Removal of Copper and Magnesium Cations from Aqueous Solutions by Clinoptilolite Zeolite Adsorption

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Abstract. The aim of this study is to determine the potentials of clinoptilolite zeolite in removing selected heavy metals, that are copper and magnesium in aqueous solutions. The removal of both metal cations has been studied by using the batch techniques. Three experimental variables were carried out under predetermined conditions of contact time (20 – 100 minutes), effect of dosage (0.20 – 1.00 gram), and effect of pH solution (pH 2 to 10). Adsorption capacity of zeolite towards heavy metal removal was then determined at various initial concentrations of metal ions between 20 to 100 ppm. Results obtained shows that adsorption of Cu2+ and Mg2+ on zeolite has been shown to depend significantly on the pH, adsorbent amount and contact time. The significant value of pH was reached at pH 6, followed by 1 hour of contact time for 1 gram of adsorbent; for both metal ions studied. Studies on the rate of uptake of heavy metal ions by the zeolite indicated that the process was quite rapid and maximum adsorption occurred within the first hour of contact. The results show that high silica zeolite such as clinoptilolite is a promising adsorbent as they combine high adsorption capacities and molecular sieve properties.

1. Introduction

Copper naturally occurs in soil, water, and sediment as a reddish metal and a vital micronutrient at low levels of intake to humans and animals. Increment of copper through mining, domestic wastewater, fertilizer and other major industries however resulted in copper released into soil. Normally copper will be strongly attached to the organic matter in surface soil and immobilize, but if soluble copper compounds are released into the water body, it can be taken up by animals and plants, end up in the food chain, and eventually became a serious threat to all living forms due to their toxicity and persistence in the environment. Magnesium present in most minerals such as magnesite and dolomite, washed from the rocks and also end up in water naturally. Other than that, excessive fertilizer application and cattle feed may add up magnesium and lead to the increase of water hardness which will make the wastewater treatment cost surges. Toxic heavy metals have also been contaminated the ground water resources at industrial and commercial areas, risking the drinkable water sources [1] where prolong exposure to them largely has caused skin irritations, kidney problems, and insomnia [2]. Hence it is obligatory to reduce or remove the heavy metals contamination. Numerous methods of removing dissolved heavy metals therefore have been implemented such as reverse osmosis, ultrafiltration, chemical precipitation and electrodialysis [3]. Activated carbon adsorption is also considered as one of the effective methods to...
remove heavy metals in wastewater, however it is less suitable as production and regeneration of spent carbon are then costly [4]. Consequently, a low cost of adsorbent such as natural zeolite has been employed to overcome the problem.

Adsorption and ion exchange method using zeolites is much reliable due to its low cost of zeolites are used. The obvious fact is that zeolite is famous for the ability towards the ion-exchange because they have enclosed interconnected cavities occupied by water molecules and large metal cations [5]. Furthermore, natural zeolites can be modified in many different ways in order to enhance its ability as adsorbent to trap contaminants in liquid forms. Natural zeolites also exist in abundance, biodegradable and required a low technology system to be acquired and processed [6]. However, the application of single heat activation for the adsorption of heavy metals has not been documented with regard to the application as an adsorbent. Therefore, the novelty of this study is the simple steps of zeolite activation and later used to remove heavy metals in aqueous. Natural zeolite hence would provide a promising of green, eco-friendly and sustainable adsorbent for the industrial’s utilization.

Natural zeolites occurred as hydrated aluminosilicate minerals, and can be found in igneous and metamorphic rocks as crystallized or as smaller diameter grains mostly in sedimentary rocks. Natural zeolites are primarily formed by alteration of glass-rich volcanic tuff with some intervention of fresh water in playas lakes or by seawater [7]. Zeolite’s structures comprise of three-dimensional matrix of SiO4 and AlO4 tetrahedra. The aluminium ion is small enough to occupy the position in the centre of the tetrahedron of four oxygen atoms, while the isomorphous replacement of Si4+ by Al3+ produces a negative charge in the lattice [8]. The net negative charge is then will be balanced by the exchangeable cation either by sodium, potassium, or calcium with either lead, cadmium, zinc, or/and manganese [9]. The relatively innocuous exchangeable cations therefore make zeolite predominantly suitable for removing undesirable heavy metal ions from industrial effluent waters. In this research work, we studied the capability of clinoptilolite zeolite to adsorb heavy metals such as copper and magnesium from a synthetic aqueous solution. The adsorption study was performed under various parameters such as contact time, adsorbent dosage, and different pH solutions. At the end of the study, the optimum removal of studied metals was presented to determine the effectiveness of the adsorbent.

2. Materials and methodology
Zeolite raw sample was obtained in granular forms from Messawa Village, Sumarorang District, Indonesia. Sample was later pulverized using the Fritsch Pulverisette 9 vibrating cup mill at an optimum speed of 950 rpm for 120 seconds to become fine powder to maximize the zeolite’s efficiency for adsorption of heavy metal ions, before carefully sieved through a 63µm sieve and rinsed three times with distilled water to clean the organic impurities. Zeolite sample then oven-dried at 120°C for about 4 hours prior to the laboratory experiments. The dehydration of zeolite until loss of water molecules causes the existing cavity to be more effective in absorbing heavy metals in the wastewater effluent [10]. In this work, zeolite undergone only a physical activation to study the properties almost its existing state without much modification but improving its adsorption capability.

The reagents used in this work were supplied by Merck as analytical grade and deionized water was used throughout the experiments. Metal ions studied in this work were copper and magnesium. The stock solution of copper and magnesium were prepared from copper sulphate (CuSO4.5H2O) and magnesium chloride (MgCl2.5H2O) in distilled water.

2.1. Physico-chemical characterizations of zeolite
The chemical composition of the investigated zeolite was determined by X-ray fluorescence (XRF) spectrometry, while the mineralogical analyses of the raw material was performed by X-ray diffraction (XRD). The determination of pH in zeolite was done in the ratio of distilled water: soil at 1:2.5 [11] using the pH meter (Hanna Instruments). The pH meter was first calibrated using the appropriate buffer solution (at pH 4.0 and 7). The reading is taken after the pH meter showed constant readings. The amount of organic matter in the soil was determined by mass loss on ignition (% by weight). Soil moisture content was determined by mass loss following drying (% by weight).

The elemental compositions and crystalline peaks present in the zeolite sample are presented in Table 1 and 2 below. Organic matter content in the zeolite is found to be moderate [12], while pH determined
the sample as slightly alkaline. Normal pH range for clinoptilolite zeolite is 8.00 – 8.54 that is highly alkaline. Based on the XRF element analysis in the sample, the percentage of silica (SiO₂) is 63% while for alumina (Al₂O₃) is 12.30%. Thus, the value for Si/Al ratio is 5.12 which directly determines that the primary crystalline phase of zeolite is clinoptilolite [13].

| Chemical Composition | Percentage (%) | Physical properties |
|----------------------|----------------|---------------------|
| SiO₂                 | 63.00          | pH 7.5±0.12         |
| Al₂O₃                | 12.30          | OM 5.32±0.79 %      |
| SiO₂/Al₂O₃ (ratio)   | 5.12           |                     |

Table 2. Crystal peaks for XRD of zeolite.

| 2θ  | d (nm)  | Miller Index (hkl) | Mineral Phase |
|-----|---------|--------------------|---------------|
| 6.51| 1.356   | 110                | Mordenite     |
| 9.75| 0.906   | 200                | Mordenite     |
| 9.88| 0.896   | 020                | Clinoptilolte |
| 13.46| 0.657  | 111                | Mordenite     |
| 19.62| 0.452  | 400                | Mordenite     |
| 20.48| 0.425  | 100                | Quartz        |
| 22.36| 0.398  | 131                | Clinoptilolit |
| 22.49| 0.395  | 330                | Clinoptilolit |
| 22.82| 0.390  | 240                | Clinoptilolit |
| 26.63| 0.334  | 011                | Quartz        |
| 26.65| 0.347  | 202                | Mordenite     |
| 25.67| 0.322  | 511                | Mordenite     |
| 29.41| 0.304  | 104                | Calsite       |
| 30.05| 0.297  | 151                | Clinoptilolite |

Mordenite (JCPDS 01-070-0232) has an orthotrombic crystal phase, while quartz (JCPDS 01-086-1560) has hexagonal crystal system with chemical formulae of oxide silicone (SiO₂). Clinoptilolite (JCPDS 25-1349) in other hand has a monoclinic crystal system with the unit cell parameters: \(a = 17.62\,\text{Å}, b = 17.91\,\text{Å}, c = 7.39\,\text{Å} \text{ dan } \beta = 116.40^\circ\), which present as the major fraction of the zeolite sample [14]. The XRD analysis hence confirmed that the raw material sample is a clinoptilolite zeolite origin.

2.2. Batch adsorption studies

The adsorption of copper and magnesium ions from the prepared synthetic aqueous solutions onto zeolite was investigated in a laboratory batch experiments, carried out in a 100 mL of conical flask, made in triplicates and shake for an hour. At the end of the fixed time interval, the adsorbent was removed by filtration, while the equilibrated metal concentration was determined in the filtrate by means of the atomic absorption spectrophotometer (AAS) using the air-acetylene flame. Four experimental series were performed. The final concentration of metals was then measured by atomic absorption spectrophotometer using standard methods for examining water and wastewater [15]. The presented data are mean values of all assays carried out in triplicates.

The percentage of metal removal and the amount of metal ions adsorbed by the zeolite were calculated using the following equations:

\[
\% \text{ Adsorption} = \frac{c_i - c_f}{c_f} \times 100
\]
where $C_i$ is the initial concentration of metal ions (mg/L), $C_f$ is the concentration in the final solution (mg/L), respectively.

3. Results and discussion

The physicochemical characteristics of zeolite after activation were determined before using in the batch study, such as pH, moisture content, organic matter content, and mineralogical and chemical composition analyses. Subsequently, the effect of several effective variables on the adsorption event including contact time, dosage and pH of the synthetic solution were further examined.

3.1. Physicochemical characteristics of zeolite

The pH of activated zeolite ranged between 7.20 - 7.52, determined as slightly alkaline. The moisture content of the zeolite sample was 0.10 % and the organic matter in the zeolite was 4.70 - 6.21 %, classified as low moisture and moderate respectively. Figure 1 showed the X-ray spectrum for clinoptilolite zeolite and the apparent peaks indicates the presence of mordenite, clinoptilolite and quartz, as determined by XRD analysis. Table 2 further shows the average chemical compositions in zeolite using XRF analysis.

Table 2. Average chemical composition of clinoptilolite zeolite.

| Main element (%) | Sample composition |
|------------------|--------------------|
| SiO$_2$          | 63.00              |
| Al$_2$O$_3$      | 12.30              |
| Fe$_2$O$_3$      | 6.66               |
| CaO              | 14.30              |
| K$_2$O           | 2.18               |
| Na$_2$O          | 1.16               |
| TiO$_2$          | 0.58               |
| MnO              | 0.16               |
| CuO              | 0.053              |
| SrO              | 0.181              |
| ZnO              | 0.023              |
| ZrO$_2$          | 0.042              |
| SiO$_2$/Al$_2$O$_3$ (ratio) | 5.12 |

Figure 1. Spectrum for the development of clinoptilolite zeolite X-rays
Both XRD and XRF results thus confirmed that clinoptilolite as the dominant mineral phase in the zeolite sample, where the ratio Si to Al is 5.12. Previous study stated that the final ratio Si/Al between 2 to 5 for zeolite is known as a middle molecule sieve [16] which determines the strength capacity of ion exchange and escalate the cation attractions to settle inside the pores and channels [17].

3.2. Effects of contact time
To study the effects of contacting time on the adsorption of metal ions by zeolite, 1 gram of sorbent has been added into 100 mL of 50 ppm metal ions solution in different containers, as depicted in Figure 2. The range of 20, 40, 60, 80 and 100 minutes were selected based on optimal results in previous studies. Results indicated that the percentage of metal ion adsorption by zeolite increased sharply with increasing time of equilibration and reached the plateau after 60 minutes before attaining equilibrium adsorption for both copper and magnesium metals. The high sorption rate occurred in the initial 60 minutes has been similarly reported in another work by [18], whom concluded the obtained results was due to the highly gradient of metal ions’ concentration compared to the surface of clinoptilolite and the diffusion of metal ions is resulted by the intra-particle diffusion mechanism. Furthermore, the enhanced elimination efficiency of the metal ions with increasing contact time might be elicited by the improving number of oxygen functional groups in longer time, thus elevated more active sites for the chelation of metal ions [19].

![Figure 2. Effect of contact time on the metal ions removal (Co: 50 ppm), mass =1 gram, V=100 mL, speed=135 rpm.](image)

3.3. Effects of adsorbent dosage
Five varying amount of sorbents (at 0.2, 0.4, 0.6, 0.8 and 1.0 gram) was determined to study the sorption capacity of metal ions on the zeolite in constant solution volume of 100 mL. The samples undergone about 1 hour stirring period. Figure 3 presents the effect of dosage on adsorption of metal ions using zeolite. The results indicated that the adsorption percentage elevated with the increasing mass of the sorbent, where the optimum dosage was achieved by 1 gram of zeolite at almost 80% of copper. Consequently, the number of zeolite adsorption sites or surface area increases with the augmented weight of adsorbent, resulted in a higher metal removal at the end of the experiment. This is also influenced by the greater availability of the exchangeable adsorption sites vacant over the larger sorbent surface area [20], which allows easier penetration of adsorbate into the adsorption sites. A similar result has been documented previously [21].
3.4. Effects of pH solution

Figure 4 shows the effect of pH on the adsorption of heavy metals onto zeolite. The pH value of the studied solution was prepared in a range from 2 to 10 (2, 4, 6, 8, 10) and adjusted using hydrochloric acid and sodium hydroxide. The adsorption efficiency was increased from pH 2 to 6 before slightly decreased at pH 7 and above, due to the metal ions experienced precipitation. Adsorption of magnesium is much lower than copper but still showing the same trends as copper. It shows that at lower pH, adsorption sites are not much or might be saturated by $\text{H}^+$ which slows down the adsorption of both metals. As the pH increases, more sorption sites became available where copper is better precipitated compared to magnesium in this study. The result shows that solution in pH 6 is the most effective value of pH and thus indicated the maximum adsorption (at 70 % and 80 %) to remove both heavy metal ions effectively. The pH of medium affects the adsorption capacity of the heavy metals substantially, where pH value affects the ability of metal ions to bind on the surface of the adsorbent and change the nature of the adsorbent chemically [22]. As being presented in Figure 4, at pH 2 and 4 the adsorption of Cu and Mg is low as the adsorption sites were saturated by $\text{H}^+$. As the pH increased, more negatively charged on active sorption sites became available; hence adsorption level of the positively charged metal ions increased which was mainly influenced by the ion exchange and electrostatic attractions at metal binding sites occurred on the adsorbent [23]. The obtained results are consistent to many previously reported studies, where the optimum removal efficiency of different metal ions has been achieved at pH 6 and at range 45% to 82% by mostly silicate minerals [19, 23].

Figure 4. Effect of pH solution on the metal ions removal (Co: 50 ppm), mass =1 gram, time=1 hour, $V=100 \text{ mL}$, speed=135 rpm.
3.5. Determination of adsorption capacity

The adsorption capacity of zeolite in copper and magnesium stock solutions was later determined experimentally for each metal, under the optimum conditions. The equilibration time was fixed at 1 hour and the stirring rate was kept constant at 135 rpm. The studied initial concentration of metal ions in solutions were varied in the region of 20 to 100 ppm (20, 40, 60, 80 and 100 ppm). Figure 5 illustrates the adsorption capacity was significantly decreasing constantly as the metal concentration is higher. The removal efficiency decreases from 100 to 35 % and 70 to 25 %, for copper and magnesium respectively. At higher concentrations, residual copper and magnesium ions remained in the aqueous solution which makes the ratio of initial number of the metal ions to the accessible active sites of adsorbent is high; therefore the removal efficiency is dropping and decreased [24]. This shows that all the parameters studied was equally crucial to remove heavy metals in solution efficiently and effectively. The application of the studied parameters will therefore speed up the removal of heavy metal ions in wastewater.

![Graph](image)

Figure 5. Determination of adsorption capacity by keeping all the parameters constant; mass=1 gram, time=1 hour: V=100 mL: speed=135 rpm: pH=6.

4. Conclusion

The characterization of zeolites through XRF and XRD analyses have confirmed that the zeolite sample used in the treatment is a Clinoptilolite zeolite. Clinoptilolite is the sorbent with a high tendency to adsorb metal cations as it has large pore size due to the crystalline shape. The high adsorption capacity of zeolite also helps increase the removal of heavy metal by trapping the ions. The application of zeolite for removal of heavy metals therefore shows significant results in the order of Cu > Mg in all tested parameters. Adsorption of Cu$^{2+}$ and Mg$^{2+}$ by zeolite however depends significantly on the tested pH, adsorbent amount and contact time throughout the experiments. Analyses on the rate of uptake of heavy metal ions by the zeolite indicated that the process was quite rapid and maximum adsorption occurred within the first one hour of contact. Therefore, zeolite adsorbent is a promising option for the efficient, economic, and eco-friendly treatment of aqueous wastes containing mixed metal ions.

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