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REMOVAL OF BORON USING ACID-MODIFIED ZEOLITE AS AN ADSORBENT

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ABSTRACT

One of the major industrial concerns is the toxicity of heavy metals such as boron in the petrochemical industry wastewater. In this study, the efficiency of natural zeolite (clinoptilolite) and zeolites modified with sulfuric acid is studied as a cheap and available adsorbent for the removal of boron from aqueous solutions. The results showed that the modified zeolite tends more to attract blond compared with the unmodified zeolite. In addition, parameters such as initial concentration of boron, sorbent particle size, amount of adsorbent and pH, the absorption rate is effective. Blond adsorption maximum was obtained at pH 8. Furthermore, the maximum adsorption capacity in adsorbent modified was observed by acid 1M. 240min balance was appropriate between absorbent and adsorbent contact time and the adsorbent 480 g/L optimum zeolite to obtain maximum adsorption. Removal of boron is 92.35 percent in optimum condition. So this adsorbent has a high potential for use in industrial waste water treatment plants. It also included three Langmuir, Freundlich and Dubinin - Radushkevich isotherm and two Freundlich adsorption models well described the adsorption of boron on adsorbents.

Keywords: adsorption, heavy metal, boron, zeolite, clinoptilolite

INTRODUCTION

Today, with the development of industry and industrial development, the risk of contamination of heavy metals increases in the environment, more than ever. A lot of water contaminated with heavy metals in industrial areas and factories, metallurgical and mining extraction areas. Environmental pollution with heavy metals results in serious problems for humans and other organisms in the environment. Because these elements are not biodegradable and can accumulate in the tissue of living organisms [1].

Common methods of removing heavy metals from wastewater industries include processes such as precipitation, coagulation, ion exchange, electro-dialysis, electro coagulation, reverse osmosis, evaporation and filtration [3, 2]. Although there are several methods for removing metals, however, most of the above-mentioned processes have significant disadvantages such as high energy needs and thus costly process, low efficiency, high amounts of sludge, sludge disposal problems containing large amounts of heavy metal, requires certain chemicals and costly restoration process [2,4]. Therefore, due to technical constraints and economic methods, the search for new ways of attracting are highly recommended and in this regard by the absorbent is considered as a new option.

Boron is the metalloids. Metalloid are elements which their properties are between metal and nonmetal. There is no set definition for metalloids, but the overall effect is characterized by:

1- Metalloids usually found in the form of an amphoteric oxides.

2. Metalloids are usually semiconductors. [5]

Boron is an element with the chemical symbol of B and atomic number 5. It is a common ingredient that naturally is found on land, they are soluble in water. Boron is not found freely at ground level, and always is combined with another chemical element. Most industrial applications of boron include sodium perborate bleach and boron compounds in the coating glass fibers. [6, 7] Boron polymers and ceramics play a key role in the industry as structural material high strength, low weight and stable. Boron compounds and silica-based glass ceramics makes this material to be resistant against sudden temperature changes. [8] Boric acid is used as an insecticide, especially against ants, fleas and cockroaches. [9] Pharmaceuticals also has a number of organic compound made of boron or are being studied.

The extensive studies are conducting on the use of adsorbents for ion-exchange properties. The advantages including low cost, high availability, rapid adsorption and adsorption capacity, revitalize and re-use capabilities has made adsorbents to develop using to remove heavy metals. One of the adsorbents that numerous studies have been concentrated on it in recent years, were zeolites that there are both natural and synthetic. [10,11] Zeolites are a large family of aluminosilicate minerals that were known by the 18th century for scientists and mineralogist, but until about 70 years ago, researchers did not conducted any significant scientific or practical work. Later, the unique physical and chemical properties of zeolites drew the attention of researchers. Normally this type of material are found in the pores and spaces available volcanic rocks and sedimentary and hydrothermal environments. Very diverse and endless applications led this category in some countries to be known as magical minerals. [12] A combination of scarcity, beauty, complexity and uniqueness of the characteristics of the mineral is magic. Clinoptilolite applications such as gas absorbers, additives in the feed, a control agent and as a water filter for drinking water and aquariums, and ammonia and other toxic gases can easily absorb water and air. [16-13] Clinoptilolite due to the large amount of space, high resistance to high temperature, and the neutral chemical structure is very suitable for this work.

The aim of this study was to enable the zeolite clinoptilolite as a cheap and available compared with sulfuric acid uptake by natural clinoptilolite zeolite and the evaluation is done based on the removal of boron as an environmental pollutant.

METHODOLOGY

This study is an experimental pilot-scale test that was conducted in the Department of Chemistry of Islamic Azad University, North Tehran branch. For samples containing boron borax salt product of Merck Germany was used and different concentrations of boron were prepared between 25 to 150 mg in a volume of 1000 ml. To measure the amount of boron atomic adsorption according to the ICP method provided in standard methods were used for the Examination of Water and Wastewater [15]. The zeolite used in this study were obtained from the company of Afrazand before and after correction is provided in Table 2. Other chemicals used in this study were prepared with analytical grade from Merck. The most common laboratory tests on soil samples, testing for moisture content, specific surface area, determined by the pH and CEC. With the detailed information of the property are some of the other physical properties predictable and overall evaluation.

CEC (cation exchange capacity) generally refers to the maximum amount that a certain weight of soil cation (zeolite) is able to attract or keep. The capacity in terms of mEq per hundred grams of soil are dry. In determining the amount of exchangeable cations in the soil has used the ion substitution. So that extracts all adsorbed cations in the soil with a certain weight of other cationic substituting. (Usually is used for the solution of ammonium acetate.)

Precise measurement of surface area and porosity is very important in many applications such as catalysts, nano absorbers, compounds and additives, pharmaceuticals and food industries and so on. Porosity measured by the method is adsorbed based on adsorption material. If the conditions have to be taken where a layer of molecules adsorbing material on the surface exists by determining the average thickness of a single molecule, a molecule occupies the surface can be calculated and therefore can be measured based on article absorbed the entire surface area of the sample. The most suitable materials for this purpose, some of the substances that are gases or vapor, and small molecular size can penetrate into the pores with dimensions of a few tens of nanometers. [17]

To determine the density of a non-destroyed sample is relatively simple. Because by dipping a cylindrical sample into the mass of the earth and knowing the weight and volume of soil that fills the cylinder density is calculated according to the following formula. [18]

Tests to determine the moisture content of raw zeolites and zeolite by comparing the weight of the dried zeolite has been achieved with the heat in the oven. [18]

Soil pH measurement is one of the most important soil properties that indicates the type of cation is adsorbed on the surface of colloids, pH meter is used to calculate it. The device electrode tip is made of sodium silicate is sensitive to the concentration of hydrogen and if hydrogen concentrations in and out of the electrode is not the same. The difference reports between the potential differences to system.

Table 1 - Physical properties of clinoptilolite

pH	Humidity	Density(g/cm)	Special area (m^2/g)	CEC	Name of adsorbent
7.1	52	2.31	21.005	86.95	**clinoptilolite**

In order to prepare the unmodified zeolite adsorbent was milled and graded by Alec (Alec standard ASTM) was isolated in three sizes. To separate impurities must granulated zeolite should be disturbed for 7 hours in distilled water, then the liquid phase is separated by standard sieve and then washed several times with distilled water and was dried at 70 ° C and the desiccating maintenance.

The chemically modified zeolite is mixed with sulfuric acid of 0.5, 1 and 1.5 molar ratio of mass to volume of one to ten and is stirred for 24 hours. Then washed with distilled water and make it smooth. Rinse will continue until the water pH reaches to 7. Zeolites are dried at a temperature of 70 ° C and keep in desiccator. Whereas quantitative analysis is done at all stages, care is required to prevent loss of samples.

Uptake experiments were fixed to determine the optimum pH, initial concentration of boron, the concentration of acid appropriate to modify zeolite adsorbent particle size determination in order to obtain the maximum adsorption isotherms. In each case the adsorption capacity is calculated as follows: [19]:

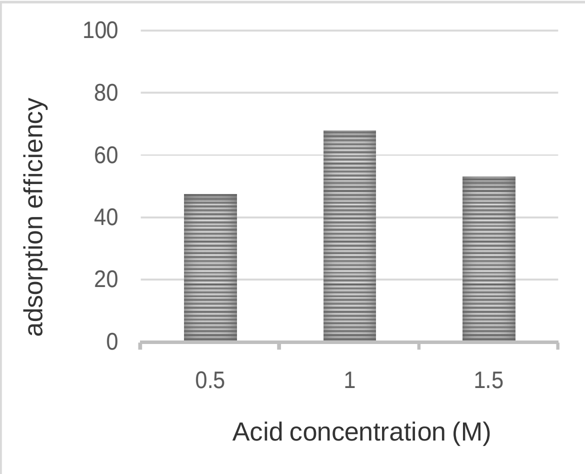
$$Q_e = \frac{V(C_i - C_t)}{m}$$

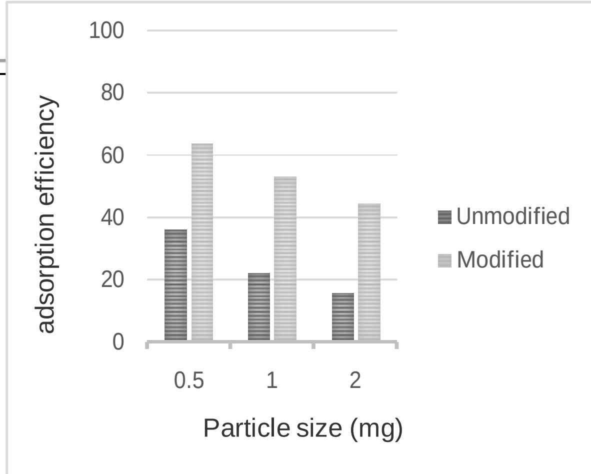
Q_e is the amount of boron adsorbed per unit mass of adsorbent, Ci is the initial concentration of boron in the solution, C_t is the secondary concentration of boron in time t, V is the volume of the solution, and m is the mass of adsorbent.

Boron adsorption isotherms were developed to determine the adsorption efficiency over time (balance) determined in accordance with isotherm model. All the experiments were repeated twice in order to reduce the error rate. In order to avoid any error all utensils used pickling and eventually was washed with deionized distilled water.

Table 2 - raw and modified zeolite chemical composition (weight percent)

Modified zeolite	Raw zeolite	chemical formula	chemical composition
87.07	67.44	**$Si O_2$**	**Silicon oxide**
5.92	10.9	**$Al_2 O_3$**	**Aluminium oxide**
0.83	0.84	**$Fe_2 O_3$**	**iron oxide**
0.28	0.19	**$Ti O_2$**	**Titanium oxide**
0.91	1.24	**Ca O**	**Calcium oxide**
0.55	0.33	**Mg O**	**Magnesium oxide**





2.93	4.39	**K_2O**	**Potassium oxide**

Fig. 1 - Effect of acid concentration on the modified zeolite (left), Fig. 2 - effect of particle size of the zeolite on the adsorption (right) (60 min, pH = 7)

RESULTS

Modification is done by various substances to increase their adsorptive capacity, which in this study, the modified zeolite is used for sulfuric acid. Zeolite modified with acid hydrogen ions are replaceable in the most important ion. Since the concentration of the acid can be effective in the reform process, zeolite were exposed to different concentrations of acid. XRF test results showed (Table 2) the raw zeolite was under the influence of acid, has been changed that ultimately leads to variation in the absorption of boron so that it is clear from Figure 1 for boron acid-modified zeolites with a molar concentration higher efficiency than other concentrations are generally modified to unmodified zeolite to absorb boron have higher efficiency.

Also by reducing the adsorbent particle size, as shown in Figure 2, the adsorption percentage is increased. Usually in the process of adsorption, pH aqueous solution is very important as a control parameter because it determines the type of ion adsorbing material and adsorbent surface charge that this situation will affect the reaction between the adsorbent and adsorbing material. It was found that adsorption efficiency is lower at acidic pH. The effect of hydrogen ion concentration on boron uptake by zeolite is shown in Figure 3. As it is clear that regardless of the type of zeolite (modified and unmodified) increased with increasing pH at acidic pH lower adsorption efficiency and adsorption efficiency, so that the pH of 2 to 10, the adsorption of boron increased by the unmodified adsorbent from 15.12 to 35.87 and the modified adsorbent are 29.39 to 62.13, respectively. The boron adsorption maximum was obtained at pH 8 for the boron uptake by unmodified and modified zeolite, is respectively, 43.5 and 66.96.

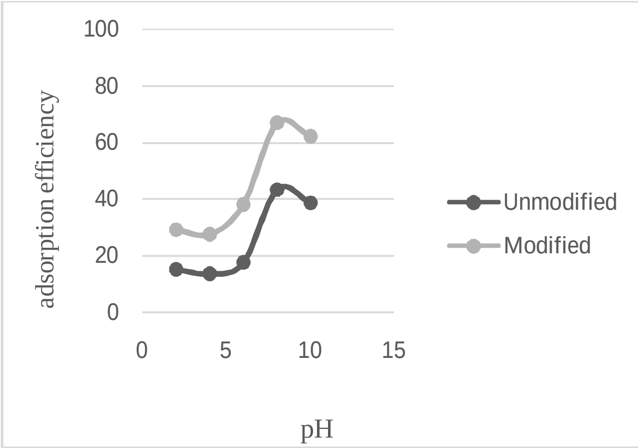


Fig. 3 - effect of pH, the adsorption efficiency of boron (process time of 60 minutes and 3 g of adsorbent)

To examine the effect of adsorbent dosage on the adsorption process showed that increasing the amount of adsorbent, the adsorption also was increased, so that according to Figure 4 adsorption of boron was increased by increasing the adsorbent of 20 grams per liter to 480 to grams per liter of none modified zeolite 10.1 52.01 and from 16.44 to 69.1 for the modified zeolite while increasing the amount of zeolite of 480 grams per liter to 600 grams per liter of zeolite adsorption efficiency for uncorrected and corrected respectively to 52.26 and 69.56.

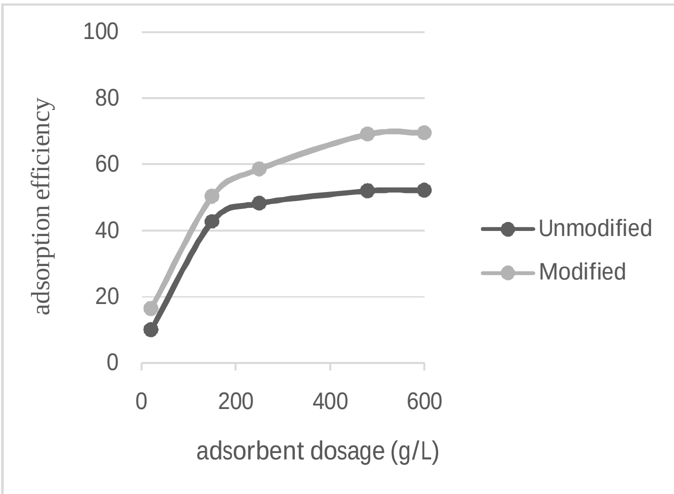


Fig. 4 - effect of adsorbent dosage on boron uptake efficiency (process time of 60 minutes, pH = 8)

The effect on the adsorption process of B is shown in Figure 5. The process also increases the adsorption of boron. Most of the boron adsorption occurred fast in first 50 minutes and then, time has reduced the amount of adsorption. Removal of boron in

300 minutes by unmodified and modified zeolite, is respectively, 52.63 and 92.87 and 52.01 and 92.35 in the 240 minutes, these numbers are reduced. These results indicate that the equilibrium time of 240 minutes.

Figure 6 shows the effect of boron concentration on the removal and absorption. It is known as the equilibrium of adsorption capacity increases with increasing initial concentration of boron. In fact, the solution is more concentrated in terms of the number of ions is better adsorbed. While the reverse shows the removal process. So that the removal rate decreases with increasing initial concentration

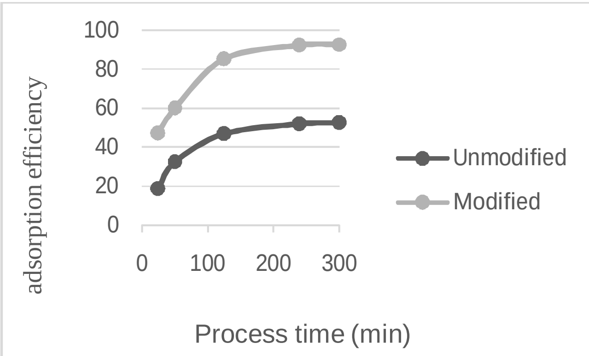


Fig. 5 - Effect of Boron adsorption process efficiency (the amount of 480 grams adsorbent and pH = 8)

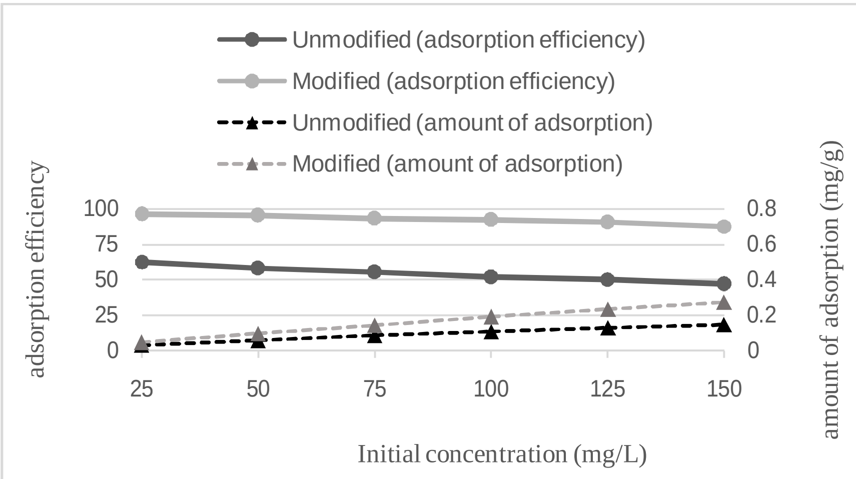


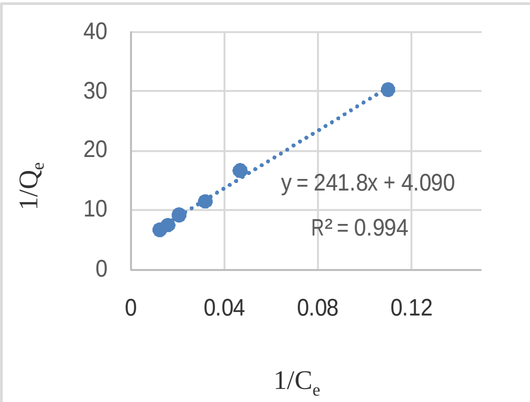
Fig.6 - Initial concentration of boron removal efficiency (the amount of 480 grams absorbent and pH = 8 and 240 min)

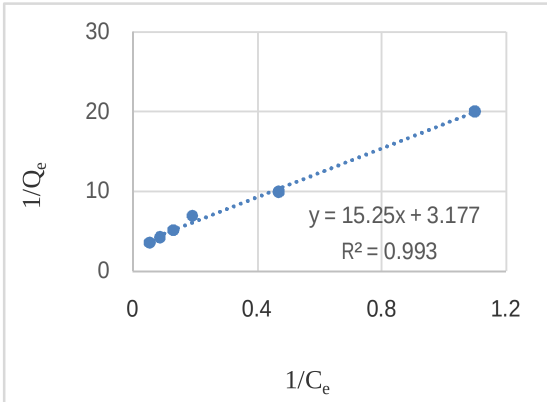
Equilibrium adsorption isotherms are discussed by plotting the concentration of boron in the solid phase to the concentration of these compounds in solution phase. Coefficients adsorption capacity (Q_{Max}) and Langmuir constant (K) Langmuir isotherm adsorption of boron on unmodified and modified zeolite is shown in Table 3. Langmuir isotherm constant fundamental characteristic dimensionless parameter called the balance, (R_L) is defined by the following equation. [20]

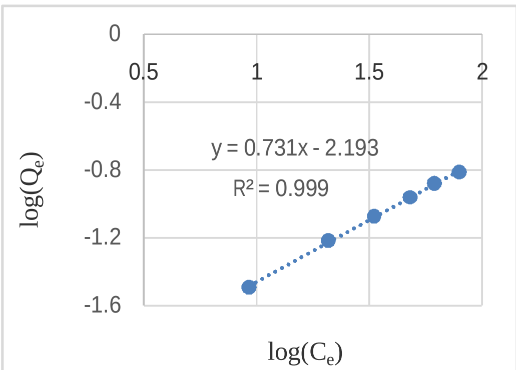
$$R_L = \frac{1}{1+KC_i}$$

Ci initial concentration of B, K and R_L indicate the type of isotherm is Langmuir constant. 1> R_L> 0 is for optimal adsorption, R_L> 1 to unfavorable adsorption, 1R_L = 0R_L = to linear and irreversible adsorption.

Fig. 7 - Langmuir isotherm adsorption of boron by unmodified zeolite (left), Fig. 8 - Langmuir isotherm adsorption of boron by modified zeolite (right)







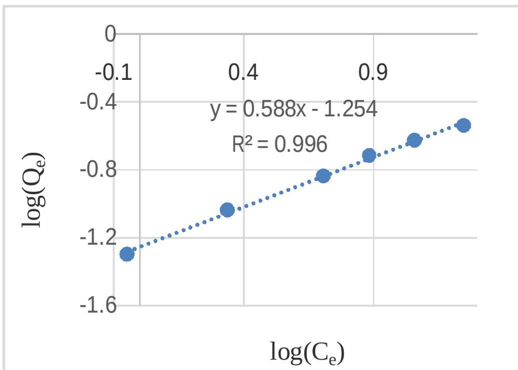
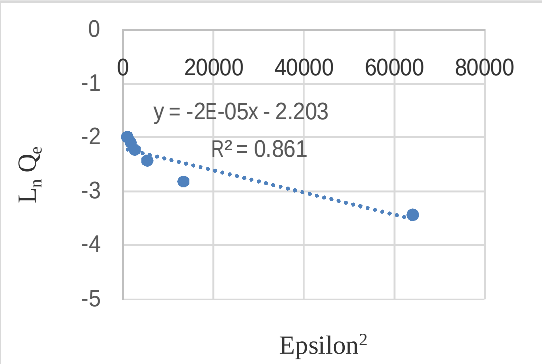


Fig. 9 - Freundlich isotherm adsorption of boron by unmodified zeolite (left) Fig. 10 - Freundlich isotherm adsorption of boron by modified zeolite (right)

By charting the log C_e against log Q_e values of n and K were obtained for boron uptake on the zeolite unmodified and modified,. The R^2 value that indicating the compliance with isotherm data is being evaluated. Freundlich coefficient (n) must have values ranging from 1 to 10 in order to be considered for optimal adsorption.



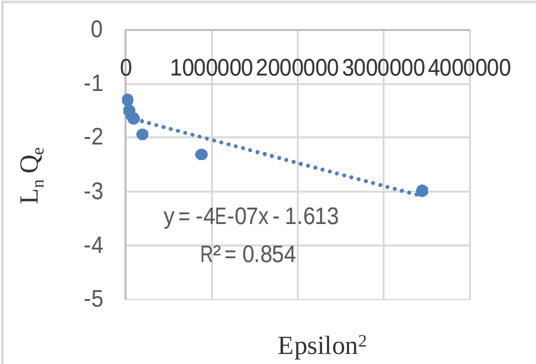


Fig. 11 - B by zeolite adsorption isotherm DR unmodified (left) Fig. 12 - DR isotherm absorption of boron by modified zeolite (right)

After charting Ln Q_e against ε^2 value β and the value E is calculated. As is clear from Figures 11 and 12 to determine the coefficient of Langmuir isotherm and Freundlich isotherms to be very low. This amount represents less compliance with experimental isotherm is D-R

Table 3 shows the results of drawing isotherms different:

Table 3: The parameters of the Langmuir isotherm, Freundlich and DR on the uptake of boron

Type of absorbent	Langmuir model			Freundlich model			D-R model		
	R^2	K	Q_{max}	R^2	n	K	R^2	β	E
Unmodified zeolite	0.9949	0.017	0.244	0.999	1.367	0.0064	0.8613	-2E-05	**158.11**
Modified zeolite	**0.9936**	**0.208**	**0.315**	**0.9966**	**1.7**	**0.055**	**0.8545**	**-4E-07**	**1118.03**

DISCUSSION

Zeolites according to their chemical structure that received during the formation and based on different values of interchangeable cations in their chemical structure show different capacity to adsorb a variety of metals. As the other researchers have noted, different capacity and raw zeolite has a high capacity to adsorb heavy metals. It was also found adsorption capacity in these minerals depends on the nature and the concentration of acid used in the process of modification. [21] Zeolite modified with acid hydrogen ions is interchangeable in the most important ion. Substantially increase the adsorptive capacity of modified zeolite with acid for adsorption of boron in the form of natural zeolite plays a dominant role of hydrogen ions as a replaceable ion. Therefore, when the most exchangeable sites in the zeolite is occupied by small hydrogen ions access to the deep-absorbing boron ions will be easier. [21] Reducing the absorbent particle size is due to increased surface to volume ratio, and finally due to an increase in surface area, the number of ion exchange sites and total efficiency adsorption of boron increases. It was also observed that adsorption efficiency is lower at acidic pH. The zeolite adsorbs preferably hydrogen ions better than boron ions and occupied the hydrogen ions sites and inhibit binding of boron cations to zeolite. In addition, due to their small size and high mobility of hydrogen ions, the ions enter the pore zeolite and replaced easily interchangeable ion of zeolite. So in terms of acid and increases by reducing the pH of the property. With increasing pH, hydrogen ion concentration is low, and this increases the adsorption of boron. [22 and 23]

To examine the effect of adsorbent dosage on the adsorption process showed that increasing the amount of adsorbent adsorption also increases, because the number of active sites increased on the adsorbent that can be adsorbed by the boron.

In an adsorption process, the initial concentration of adsorbing ions in the solution plays a key role as a driving force to overcome the resistance of mass transfer between a liquid phase and solid phase. It is expected that with increasing the concentration, the amount of adsorbed ions increases. [24] Therefore, according to figures can be seen that the first solution is more concentrated in terms of the number of ions, the adsorption can be done better and second adsorption rate was high at the beginning of the process. There was a relatively high level of adsorbent prepared at the start of the process, in other words, the presence of active sites adsorbed rapidly boron. However, the number of active adsorptive sites is gradually reduced by increasing process time and increasing the number of ions adsorbed on the adsorbent, so that significantly reduced rate of adsorption leads to the formation of balance adsorb.

In an adsorption process, the initial concentration of adsorbing ions in the solution a key role as the driving force to overcome the resistance has the mass transfer between a liquid phase and solid phase. It is expected that with increasing concentration, the amount of adsorbed ions increases. [25] But copper adsorption is reversed by natural and modified zeolite, high efficiency at low initial concentration is because the adsorption sites are available and are easily occupied. But in higher concentrations of accessible sites is low compared to the number of moles of copper removal rate and thus removal percentage will be dependent on the initial concentration. Also according to figures observed at the beginning of the process, the adsorption rate was relatively high and was related to the existence of the adsorbent prepared at the start of the process, in other words, there is adsorption of the active sites that adsorbed copper quickly. However, the number of active sites attracted decreases gradually increasing process time and increasing the number of ions adsorbed onto the adsorbent. "Horsfal" reinforces the idea, stating that a reduction in the removal of an increase in the initial concentration is due to the increasing number of competing ions available for adsorption sites on the adsorbent and finally, the lack of sites in high concentrations. Meanwhile, higher concentrations decrease the average distance between adjacent electrically charged components adsorbed effects on the distribution so the ability to adsorb components in the migration change the adsorbent surface and thereby reducing ions on the adsorbent. [26]

Adsorption isotherm is an important factor in adsorption system design. In fact, the interplay between adsorption and adsorption isotherm describes the adsorbing body. So, it is considered always a major factor to determine the capacity of an adsorbent and adsorbent to optimize consumption. Maximum capacity of adsorption coefficient (Q_{Max}) and Langmuir constant (K) Langmuir isotherm are shown in Table 2. Coefficient of determination (R^2) to capture raw and refined copper on zeolite is 0/99 that shows a good model fit of Langmuir monolayer is modified by zeolite to absorb copper and the compliance may be due to the homogeneous distribution of site adsorption on the adsorbent surface, because Langmuir isotherm adsorbent surface is as homogeneous.

RECOMMENDATIONS

- Adsorption properties of zeolite modified by modifying agents such as nitric acid, phosphoric acid, hydrochloric and types of surfactants.
- Check the efficiency of adsorption of boron by synthetic zeolite and comparison with unmodified and modified zeolite.
- The use of zeolite clinoptilolite as affordable and accessible in order to remove

other contaminating elements and ions that adequate performance and economic justification.

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