REMOVAL OF COPPER BY THE ACID-MODIFIED CLINOPTILOLITE

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ABSTRACT
The study aims to investigate the efficacy of natural zeolite of clinoptilolite and also its modified type with sulfuric acid 1 M as adsorbent and solvent for removal of contaminated soluble copper concentrations with 100ppm emissions. Absorption methods by mixing absorption and solution were used to attract and measure the absorbed doses and the experimental studies of physical relationships of Langmuir isotherm were compared with Freundlich, and the results showed that increasing the concentration does not increase absorption. The study also examined the effects of time. The maximum average intake in this study was 89.7% at for copper 300 minutes and studies show that the increased time, increased the absorption percentage. Also the effect of pH value was studied, which for copper maximum uptake was at pH = 7, and absorption efficiency was 92.7%. The weight in grams of zeolite was also investigated; the results showed that increasing the amount of zeolite, further absorption takes place.

Keywords: Adsorption, Heavy Metal, Copper, Clinoptilolite, Water Treatment Plants

INTRODUCTION
Zeolites are a large family of minerals consists of Aluminosilicates silicate that from 18th century were known to scientists and mine experts but about 70 years ago, researchers did not have done any significant scientific or practical work on it. After understanding their unique physical and chemical properties, it drew the attention of researchers. Natural materials typically are found in volcanic rocks and in holes and thermal spaces and environment and in sedimentary rocks. Today, more than 50 species and 200 types of natural and synthetic zeolite is known to have multiple applications and valuable materials have been found in various fields of science. A combination of scarcity, beauty, the complexity and uniqueness of the characteristics of the mineral are magic. Yet, many researchers have investigated different applications of zeolites in scientific and industrial fields, the investigations and these studies caused the synthesis of amorphous aluminosilicate, and the exchange of trade and were used to soften and remove the hardness of water. Other well-known industrial applications of zeolites are in the areas of recruitment and the catalyst (Gottardi and Galli, 1985; Breck, 1974). The physical and chemical properties of zeolites have been used in terms of functional properties of ion exchange, which was studied about 140 years ago (Berck, 1964; Vaughan, 1980). So far, many studies have taken place on the phenomenon, especially on clinoptilolite zeolite ion exchange. Heavy cation adsorption of heavy industrial waste, municipal and agricultural assistance zeolite were also examined in-depth. In order to prepare the sorbent surface for optimal absorption processes that is elected, new modifiers (reagent tailoring or surface modifiers) are used. These reagents have zeolite properties and features new seating positions in the cause, so the zeolite has called tailored (Cleseri et al., 1989).

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have a dual nature this means that are dissolved both in the acid and the base (Cleseri et al., 1989). Heavy metals are elements that are found in abundance in the earth’s crust and they are entered into the environment during various industrial processes and through the industrial waste. Many of these metals are toxic and dangerous; and while entering the food chain and accumulate in living tissue will have wide risks on human health. Copper is one of these heavy metals that should be considered that is shown with the chemical symbol of Cu in the periodic table (Derived from the Latin word of cuprum). Copper, silver and gold are all in eleventh place in the periodic table thus, they show some common behaviors. All the elements of an electron in d orbital and some electron in s orbital. The common feature of all these elements is their ductility and high electrical conductivity. D layer that is filled with electrons so will not be imported in the nuclear reaction but metallic bond is done through electrons of s orbitals. Unlike metals, which have a half-full d layer, copper do not have metal features of covalent bond, and is relatively weak. This is due to the low hardness and high ductility of a single crystal of copper (George and Edmund, 1992). Copper has many applications, such as copper wire, copper pipe, doorknobs and other fixtures, electrical magnets, motors, especially electromagnetic motors, vacuum tubes, cathode ray tubes, musical instruments, especially wind instruments, have applications in chemistry compounds, such as Fehling’s solution, copper sulfate is used as a poison and a water purifier. All copper compounds should be treated as if they were toxic (unless the contraction is specified). The metal is a fire hazard in powder form. 30 g of copper sulfate is fatal to humans. Copper in drinking water at concentrations higher than 1 mg per liter can stain clothes and items in the water. Safe level of copper in drinking water for humans varies depending on the source, but the border is between 1.5 to 2 mg per liter.

The study aims to modify clinoptilolite zeolite as a cheap and readily available and compared with sulfuric acid uptake by natural clinoptilolite zeolite and then evaluates different parameters in order to obtain maximum absorption of copper as a water contaminant.

MATERIALS AND METHODS
Methodology
The study was released in lab-scale pilot study at the Faculty of Chemistry, University of North Tehran Branch. For samples containing copper nitrate 3 Abe copper (Cu(NO₃)₂. 3H₂O) Germany Merck product was used. And different concentrations of copper were prepared between 25 and 150 mg in a volume of 1000 ml.

![Figure 1: XRD spectra clinoptilolite](image)

To measure the amount of copper atomic absorption according to the method provided in standard methods were used for the examination of water and wastewater (Terasaki et al., 1993). The zeolite used in this study was obtained from the company Afrazand before and after modification is provided in Table 1. Other chemicals used in this study were prepared with analytical grade from Merck.
The desired zeolite is separated under three different meshes by standard ASTM\textsuperscript{1} sieves and zeolite available is divided in sizes 0.5, 1.5 and 2 mm and then is washed with water so that any particles is removed and measured in it which can disrupt the absorption process. After several washing stage zeolite filter with filter paper and dried in an oven at 50 ° C to. 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 stirred for 24 hours. Then washed with distilled water and make it smooth. Rinse will continue until the water pH to 7. Zeolites are dried at a temperature of 70 ° C and keep desiccator. Whereas quantitative analysis is done at all stages, care is required to prevent loss of samples. To search for samples of synthetic zeolite crystal phase, subjects were separated in the XRD system and exposed to X-ray. The results of these tests are specified in Table 1. Uptake experiments were fixed to determine the optimum pH, the initial concentration of copper, the concentration of acid appropriate and to modify zeolite sorbent particle size determination in order to obtain the maximum absorption isotherms. In each case the absorption capacity is calculated as follows (Dang \textit{et al.}, 2009):

\[
Q_e = \frac{V(C_i - C_f)}{m}
\]

\(Q_e\) is the amount of copper absorbed per unit mass of adsorbent, \(C_i\) is the initial concentration of copper in the solution, \(C_f\) is the secondary concentration of copper at time \(t\), \(V\) is the volume of the solution, and \(m\) is the mass of adsorbent. Data obtained using the Langmuir and Freundlich equation isotherms were analyzed and reaction rate constants and constants of different adsorption isotherms for interpretation and absorption capacity were excluded. All the experiments were repeated twice in order to reduce the error rate.

\[\text{Table 1: Chemical composition of raw and modified zeolite (weight percent)}\]

<table>
<thead>
<tr>
<th>Modified zeolite</th>
<th>Raw zeolite</th>
<th>Chemical formula</th>
<th>Chemical composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>87.07</td>
<td>67.44</td>
<td>Si O(_2)</td>
<td>Silicon oxide</td>
</tr>
<tr>
<td>5.92</td>
<td>10.9</td>
<td>Al(_2)O(_3)</td>
<td>Aluminium oxide</td>
</tr>
<tr>
<td>0.83</td>
<td>0.84</td>
<td>Fe(_2)O(_3)</td>
<td>iron oxide</td>
</tr>
<tr>
<td>0.28</td>
<td>0.19</td>
<td>Ti O(_2)</td>
<td>Titanium oxide</td>
</tr>
<tr>
<td>0.91</td>
<td>1.24</td>
<td>Ca O</td>
<td>Calcium oxide</td>
</tr>
<tr>
<td>0.55</td>
<td>0.33</td>
<td>Mg O</td>
<td>Magnesium oxide</td>
</tr>
<tr>
<td>2.93</td>
<td>4.39</td>
<td>K(_2)O</td>
<td>Potassium oxide</td>
</tr>
</tbody>
</table>

\[\text{RESULTS AND DISCUSSION}\]

\textbf{Results}

After drying of the zeolite with different mesh placed in the vicinity of the copper solution, for 24 hours (Of course solutions were stirred in the mixer) and after this period of re-using filter paper copper solution was separated from the zeolite and copper samples was placed to measure the amount of atomic absorption and it was concluded that based on Figure 2 zeolite with a diameter has more than 0.5 absorption, and in addition to the zeolite with a diameter of 1.5, the amount absorbed is greater than the zeolite with a diameter of 2.

As well as to evaluate the absorption efficiency of the three types of zeolite modified with sulfuric acid in the same condition was in contact with copper solutions that its result can be seen in Figure 3.
The effect of pH, the liquid environment on absorption efficiency by zeolite sample of the copper solution is considered with a pH between 3 and 7 and put in contact with the zeolite. For this purpose, 10 ml of the copper solution with different pH was poured in the flask and 3 grams of zeolite added to it and stirred for an hour in a mixer. The resulting solution is filtered with the finest filter paper. The same steps repeated for other parameters including the amount of zeolite and repeat the process. The effect of pH on copper absorption by zeolite shown in Figure 4. As is clear regardless of the type of zeolite (modified and unmodified) is low at acidic pH lower absorption efficiency and process efficiency increased with increasing pH, copper is absorbed by the unmodified absorbent was 14.8 at pH 3 that at pH 7 reached to 64.7 and in the modified adsorbent increased from 23.4 to 92.7.

Effects of time on copper absorption process are shown in Figure 5. The process time also increases copper absorption. To balance the absorption of Cu in 200 minutes for unmodified and modified zeolite is respectively, 62.8 and 88.3.

The effect of adsorbent dosage on the adsorption process showed that was significant increasing the amount of absorbent absorption. According to tests performed for the unmodified and modified zeolite adsorption in the amount of 500 grams per liter was 59.82 and 89.4, respectively.
The graph related to affect of initial concentration of copper on the graph shows the efficiency of removal process is reversed. So that the removal rate decreases with increasing initial concentration.
Equilibrium adsorption isotherms are discussed plotted against the concentration of copper concentration of these compounds in solution phase. Coefficients of absorption capacity (QMax) and Langmuir constant (K) Langmuir isotherm absorption of copper on Unmodified and modified zeolites are shown in Table 2.

Plotting the Log C_e against log Q_e values of n and K for copper adsorption were obtained on unmodified and modified zeolite. Freundlich coefficient (n) must have values ranging from 1 to 10 in order to be considered for optimal absorption.

The results of the drawing the Langmuir isotherm and Freundlich are summarized in following table:

<table>
<thead>
<tr>
<th>Type of absorber</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R²</td>
<td>K</td>
</tr>
<tr>
<td>Unmodified zeolite</td>
<td>0.9989</td>
<td>0.011</td>
</tr>
<tr>
<td>Modified zeolite</td>
<td>0.9992</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Discussion
Zeolite used in this study has sampled on clinoptilolite of Mining Garmsar, Semnan province. An important feature of the zeolites is the ability to attract and the loss of water without damaging the crystal
structure. Pores in zeolite structure can control molecules or ions that pass of it. As a result, it can act as a chemical sieve causing the ions to pass through it while blocks other materials (Aftabi and Anvary, 1992; Trasaki et al., 1993)[10]. The absorptive capacity of modified zeolite is increased substantially to absorb acid copper compared with the natural form of zeolite. This increase is due to the dominant role of hydrogen ions as an interchangeable ion zeolite so when most sites replaceable small hydrogen ions are occupied access to the deep absorbing copper ions will be more easily (Panuccio et al., 2009). Reducing the sorbent particle size due to increased surface to volume ratio, and finally due to an increase in specific surface area, causes an increase in the number of further ion exchange sites and a total efficiency of copper absorption.

As is known, pH changes are effective on copper absorption. Because the pH of the absorbent affects surface charge and copper ions charge. The zeolite absorbed preferably hydrogen ions better than copper ions. In addition, due to their small size and high mobility of hydrogen ions, the ions enter the pore zeolite and easily replaced the interchangeable ion of zeolite. So increases in terms of increasing acid and lowering the pH of the property. With increasing pH, hydrogen ion concentration is low and the absorption of copper will increase. The best point of pH for Cu absorption by zeolite is the neutral range that has the absorption of about 92.6 percent (Motsi et al., 2009; Wan and Hanafiah, 2008).

In an adsorption process, the initial concentration of absorbing 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 (Wan and Hanafiah, 2008). But copper absorption is reversed by natural and modified zeolite, high efficiency at low initial concentration is because the absorption 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 absorption 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 absorption of the active sites that absorbed 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 absorbent 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 absorbent surface and thereby reducing ions on the adsorbent (Quintelas et al., 2009).

The effect of absorbing as expected increases in the absorption of copper by increasing the absorbent absorption. The reason for this increase is that by increasing the amount of absorbent, absorption of the active sites increased that can be available to the copper absorber (Wan and Hanafiah, 2008). Adsorption isotherm is an important factor in absorption system design. In fact, the interplay between absorption and adsorption isotherm describes the absorbing body. So, it is considered always a major factor to determine the capacity of an absorbent and adsorbent to optimize consumption. Maximum capacity of absorption 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 absorbent surface, because Langmuir isotherm absorbent surface is as homogeneous.

Although Langmuir monolayer adsorption model was suitable to describe the experimental data obtained from the appropriate absorption, however, the process of absorption was also evaluated by Freundlich model and it was determined that Freundlich model well describes the Langmuir model of copper absorption. In general, the coefficient of determination Freundlich model than Langmuir model so Langmuir isotherm model selected and introduced to predict the behavior of copper absorption of the water by modified zeolite adsorbent sulfuric acid.


