the accessibility to the aluminum atoms will be influenced (22). In a previous study, it was treated with nitric acid a zeolite (mordenite) which caused an increase in the volume of the micropores and in the surface area, which improved the adsorption characteristics of this zeolite. The treatment with nitric acid caused the dealuminization of the mordenite and the dimension of this, increased with the acid concentration (24). The process of dealuminization causes a partial rupture of the Al-O-Al and Al-O-Si bonds, this could occur due to an acid treatment, which contributes H^+ ions. This phenomenon is manifested by decreasing the Si / Al ratio, which suggests the formation of dealuminized bonds Al-O- and Si-O- which are possible exchange sites, these are widely distributed in the zeolites, forming broken tetrahedra of aluminum and silicon, producing proton exchange sites, such as: Al-O-H and Si-O-H (23). When get in touch a zeolitic material in contact with an acidic solution, an ion exchange of H^+ will be carried out between the solution and the exchange sites, achieving an increase in the pH values of the solution, its structure will be dealuminized but its thermal stability and the size of the pores will be modified, which will increase the capacity of adsorption, will be very convenient for later uses. The aluminum that is released from the zeolitic structure, through an acid treatment, can be easily reincorporated into the structure of the zeolite if it adjusts the pH value of the solution (25), which indicates a degree of reversibility in this process (26). A chemical attack can modify the zeolites. In order to expand the pore system and improve its adsorption capacities the zeolites are subjected to an acid treatment, this conditioning weakens the Al-O bonds, dealuminized the structure, which causes openings and certain defects in the structure of the zeolites, increasing the surface area, which is reflected in an increase in the adsorption capacity. A simple and economical way to increase the adsorption capacity of a natural zeolite is to subject it to an acid treatment (27). The zeolites have pre-existing native cations in their structure, which, after an acid treatment are replaced by protons, during this transition the zeolites are modified to protonated forms (H-form Zeolite) (28).

One of the techniques that is most chosen for the study of the characteristics of pores in a solid material, is the physical adsorption of gases (12). In the Table 3 the results of the surface area analyze of the zeolites before and after the acid treatment are shown. To calculate the % difference in the surface area the following equation is used:

$$\% \Delta = \frac{A_t - A_{wt}}{A_t} * 100 \quad (3)$$

Where: A_t and A_{wt} are the surface area with treated Zeolite (TZ) and Natural Zeolite (NZ) respectively ($m^2 g^{-1}$).

Surface Area	Natural	Treated	% Δ
Multipoint BET ($m^2 g^{-1}$)	28.68	52.60	45.48
Langmuir Surface Area ($m^2 g^{-1}$)	44.06	74.66	40.99
BJH Method ($m^2 g^{-1}$)	25.16	39.89	36.93
t-Method External Surface ($m^2 g^{-1}$)	22.98	32.37	29.01
t-Method Micro Pore Surface ($m^2 g^{-1}$)	5.70	20.23	71.84

Table 3. Surface Area of zeolite

When a zeolite is in contact with an acidic solution, its surface area increases, improving its adsorption capacity, since in turn there is an increase in the exchange sites. With the multipoint BET method, a near double increase is recorded, which is very convenient for a material to be used as an adsorbent, it should be noted that the increase is not due exclusively to the formation of new pores, but also to the fact that according to the exposed by Kuehne et. al., 1998, the existing pores were unblocked by the acid solution, increasing the surface area (29). According to the surface area method of Langmuir, the increase was also significant. According to BJH method, the mesopore size distribution showed a considerable increase but the most considerable increase was registered in the distribution of micropores, that were calculated by the t-plot method.

Two analytical methods were used to determine the elemental composition of the zeolites (**Table 4**), for both methods the changes before and after being in contact with the acid solution show significant changes.

According to the two analytical methods used, a considerable loss of Na^+ can be observed; K^+ , Ca^{2+} and Mg^{2+} suffer loss but to a lesser extent, Ti, Mn, and Fe do not change their concentration practically. This behavior can be explained by the fact the zeolites show negative charge of the framework, which comes from tetrahedrally coordinated aluminum, is counterbalanced mainly by monovalent cations (Na^+ , K^+) as well as by divalent cations (Ca^{2+} , Mg^{2+}) (30,31); these elements were exchanged for H^+ ions of the acid solution that was used for the treatment, quantifying this exchange as a loss of the same ones.

Using the X-ray diffraction (XRD) patterns (no show), it was determined the presence of Clinoptilolite-Ca (Heulandite) ($Ca_{3.16}Si_{36}O_{72} (H_2O)_{21.80}$), Stellerite ($Ca_2Al_4Si_{14}O_{36} \cdot 14H_2O$), Quartz (SiO_2), Calcite ($CaCO_2$), anortite ($CaAl_2Si_2O_8$) and other trace compounds. XRD pattern of natural zeolite (no show) 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. In order to determine if the crystallographic structure of the zeolite had undergone a significant change when in contact with an acid solution, diffraction patterns of X-rays of both materials were acquired. **Figure 3** shows a transposition superposition of both patterns. It can be observed that the patterns are almost identical, being able to affirm that the crystallographic structure did not suffer significant changes.

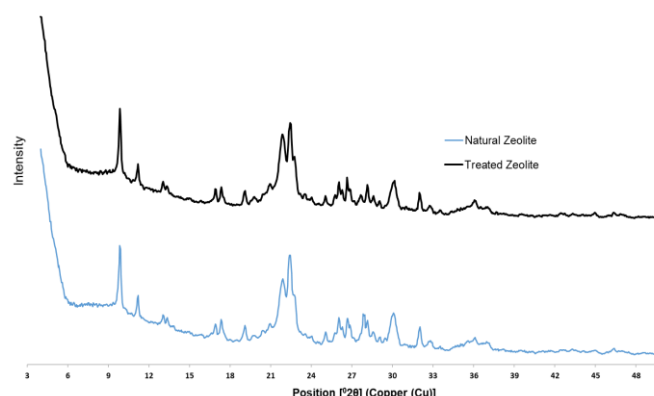


Fig 3. Comparison of patterns of NZ and TZ

This behavior is consistent with what was observed in some previous studies which is congruent with the established in several previous studies (32–34). This behavior is consistent with what was observed in some previous studies. A considerable tolerance to acid attacks has been observed in zeolites, mainly in the Clinoptilolite. With an acid treatment changes are observed, but these do not destroy the crystallographic structure; and the changes presented will be based on the content of cations, the amount and type of impurities and the conditions of the process (35), this behavior was evidenced that there are no significant changes in XDR patterns of natural and treated zeolites.

Used Hitachi Scanning Electron Microscope SU 3500, with the following working conditions: vacuum 60 Pa, Accelerating Voltage 15KV, magnification 30x and 200x obtain photomicrograph of zeolites, in order to determine if surface morphologies had undergone an obvious change. In **Figure 4A** a zeolite particle without acid treatment (NZ) is shown and in **Figure 4B** an approach of one of the macropores of the same particle is presented

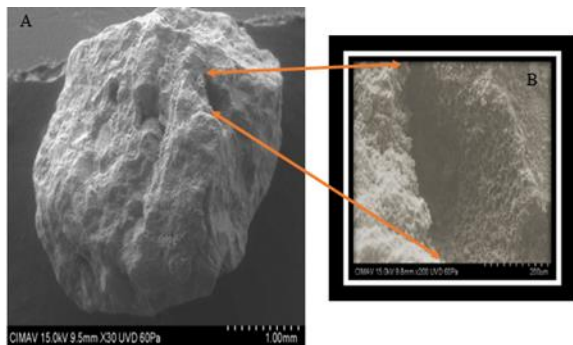


Fig 4. Microphotograph of Natural Zeolite (NZ)

Figure 5A shows a particular zeolite that was used to neutralize a solution with a pH value of 2.0, **Figure 5B** shows an approach of a macropore of the same particular in question.

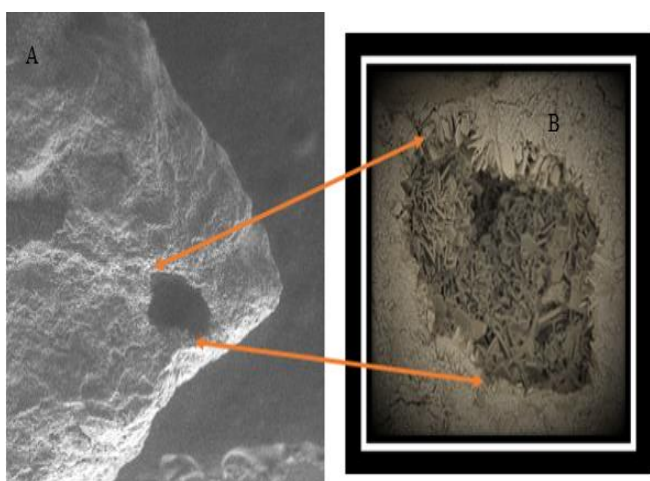


Fig 5. Microphotograph of Treatment Zeolite (TZ) (A 30x and B 200x)

In order to achieve a better understanding of the complex structure of a porous material, imaging techniques should be used. These help to solve the complex structure of a material on a scale from macro to nanoscale, for this the complete integration of the most modern methods is required, this being a challenge that still remains unfulfilled in most studies (36). With the use of electron microscopy techniques, a detailed study of the structures of a zeolite granule can be made, combining the macro and nano scales. It is only of utmost importance to emphasize that a careful evaluation of the measurements of the images is required to be representative (36,37). At first sight, no significant changes in the structure of the zeolite can be observed, even after suffering an acid treatment. It is observed that in the pores of the untreated zeolite (NZ) are clogged by microcrush material, while in the zeolite that was subjected to an acid treatment, the structures are observed free of material, this is consistent with that mentioned in previous studies (29).

C. Adsorption Experiments

Clinoptilolite has a cage-like structure with pores and channels running through the crystal. The cage consisting of SiO₄ and AlO₄ tetrahedral joined by shared oxygen atoms carries a net negative charge which is balanced by the presence

of exchangeable cations, generally calcium, magnesium, sodium, potassium and iron. These ions can be readily displaced by other cations that have stronger interaction with the negative structure of the zeolite framework, for example heavy metals. This phenomenon is known as cationic exchange, and it is the very high cationic exchange capacity of Clinoptilolite which makes it a potential adsorbent for removing cations from an aqueous solution [26].

According to the results of the experiment, a high degree of removal of metal ions in aqueous solution is observed by means of a zeolite that was subjected to a previous acid treatment. This method is efficient process of removal of heavy metal ions from wastewater containing lower pollution concentrations. The results of these studies are presented as a function of the % removal of each metal (Figure 6) and the maximum adsorption capacity, the mg of the metal removed in question as a function of the amount of Zeolite used, after exposed to an acid treatment (Figure 7). The percentage of removal of the metals increases as the amount of adsorbent increases for the case of copper and zinc, in the case of lead the removal remains constant, being the removal practically total. Even with the lowest amount of adsorbent material, the removal of lead is practically total, this being due to the fact that the affinity of lead for this adsorbent material is very high, being congruent as established in several previous studies (30,38–41).

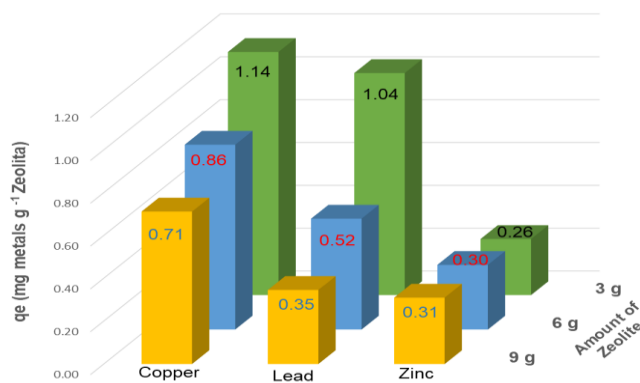


Fig 6. qe versus amount of zeolite

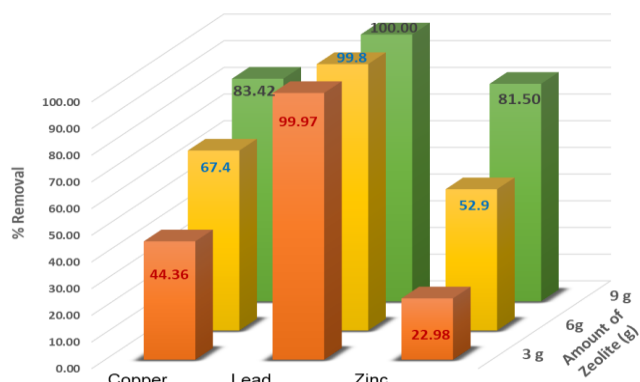


Fig 7. % Removal Metals versus Amount of Zeolite

The results show that the elimination of copper, lead and zinc species follows the Pb >> Cu > Zn sequence, which is congruent in previous studies (42).

IV. CONCLUSIONS

The Zeolitic material with which the test was carried out is efficient for the neutralization of an acid solution, when there is constant agitation.

A contact time of 15 minutes is sufficient to achieve the pH values necessary to comply with NOM-001-SEMARNAT-1996 and the Federal Code of Regulations (CFR) of the United States of America in the Title 40, Chapter I, Subchapter N of part 440.

For an acid solution with an initial pH of 2.0 with 150 g / L it will be enough to remedy the pH values and there is no risk that with this concentration the solution will raise its pH values to the point of alkaline and make it impossible to reuse them / or poured into a body of water, therefore, the basic parameters of design are the contact time and the dose of zeolite.

Therefore, the basic design parameters, for subsequent scaling, were: 15 minutes of contact time, with constant agitation at an initial pH of 2.0 and a zeolite concentration of 150 g / L.

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

With an acid treatment, the zeolitic material used suffers from dealumination in its structure, but this is minimal, taking into account 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 aluminum content of zeolites increased their adsorption capacity as a result of increasing ion exchange capacity of zeolites. The capacity of adsorption by means of a zeolite improves when an acid treatment is carried out.

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