Removal of Hazardous Contaminants from Wastewater Using Natural Zeolite

Ali M.M.*, El-SayedE.E, KamelM.Z.b

*Deputy Director and Operation Manager at Central Laboratory for Environmental Quality Monitoring (CLEQM), National Water Research Center (NWRC), El-kanater, Qalubiya, Egypt
bResearcher at CLEQM

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Abbreviations:
NH₃: ammonia; NH₄⁺: ammonium; Al: aluminium; Ba: barium; Cd: cadmium; Cr: chromium; Cu: copper; Fe: iron; Mn: manganese; Pb: lead; Ni: nickel; and Zn: zinc; XRF: X-Ray fluorescence; XRD: X-Ray diffraction; ESM: Electroscaning Microscope

Corresponding Author:
Ali M.M.*
Deputy Director
Email: mahaali_59 ( at ) yahoo ( dot ) com

El-Sayed E.E
Researcher

Kamel M. Z.
Researcher

Abstract
Water scarcity challenges are currently facing many countries worldwide. Egypt is not an exception from this fact. In addition, water pollution within the Egyptian different water ways adds another challenging dimension. On the other hand, Egyptian government is wasting no time or efforts towards preventing the pollution sources and/or de-pollution of the different water ways through different mechanisms. Research community within the Egyptian authorities is doing its best to find practical, sustainable, and technological approaches for the de-pollution. Among this effort is the utilization of natural zeolite as an adsorbent for certain pollutants. Natural zeolites are environmentally and economically acceptable, their effectiveness in different technological processes depends on their physical and chemical properties that are tightly connected to their geological deposits hydrated aluminosilicate materials with exceptional ion-exchange and sorption properties. Natural zeolite was identified using X-Ray fluorescence (XRF), X-Ray diffraction (XRD) and Electroscaning Microscope (ESM) as clinoptilolite. In this study, the adsorption behavior of natural (clinoptilolite) zeolites with respect to ammonia and heavy metals (Al, Ba, Cd, Cr, Cu, Fe, Mn, Pb, Ni, and Zn) has been studied in order to consider its application to purify wastewaters. The batch method has been conducted, using ammonia and heavy metals concentrations in solution under variables conditions of pH values (4-10), contact time (up to 3 hour), weight of adsorbent (0.5-2.0 g) and different initial concentrations of contaminants (1-10 ppm of ammonia and heavy metals). The obtained results revealed that the removal efficiency of clinoptilolite for ammonium was ranged from 70-92%, while it ranged from 70-99% for heavy metals at various conditions. The current study has confirmed the excellent performance of low cost natural zeolite for removing ammonia and heavy metals from wastewaters.

Citation:

1. Introduction

Egypt has been suffering from severe water scarcity in recent years. The River Nile is the lifeline of the country as it services the country’s industrial and agricultural demand and is the primary source of drinking water for the population. Rising populations and rapid economic development in the countries of the Nile Basin, pollution and environmental degradation are decreasing water availability. Industrial effluents are often highly toxic, containing heavy metals that can combine with the suspended solids in domestic wastewater to form muck. Heavy metals are not degradable and have increasing significant owing to their harmful effect on human physiologies and other biological systems when they exceed the tolerance levels and
become an ecotoxicological hazards of prime interest (Aguiar et al., 2002).

The presence of ammonia in the environment is a major concern due to its toxicity. Ammonia is an important nitrogen ion form in aqueous solution. Its pollution mainly results from fertilizer factories discharge, municipal sewage and agricultural wastes. The most dangers effects were presented when higher concentration of ammonia causes a sharp decrease of dissolved oxygen and obvious toxicity to aquatic organisms.

All of these factors combine together needs to be controlled. Removal of these contaminants requires cost effective technologies. Currently, adsorption is believed to be a simple and effective technique for water and wastewater treatment and the success of the technique largely depends on the development of an efficient adsorbent (Babel and Kurniawan, 2003). Activated carbon, clay minerals, biomaterials, zeolites, and some industrial solid wastes have been widely used as adsorbents for adsorption of ions and organics in wastewater treatment (Hedström, 2001).

Natural zeolite is one of the most important methods are explored as an effective adsorbent (Bolan et al., 2003). Zeolites constitute a major class of natural and synthetic aluminosilicate crystalline microporous materials as shown in Figure (1). Their structure shows unique physicochemical properties. Because of these properties, the zeolites have found a wide spectrum of environmental and industrial applications (e.g. molecular sieves, ion-exchangers, adsorption, catalysis, soil remediation, and energy (Tsitsishvili, 1992; Kalló, 2001). Natural zeolite has advantages over other cation exchange materials such as commonly used organic resins, because they are cheap, they exhibit excellent selectivity for different cations at low temperatures, which is accompanied with a release of nontoxic exchangeable cations (K\(^+\), Na\(^+\), Ca\(^2+\) and Mg\(^2+\)) to the environment, they are compact in size and they allow simple and cheap maintenance in the full scale applications. Utilization of natural zeolite has been focused on ammonium and heavy metal removal due to the nature of ion exchange and some review papers have been appeared (Kessraoui Ouki et al., 1994; Caputo and Pepe, 2007). Many investigations have been conducted using natural zeolite for ammonia and metal ion adsorption (Kalló, 2001). However, these researches focused on single metal ion and its affinity to zeolite. While for wastewater systems, there are different types of contaminants and may contain a mixture of metal ions.

In this study, the adsorption properties of the natural zeolite from Alyaman with respect to ammonia and some heavy metal in solution were investigated under various conditions.

**Justification of Research**

Water pollution in the different irrigation and drainage channels in Egypt is a challenging issue. This pollution prevents water managers from recycling the drainage water especially in the era of the Egyptian water scarcity. Therefore, de-pollution and removing whatever pollutants from different water ways are targets for the Egyptian scientific community towards supporting decision makers in facing the various water challenges in Egypt. The current research is considered a break-through in finding a safe and efficient substance available in the Egyptian environment that can reduce the pollution load from the different water ways. The current research started with utilizing the natural zeolite in a laboratory scale to evaluate its efficiency and has proven its efficiency for this scale. The research authors are planning to upscale the experiment to a laboratory channel for a further research indoors step towards further evaluation.

2. **Experimental**

2.1. **Identification of zeolite**

Natural zeolite samples were provided by Egyptian company (Technolab El-Bahaa group). Chemical analysis of zeolite sample was determined by X-Ray fluorescence (XRF) spectroscopy using Axios, sequential WD- XRF spectrometer, PAN analytical 2005. The X-Ray powder diffraction (XRD) was analyzed using a PAN analytical X-Ray Diffraction equipment model X Pert PRO. Zeolite sample were investigated using Electroscanning microscope (ESM).

2.2. **Zeolite sample preparation**

The sample was ground in a ball mill and particles smaller than 0.25 mm were used for the sorption experiments. The zeolite sample was washed with distilled water to remove any non-adhesive impurities and small particles, and then, dried at 70°C for 24h to remove moisture. The used particle size of zeolite was ranged between 0.25–0.5 mm to maximize the adsorption capacity of zeolite to ammonia and heavy metals ions.

2.3. **Pollutant samples preparation**

Different concentrations of ammonia (1, 5 and 10 mg/l) were prepared using crystalline NH\(_4\)Cl (Aldrich, Milwaukee, WI). Ammonia was measured using ion chromatography (model Dionex ICS 5000). Inorganic chemicals were supplied by Merck as analytical grade reagents and deionized water was used.

The metal ions studied were Al, Ba, Cd, Cr, Cu, Fe, Pb, Mn, Ni, and Zn. The multi-standard stock solution (1000 mg/l) was used to prepare different concentrations of heavy metals (1, 5 and 10 mg/l), in deionized water. The metals were analyzed using ICP-MS (Perkin Elmer, NexIon 300D) financed by Science technology and Development Funds (STDF).

2.4. **Batch adsorption studies**

The efficiency of natural zeolite to remove ammonia and metal ions from wastewater was evaluated under different condition (mass of zeolite, pH, initial pollutants concentrations and contact time).
The ion exchange of ammonia and heavy metals on natural zeolite was carried out using the batch method. Batch adsorption experiments were conducted using 0.5, 1.0 and 2.0 g of absorbent to 100 ml of solutions with varying concentrations of ammonia and heavy metals (0.5, 1.0 and 2.0 g). The drops and negligible volumes of sodium hydroxide (NaOH) or hydrochloric acid (HCl) were adding to the solution system to adjust the tested pH (4, 6, 8 and 10).

The equilibrium state for zeolite under investigation was obtained by using the constant weight of absorbent (0.5, 1.0 and 2.0 g) in 100 ml of prepared solution of ammonia and heavy metals in glass bottles and kept on constant agitation shaker (100rpm at 25°C) to enhance the interaction of the clinoptilolite with ammonia and heavy metals solution. It was observed that the absorbed ammonia and heavy metals ions and absorbent reached to equilibrium after 2 hours. However, the experiment was kept for 3 hours to ensure that the absorption process reached to complete equilibrium. The experiments were performed in duplicate. After that the samples were filtered using filter paper and the concentration of ammonia and different heavy metals ions were measured. The removal efficiency of zeolite was calculated by the following equation:

\[
\text{Treatment efficiency (\%)} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]

Where, \(C_0\) is the initial concentration of metals ions (mg/l) and \(C_e\) is the concentration of the metal (mg/l) at definite contact time (1, 2 and 3 hours).

3. Results and Discussion

3.1. Identification of studied zeolite

Chemical analysis of zeolite sample by X-Ray fluorescence (XRF) spectroscopy was presented in Table (1). The mineralogical characteristics of the natural sorbent as shown in Figure (2) and Table (2), while Figure (3) presents the Electrosclanning microscope (ESM) for zeolite sample. The above investigation indicates that the obtained type of zeolite in this study is clinoptilolite.

3.2. Batch study

The ammonia and heavy metal uptake is attributed to different mechanisms of ion-exchange processes as well as to the adsorption process. During the ion-exchange process, metal ions had to move through the pores of the zeolite mass, but also through channels of the lattice, and they had to replace exchangeable cations (mainly sodium and calcium). Diffusion was faster through the pores and was retarded when the ions moved through the smaller diameter channels. In this case the metal ion uptake could mainly be attributed to ion-exchange reactions in the micro porous minerals of the zeolite samples.

3.2.1. Weight of absorbent.

Tables (3-5) represent the removal efficiency of the studied zeolite with various weight of absorbent at different contact time and initial concentration of pollutants (ammonia and heavy metals). The obtained data revealed that, the maximum removal efficiency was obtained with 2 g of absorbent.

3.2.2. Effect of pH

The pH of the solution is an important controlling factor for the adsorption of ammonia and heavy metals on the sorbents with the effect of metal type and binding sites on surface metal. The effect of pH on the adsorption of ammonia and metal ions at different initial concentrations (1, 5 and 10 mg/l with 2 g of zeolite) respectively at 25°C are presented in Figures. 5-15. The obtained results showed that the adsorption of ammonia and metal ions onto zeolite is affected by pH.

The ability of Al-Yamane Clinoptilolite under investigation to remove ammonia from solutions were increase with increasing pH (i.e pH=10 compared to pHs 4 and 6). This is due to the fact that hydrogen ion (H+) themselves is strong competing ions and partly that the solution pH influences the chemical groups on to the adsorbent surfaces. For a multi component system there was a competitive effect between ammonium ions and other cations such as Ca\(^{2+}\), Mg\(^{2+}\), Na\(^+\), K\(^+\) and the zeolite’s selectivity for ammonium ions was over other cations typically present in sewage (Lei et. al., 2008).

A clinoptilolite from New Zealand was treated with alkaline solutions (pH= 9) and evaluated to remove NH\(_4^+\) from wastewater stream. It was found that metal ions exchange capacity of the natural zeolite was increased by up to 74% and the zeolite could hold a potential maximum of 18.7-20.1 mg NH\(_4^+\)/g. The obtained data were agree with Cooney et al., 1999 who conduct a study on Australian Clinoptilolite to remove ammonium ions from wastewater. The results revealed that the highest ammonium removal efficiency was achieved when the zeolite’s exchange sites were converted to the sodium form in pH ranged from 9 to 11.

Contamination of metals ions in water supplies has steadily increased over the last decades due to over population and expansion of industrial activities. The presence of heavy metals in the environment is a major concern due to their toxicity. It has been found that many heavy metal ions cause strong health problem and damage to plants and animals. The finest clinoptilolite fractions adsorbed higher amounts of the metals due to relative enriching by higher cleavage. Inglezakis et al., 2007 presented a study of using natural clinoptilolite to remove Pb\(^{2+}\) from aqueous solutions. Clinoptilolite dust (micro size) is found to be more efficient than granular clinoptilolite. Time and temperature affected the uptake of Pb\(^{2+}\), especially in the case of granular clinoptilolite (2.5–5.0 mm). The adsorption of lead increased with an increase in pH of the solution from 6 to 10.
Table 1: X-ray fluorescence (XRF) analysis for the studied natural zeolite

<table>
<thead>
<tr>
<th>Content</th>
<th>Tz3</th>
<th>Tz4</th>
<th>Tz101</th>
<th>Tz-z</th>
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<tr>
<td>SiO$_2$</td>
<td>70.5</td>
<td>70.06</td>
<td>69.58</td>
<td>69.6</td>
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<tr>
<td>TiO$_2$</td>
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<td>11.2</td>
<td>12.07</td>
<td>0.23</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.16</td>
<td>0.15</td>
<td>0.17</td>
<td>11.59</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.56</td>
<td>2.06</td>
<td>2.18</td>
<td>2.55</td>
</tr>
<tr>
<td>MnO</td>
<td>11.09</td>
<td>0.08</td>
<td>0.16</td>
<td>0.06</td>
</tr>
<tr>
<td>MgO</td>
<td>0.48</td>
<td>0.34</td>
<td>0.52</td>
<td>0.52</td>
</tr>
<tr>
<td>CaO</td>
<td>1.01</td>
<td>1.62</td>
<td>1.16</td>
<td>1.89</td>
</tr>
<tr>
<td>NaO</td>
<td>0.35</td>
<td>0.12</td>
<td>0.4</td>
<td>0.26</td>
</tr>
<tr>
<td>K2O</td>
<td>4.57</td>
<td>5.16</td>
<td>3.03</td>
<td>4.28</td>
</tr>
<tr>
<td>P2O$_5$</td>
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<td>0.01</td>
<td>0.03</td>
<td>0.031</td>
</tr>
<tr>
<td>SO$_3$</td>
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<td>0.002</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>LOI</td>
<td>8.04</td>
<td>9.08</td>
<td>10.55</td>
<td>8.84</td>
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</table>

Table 2: The chemical characteristics of the natural sorbent

<table>
<thead>
<tr>
<th>Ref. Code</th>
<th>Mineral Name</th>
<th>Chemical Formula</th>
<th>Semi Quant [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>96-900-1618</td>
<td>Clinoptilite-Na</td>
<td>Na7.20 Si27.11 Al8.89 O97.92</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 3: Removal efficiency of ammonia and heavy metals concentrations at different contact time using natural Zeolite (clinoptilolite 2 g)

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameters</th>
<th>Contact time, Initial Conc</th>
<th>Removal Efficiency (%) at different times</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 hour</td>
<td>5.0 (mg/l)</td>
</tr>
<tr>
<td>1</td>
<td>Ammonium (NH$_4^+$)</td>
<td>81.9</td>
<td>91.1</td>
</tr>
<tr>
<td>2</td>
<td>Aluminum (Al)</td>
<td>91.6</td>
<td>90.2</td>
</tr>
<tr>
<td>3</td>
<td>Barium (Ba)</td>
<td>99.5</td>
<td>92.2</td>
</tr>
<tr>
<td>4</td>
<td>Cadmium (Cd)</td>
<td>99.5</td>
<td>98.0</td>
</tr>
<tr>
<td>5</td>
<td>Chromium (Cr)</td>
<td>99.5</td>
<td>98.1</td>
</tr>
<tr>
<td>6</td>
<td>Copper (Cu)</td>
<td>99.1</td>
<td>98.5</td>
</tr>
<tr>
<td>7</td>
<td>Iron (Fe)</td>
<td>99.5</td>
<td>95.4</td>
</tr>
<tr>
<td>8</td>
<td>Lead (Pb)</td>
<td>98.4</td>
<td>95.0</td>
</tr>
<tr>
<td>9</td>
<td>Manganese (Mn)</td>
<td>99.2</td>
<td>93.1</td>
</tr>
<tr>
<td>10</td>
<td>Nickel (Ni)</td>
<td>99.2</td>
<td>98.5</td>
</tr>
<tr>
<td>11</td>
<td>Zinc (Zn)</td>
<td>99.0</td>
<td>93.2</td>
</tr>
</tbody>
</table>

Table 4: Removal efficiency of ammonia and heavy metals concentrations at different contact time using natural Zeolite (clinoptilolite 1 g)

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameters</th>
<th>Contact time, Initial Conc</th>
<th>Removal Efficiency (%) at different times</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 hour</td>
<td>5.0 (mg/l)</td>
</tr>
<tr>
<td>1</td>
<td>Ammonium (NH$_4^+$)</td>
<td>78.3</td>
<td>81.2</td>
</tr>
<tr>
<td>2</td>
<td>Aluminum (Al)</td>
<td>84.2</td>
<td>88.4</td>
</tr>
<tr>
<td>3</td>
<td>Barium (Ba)</td>
<td>88.1</td>
<td>90.0</td>
</tr>
<tr>
<td>4</td>
<td>Cadmium (Cd)</td>
<td>99.9</td>
<td>99.9</td>
</tr>
<tr>
<td>5</td>
<td>Chromium (Cr)</td>
<td>99.9</td>
<td>99.9</td>
</tr>
<tr>
<td>6</td>
<td>Copper (Cu)</td>
<td>99.7</td>
<td>99.8</td>
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<tr>
<td>7</td>
<td>Iron (Fe)</td>
<td>99.5</td>
<td>95.4</td>
</tr>
<tr>
<td>8</td>
<td>Lead (Pb)</td>
<td>84.4</td>
<td>92.1</td>
</tr>
<tr>
<td>9</td>
<td>Manganese (Mn)</td>
<td>99.6</td>
<td>99.7</td>
</tr>
<tr>
<td>10</td>
<td>Nickel (Ni)</td>
<td>99.5</td>
<td>99.7</td>
</tr>
<tr>
<td>11</td>
<td>Zinc (Zn)</td>
<td>99.0</td>
<td>99.7</td>
</tr>
</tbody>
</table>
Table 5: Removal efficiency of ammonia and heavy metals concentrations at different contact time using natural zeolite (clinoptilolite 0.5 g)

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameters</th>
<th>Contact time, initial Conc.</th>
<th>1 hour</th>
<th>2 hours</th>
<th>3 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.0 (mg/l) 5.0 (mg/l) 10.0 (mg/l)</td>
<td>1.0 (mg/l) 5.0 (mg/l) 10.0 (mg/l)</td>
<td>1.0 (mg/l) 5.0 (mg/l) 10.0 (mg/l)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Ammonium (NH₄⁺)</td>
<td>70.2 76.3 78.9</td>
<td>80.1 87.2 87.7</td>
<td>80.0 87.0 87.1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Aluminum (Al)</td>
<td>77.2 76.20 72.3</td>
<td>82.0 92.0 90.4</td>
<td>81.0 88.2 86.7</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Barium (Ba)</td>
<td>84.0 88.0 86.1</td>
<td>97.5 93.1 88.0</td>
<td>97.3 89.1 82.1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Cadmium (Cd)</td>
<td>97.9 97.90 94.5</td>
<td>97.9 97.9 97.9</td>
<td>97.9 94.1 97.9</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Chromium (Cr)</td>
<td>97.9 91.40 96.0</td>
<td>97.9 97.0 97.1</td>
<td>97.9 95.0 95.2</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Copper (Cu)</td>
<td>91.6 94.4 92.1</td>
<td>90.6 97.0 96.1</td>
<td>91.1 95.2 95.4</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Iron (Fe)</td>
<td>72.0 90.1 91.1</td>
<td>90.1 92.2 92.0</td>
<td>91.0 95.1 92.0</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Lead (Pb)</td>
<td>97.1 95.0 93.0</td>
<td>97.7 95.1 95.4</td>
<td>95.1 96.5 94.2</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Manganese (Mn)</td>
<td>97.2 96.4 94.2</td>
<td>97.5 97.5 96.4</td>
<td>97.5 97.0 95.1</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Nickel (Ni)</td>
<td>95.1 94.2 91.1</td>
<td>97.3 97.2 96.1</td>
<td>97.0 95.0 96.0</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Zinc (Zn)</td>
<td>97.1 92.2 93.0</td>
<td>97.9 97.0 94.3</td>
<td>97.2 90.2 93.2</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1: Simplified chemical composition and structure of zeolite.

\[
\text{Me}_{n}^{n+} \text{ K}^+ \text{ Ca}^{2+} \text{ Na}^+ \text{ Mg}^{2+} \text{ Fe}^{3+} \text{ NH}_4^+
\]

Figure 2: XRD pattern of studied zeolite

Figure 3: Electrosanning microscope (ESM) for the studied Zeolite
Figure 4: The competition of cations on zeolite surface / time

(A) (B)

Figure 5: Effect of pH on removal of $\text{NH}_4^+$ using 2g of zeolite

Figure 6: Effect of pH on removal of Al using 2g of zeolite

Figure 7: Effect of pH on removal of Ba using 2g of zeolite

Figure 8: Effect of pH on removal of Cd using 2g of zeolite

Figure 9: Effect of pH on removal of Cr using 2g of zeolite

Figure 10: Effect of pH on removal of Cu using 2g of zeolite
Figure 11: Effect of pH on removal of Fe using 2g of zeolite

Figure 12: Effect of pH on removal of Pb using 2g of zeolite

Figure 13: Effect of pH on removal of Mn using 2g of zeolite

Figure 14: Effect of pH on removal of Ni using 2g of zeolite

Figure 15: Effect of pH on removal of Zn using 2g of zeolite

Figure 16: Effect of Contact time and initial Conc. on removal of \( \text{NH}_4^+ \) using 2g of zeolite
Figure 17: Effect of Contact time and initial Conc. on removal of Al using 2g of zeolite

Figure 18: Effect of Contact time and initial Conc. on removal of Ba using 2g of zeolite

Figure 19: Effect of Contact time and initial Conc. on removal of Cd using 2g of zeolite

Figure 20: Effect of Contact time and initial Conc. on removal of Cr using 2g of zeolite

Figure 21: Effect of Contact time and initial Conc. on removal of Cu using 2g of zeolite

Figure 22: Effect of Contact time and initial Conc. on removal of Fe using 2g of zeolite
**Figure 23:** Effect of Contact time and initial Conc. on removal of Pb using 2g of zeolite

**Figure 24:** Effect of Contact time and initial Conc. on removal of Mn using 2g of zeolite

**Figure 25:** Effect of Contact time and initial Conc. on removal of Ni using 2g of zeolite

**Figure 26:** Effect of Contact time and initial Conc. on removal of Zn using 2g of zeolite

**Figure 27:** Effect of Contact time and initial Conc. on removal of NH₄⁺ using 1g of zeolite

**Figure 28:** Effect of Contact time and initial Conc. on removal of Al using 1g of zeolite
Figure 29: Effect of Contact time and initial Conc. on removal of Ba using 1g of zeolite

Figure 30: Effect of Contact time and initial Conc. on removal of Cd using 1g of zeolite

Figure 31: Effect of Contact time and initial Conc. on removal of Cr using 1g of zeolite

Figure 32: Effect of Contact time and initial Conc. on removal of Cu using 1g of zeolite

Figure 33: Effect of Contact time and initial Conc. on removal of Fe using 1g of zeolite

Figure 34: Effect of Contact time and initial Conc. on removal of Pb using 1g of zeolite
**Figure 41:** Effect of Contact time and Initial Conc. on removal of Cd using 0.5g of zeolite

**Figure 42:** Effect of Contact time and Initial Conc. on removal of Cr using 0.5g of zeolite

**Figure 43:** Effect of Contact time and Initial Conc. on removal of Cu using 0.5g of zeolite

**Figure 44:** Effect of Contact time and Initial Conc. on removal of Fe using 0.5g of zeolite

**Figure 45:** Effect of Contact time and Initial Conc. on removal of Pb using 0.5g of zeolite

**Figure 46:** Effect of Contact time and initial Conc. on removal of Mn using 0.5g of zeolite
Llanes-Monter et al., 2007 evaluate the removal of heavy metals by natural clinoptilolite. Maximum metal ions exchange capacity of clinoptilolite was at pH 8. The chemical metals speciation, the pH, as well as the characteristics of the clinoptilolite are important factors to be considered on the metal ions sorption process by zeolites.

Wingenfelder et al., 2005 studied the removal of Fe, Pb, Cd, and Zn from prepared solution by a natural zeolite. The lead was removed efficiently from neutral as well as from alkali solutions, whereas the uptake of Fe, Zn and Cd decreased with low pH value. With increasing pH, the elimination of such metal ions increases.

3.2.3. Effect of initial concentrations of pollutants

The results showed that the adsorption of ammonia and metal ions onto zeolite is affected by their initial concentrations as shown in Figures (16-48). The removal efficiency of the investigated zeolite was increased as the initial concentration of pollutants decreased at 25°C. The results of the present study were agreed with Rožić et al., 2000 who investigated the removal of ammonium ions from solutions using a Croatian Clinoptilolite. They found that the highest removal efficiency for N–NH₄⁺ (88.1 %) was achieved at initial lowest concentration. With the increase of the initial concentration of ammonia nitrogen, the removal efficiency quickly decreased.

Lebedynets et al., 2004 carried out a study of NH₄⁺ sorption from synthetic aqueous solutions by a Ukraine clinoptilolite. NH₄⁺ sorption by the zeolite would be completed within 24 h for all fraction sizes, initial NH₄⁺ ion concentrations and adsorbate volumes. The adsorption capacity was controlled by pH factor. The higher adsorption capacity is higher pH values. The amounts of NH₄⁺ ions sorbed increased with increasing adsorbate volumes and decreasing initial NH₄⁺ concentration. Englert and Rubio, 2005 used a natural zeolite as an adsorbent for ammonia from aqueous solutions. The experiment showed the particles were negatively charged over a broad pH range, while the maximum removal was higher at low concentration of pollutants.

3.2.4. Effect of contact time

The ion exchange behavior of natural zeolite depends on several factors, including the contact time, framework structure, ion size and shape, charge density of the anionic framework as shown in Figure (4), ionic charge and concentration of the external electrolyte solution (Inglezakis et al., 2010).

The contact time influences the adsorption of metal ions onto zeolite. Many studies proved that, the efficiency of impurities removal in the water treatment process on the zeolites depends on the contact time and fraction size (Erdem et al., 2004). Total surface for the active sites of the zeolite increases with decreasing particle size, and increases the contact time as well as the number of direct contacts of impurity ions with the main channels.

The contact time in present study was also investigated. Tables (3-5) and Figures (16-48) present the effect of contact time on the removal efficiency. The results reveal that the pollutants removal is higher at the beginning of batch study due to the availability of surface area of zeolite for adsorption of ammonia and heavy metal ions. With time the surface adsorption sites become filled with ammonium ions and metal ions and the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles (Sprynsky et al., 2005).

Initially, the rate of different metal ions uptake was higher because all sites on the adsorbent were vacant and metal ions concentration was high, but through time the uptake rate being to decrease due to reduce of sorption sites. The obtained results were similar to that found in the study of Cheng et al., 2005 they found the optimum contact time was determined at 90 min. for metal ions removal, while the removal rate of metal ions gradually decreased with increase in contact time.
Conclusion

The complexity of aquatic systems demands special attention in the selection and preparation of materials for water purification. The unique ion exchange and adsorption properties, low coast, safety, high porosity, and excellent thermal stability of zeolite make them very suitable for many water treatment processes.

This study has demonstrated its effectiveness in reducing the contaminants (ammonia and heavy metals) from wastewater. The research revealed that the efficiency of water treatment by using natural zeolite depends on the type and quantity of the used zeolite, the initial concentration of contaminants (ammonia and heavy metals), pH value of solution and contact time of system zeolite/solution.

Further academic and applied research should be focused on the implementation of this zeolite in various waterways.

Research Highlights

1. The current research demonstrated using natural zeolites (clinoptilolite) as an effective material for wastewater treatment.
2. The effectiveness of natural zeolite as a low cost, safe for ammonium and heavy metals were depending on the type and quantity of the used zeolite, the initial concentration of contaminants, pH and contact time.
3. The removal efficiency of clinoptilolite for ammonium was ranged from 70-92%, while it ranged from 70-99% for heavy metals at various conditions.

Limitations

The research presented in the current manuscript represents the first step towards utilizing the natural zeolite in the water de-pollution of different water ways in Egypt. This research utilized the natural zeolite in a laboratory experiments and proved to be very efficient according to the results presented. Therefore, the current research is limited until now for a laboratory experimentation.

The authors plan to extend their research to a laboratory flume with a flowing water to measure the efficiency of natural zeolite in removing the different pollutants in a small scale channels as well as the other parameters such as the contact time, optimum water flow velocity, amount of zeolite needed compared to the water flow, and any side effects that might be witnessed.

Recommendations

Natural zeolite has proven its efficiency in removing certain pollutants from water within laboratory experimentation. It is highly recommended to expand the research to a laboratory channel scale towards evaluating the different parameters in the idea and before the zeolite can be professionally adopted in a field water channels with certain guidelines on the application process.

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Author's Contributions and Competing Interest

The research authors are in team work and aiming to use low cost and safe environmentally materials on wastewater treatment to overcome the water scarcity due to increasing of population in Egypt.

Future objective

We attend to implement the current experiment on large scale represented on water flume to investigate if it useful to demonstrates this module at water drainage.

References


