Regeneration and Reuse of Clinoptilolite for Recovery of Copper and Cobalt from Aqueous Solutions

Elvis Fosso-Kankeu, Antoine-Floribert. Mulaba-Bafubiandi, Jim T. Modipe and Eunice S. Maroga

Abstract—Ineffective recovery of metals from pregnant solutions during hydrometallurgical processes mainly results in residual value reporting to the liquid effluent. Previous studies have shown that zeolite can be used for the recovery of base metals from solution through ion-exchange process. The main objective of this work was to investigate the potential regeneration of used clinoptilolite in alkaline and acidic solutions. The batch adsorption tests work was conducted at room temperature using 5g of zeolite for the recovery of copper and cobalt present in aqueous solutions at concentrations ranging from 10ppm to 50ppm. The maximum adsorption rate achieved with non-regenerated zeolite was (50%), adsorption capacity was increased to 90% after regeneration with nitric and chloridric acid at 0.02 M. The poor performance of the non-regenerated clinoptilolite would be due to the high poisoning level of the zeolite whereas residual poisons have been removed through the regeneration process. It is then concluded that regenerated zeolite showed potential to be used as sorbent in the recovery of cobalt and copper from their aqueous solutions.

Keywords—Clinoptilolite, metal adsorption, regeneration, reuse

I. INTRODUCTION

The potential of zeolite for removal of metals from solutions has been extensively proven; naturally present in the soil, it can also be synthesized for commercial and research purposes. Widely available, zeolite could therefore constitute a suitable adsorbing agent for bioremediation of metal polluted effluents. High adsorption rate has been achieved by several researchers [1], [2], [3] when using both natural and synthetic zeolites for removal of metal from solutions. Metal adsorption by zeolite mainly occurs through a chemical mechanism or ion exchange process, and partly through a physical mechanism dependent on the microporous structure of the mineral [4], [5], [6]. Natural zeolite is often preferred for metal bioremediation processes because of their low cost and unique physical and chemical properties [5].

With large size of deposits around the world and wide geographic distribution, clinoptilolite is considered as the most abundant zeolite [7].

The remediation process may become more attractive if the cost of the sorption agent is low. One way of ensuring minimal cost of the sorbent is through its regeneration and reuse, eliminating the need to use new sorbent for every adsorption cycle and also ensuring the recovery of values. Acidic and alkaline media have been used as eluents for the regeneration of zeolites with different outcomes. Some researchers have claimed that acidic eluents are responsible of the degradation of zeolite and therefore reduction of their adsorption capacity, while alkaline conditions were not effective in most cases [8], [9]. Gorimbo [8] reported dealumination and reduction of adsorption capacity of clinoptilolite following exposure to high concentration of acids, while exposure to base resulted to internal formation of precipitates and clogging of the pores in the zeolite framework.

Natural zeolites found in the environment often have different structures [10] and therefore likely to exhibit different adsorption capacity and robustness following reuse. In this study clinoptilolite collected from the Vulture Greek of Kwazulu Natal Province in South Africa was tested for its potential of reuse during metal removal processes.

II. METHODOLOGY

A. Characterization of clinoptilolite

Preloaded and eluted clinoptilolite samples from previous study (cobalt and copper adsorption) were grind in a mortar and the mineralogical composition determined using the X-ray fluorescence.

B. Determination of the poisoning level

To determine the level of poisoning with residual metals, powder form of clinoptilolite was dissolved in aqua regia. The mixture was then filtered and the concentration of copper and cobalt in the filtrate was measured using atomic absorption spectrophotometer (AAS).

C. Regeneration technique

Regeneration of poisoned clinoptilolite was done using either alkaline or acidic solution. Alkaline solution was
prepared by dissolving potassium chloride in distilled water to obtain a concentration of 0.02M. The loaded clinoptilolite was immersed in the solution for one hour, then dried at 50°C for 24 h in an oven prior to use for adsorption experiments. Concentrated solution of chloridric and nitric acids were dissolved in distilled water to prepare solution solutions of 0.02 M. They were then used to regenerate loaded clinoptilolite for one or eight hours. Clinoptilolite was then dried as above before used for adsorption of metals.

D. Adsorption of metals

Batch adsorption experiments were conducted at room temperature using 5 g of clinoptilolite in 50 ml solutions of 10, 20, 30 and 50 mg/L initial concentrations of either cobalt or copper ions. Solutions of metal ions were loaded into columns in glass containing 5 g of regenerated clinoptilolite and the exposure was allowed for a period of one hour, then the effluent was collected for measurement of residual metal ions using AAS.

III. RESULTS AND DISCUSSION

A. Mineralogical composition

The mineralogical composition (Table 1) indicates that clinoptilolite studied has relatively high silica level. The Si/Al ratio was 5.91, while the (Na + K)/Ca ratio was 3.62. For typical theoretical exchange capacity, Si/Al ratio of natural clinoptilolite can generally range from 4 to 5.5 [10], implying that the clinoptilolite used in this had the capacity to exchange ions. Moreover, the clinoptilolite studied contains relatively high silica level and could be classified as high silica member, a group reported to be also rich in sodium, potassium and magnesium [10].

<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>% weight</th>
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<tbody>
<tr>
<td>1</td>
<td>Na₂O</td>
<td>1.0469</td>
</tr>
<tr>
<td>2</td>
<td>MgO</td>
<td>0.8082</td>
</tr>
<tr>
<td>3</td>
<td>Al₂O₃</td>
<td>13.0621</td>
</tr>
<tr>
<td>4</td>
<td>SiO₂</td>
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</tr>
<tr>
<td>5</td>
<td>P₂O₅</td>
<td>0.0104</td>
</tr>
<tr>
<td>6</td>
<td>SO₃</td>
<td>0.2917</td>
</tr>
<tr>
<td>7</td>
<td>Cl</td>
<td>0.2819</td>
</tr>
<tr>
<td>8</td>
<td>K₂O</td>
<td>4.1793</td>
</tr>
<tr>
<td>9</td>
<td>CaO</td>
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<tr>
<td>11</td>
<td>MnO</td>
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<tr>
<td>12</td>
<td>Fe₂O₃</td>
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<tr>
<td>13</td>
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<tr>
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<tr>
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</tr>
<tr>
<td>16</td>
<td>ZnO</td>
<td>0.0062</td>
</tr>
</tbody>
</table>

Table 1

X Ray Fluorescence results also revealed that the clinoptilolite used in this study contained Cu, Zn, Ni, Co, Fe and Mn in the form of oxides. These ions might be held on the active available sites for adsorption, during the adsorption of targeted metals they may act as competitive ions, hence reducing the cation exchange capacity of the zeolites.

B. Level of clinoptilolite poisoning

Dissolution of the clinoptilolite in the aqua regia allowed to determine the level of poisoning. It was observed that a maximum of 3.2 mg/g and 1.9 mg/g of residual copper and cobalt respectively were still occupying the binding sites on the clinoptilolite. The clinoptilolite was then regenerated into alkaline or acidic solution to free the binding sites.

C. Study of alkaline regeneration

Clinoptilolite regenerated with alkaline solution was a relative poor sorbent as it was reused for adsorption of cobalt and copper. As shown in Figure 1 below, the maximum adsorption capacities were 0.12 mg/g and 0.1 mg/g for cobalt and copper respectively, and no metal removal was achieved in diluted solutions (initial concentrations 10 and 20 mg/L).

D. Study of acidic regeneration

Regeneration with nitric acid After regeneration with nitric acid, clinoptilolite showed good adsorption capacity as it removed almost all the metal ions from the solution (Figure 2). There was no significant change of the adsorption capacity over time, however it increased with the initial concentration of metal, a phenomenon explained by the mass transfer. The regenerated clinoptilolite showed similar affinity for both cobalt and copper. The optimum time of adsorption was then one hour at which the maximum adsorption capacities were 0.47 mg/g and 0.48 mg/g for cobalt and copper respectively.

Fig. 1 Removal of cobalt and copper by clinoptilolite regenerated in alkaline solution (KCl, 0.02M)

Fig. 2 Removal of cobalt and copper by clinoptilolite regenerated in nitric acid (0.02M)
Regeneration with hydrochloric acid Despite some few disparities, the general pattern of metal adsorption by clinoptilolite regenerated with hydrochloric acid (Figure 3) was similar to the clinoptilolite regenerated with nitric acid. The maximum adsorption capacities at the optimum time were 0.42 mg/g and 0.43 mg/g for cobalt and copper respectively.

Regenerated clinoptilolite, hence the need of regeneration. On the other hand it can be seen that potassium chloride was not a good medium for regeneration; Figure 4 shows that the performance of clinoptilolite was even reduced (comparing with non-regenerated clinoptilolite) when exposed to potassium chloride. Using different chemicals (1M NaCl, KCl, CaCl and HCl) to regenerate clinoptilolite and adsorb cadmium, Gedik and Imamoglu [9] found that KCl and HCl had a poor performance. On the contrary, Vasylychko et al. [12] observed favourable cadmium removal after pretreatment with HCl.

IV. CONCLUSION
Zeolite has been an attractive adsorbent over the years because it is environmentally friendly and cheap. One critical aspect for the application of adsorption is therefore the availability and cost of adsorbents. Regeneration of adsorbent with suitable medium is then imperative. It has been demonstrated in this study that regeneration of natural clinoptilolite originating from the Vulture Greek of KwaZulu Natal Province in South Africa, is effective when using nitric acid (0.02 M) for one hour. The possible use of this clinoptilolite for more than one adsorption cycle will make it an adequate sorbent for treatment of mine effluents.

REFERENCES
Born in Cameroon, the author obtained the certificate for completion of high school in Bafoussam-Cameroon and then completed a BSc in Biochemistry at the University of Dschang in Cameroon. He then traveled to South Africa where he continued his studies and completed a B-Tech and M-Tech in Biotechnology; after a year in the consulting sector, he went back in academia to complete a D-Tech in Extraction Metallurgy focusing on Bioprocessing.


Dr Elvis Fosso-Kankeu has been a recipient of several merit awards, the more recent is the best paper award received at the International Mine Water Conference in Bunbury-Australia, October 2012.