Parameters Affecting the Removal of Copper and Cobalt from Aqueous Solution onto Clinoptilolite by Ion-Exchange Process

John Kabuba, Hilary Rutto

Abstract—Ion exchange is one of the methods used to remove heavy metal such as copper and cobalt from wastewaters. Parameters affecting the ion-exchange of copper and cobalt aqueous solutions using clinoptilolite are the objectives of this study. Synthetic solutions were prepared with the concentration of 0.02M, 0.06M and 0.1M. The cobalt solution was maintained to 0.02M while varying the copper solution to the above stated concentrations. The clinoptilolite was activated with HCl and H_2SO_4 for removal efficiency. The pHs of the solutions were found to be acidic hence enhancing the copper and cobalt removal. The natural clinoptilolite performance was also found to be lower compared to the HCl and H_2SO_4 activated one for the copper removal ranging from 68% to 78% of Cu^{2+} uptake with the natural clinoptilolite to 66% to 51% with HCl and H_2SO_4 respectively. It was found that the activated clinoptilolite removed more copper and cobalt than the natural one and found that the electronegativity of the metal plays a role in the metal removal and the clinoptilolite selectivity.

Keywords—Clinoptilolite, cobalt and copper, Ion-exchange, mass dosage, pH.

I. INTRODUCTION

COPPER and cobalt are the most important metals often found in industrial effluents such as acid mine drainage and municipal wastewater treatment plant. These heavy metals are high toxics and not biodegradables; therefore, they must be removed from the polluted streams because if the wastewaters were discharge directly into natural water they would generate a great risk for the aquatic life and a direct discharge into the sewage system would decrease our drinking water quality standard [1]. In the last decades, the removal of copper and cobalt from sewage and industrial waste effluents has been studied. Their presences in streams have been responsible for several types of health problems in animals, plants and human beings [2], [3]. Since the environment regulations on the discharge of heavy metal are getting stricter with time, it is necessary to create more efficient ways to remove them from industrial effluents [4]. Many methods have been proposed for removal of copper and cobalt from wastewater such as adsorption, ion-exchange, electrocoagulation and electrodialysis [5]. Amongst the many methods available to

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reduce heavy metal concentration such as copper and cobalt from wastewater, the most economic one is ion-exchange process [6]. Ion-exchange is a reversible chemical reaction in which ions are exchanged between a solution and an insoluble solid. Natural zeolites are among the most commonly ion-exchanger material employed in industrial wastewater treatment because of their high specific surface area and high cation exchange capacities [7]. Clinoptilolite is the most abundant and cosmopolitan zeolite and it has been widely exploited for its ion-exchange capabilities since it can easily exchange its interstitial sodium for external cations in solution [8]. In recent years, several studies have successfully conducted on the copper and cobalt removal from aqueous solutions by zeolites [2], [5]-[7], [9], [10]. Reference [10] investigated the capability of clinoptilolite as an ion exchanger and found that in every concentration range, the adsorption mass ratio of clinoptilolite to metal concentration conformed to both Langmuir and Freundlich adsorption isotherms. They also recorded an uptake of 79% and 63% of copper and cobalt removal respectively using a 0.02M HCl activated clinoptilolite. Though numerous works have been done by various researchers on the removal of copper and cobalt from wastewater, this work is presenting a new aspect to the clinoptilolite ability as an ion-exchanger by evaluating the effect of pH on the solutions of copper/cobalt and the effect of mass dosage of the clinoptilolite.

II. MATERIALS AND METHODS

A. Preparation of Clinoptilolite and Synthetic Solution

The clinoptilolite and synthetic solution used in this study were prepared as described by references [3] and [10], respectively. The clinoptilolite was washed several times with distilled water prior to the treatment with acid to remove surface adherent particles and soluble materials. The dried sample at 120°C was milled with average particle sizes of approximately 75μm. The powder was then examined using an X-ray powder diffractometer (XRD), Phillips X'pert Model 0993 and X-ray fluorescence spectroscopy (XRF), Phillips Magix Pro while the surface area was analysed using Brunauer Emmett Teller (BET), Tristar 3000. Two solutions of HCl and H_2SO_4 were prepared and having the same set of concentration each of 0.02M and 0.04M. Each of these acid solutions was used to activate the clinoptilolite; this happened by soaking the clean and dried clinoptilolite into 4 containers, each containing the different concentrations of the acids used. The containers

were open after 21 hours counting from the moment the clinoptilolite was soaked till it was put to dry in the oven (Labcon 2029K) at a temperature of 100°C for 3 hours and 45 minutes. Once dried, they were collected and put back into their respective containers and kept there to avoid any contamination. Three solutions of each metals (copper and cobalt) were prepared and each having a concentration of 1270.92 mg/L, 3812.76 mg/L and 6354.6mg/L (0.02M, 0.06M and 0.1M respectively). The concentrations were decided based on ratios which were to be used during the ion exchange between the synthetic solutions (mixture of copper and cobalt solutions).

Up to this point the procedure is similar to the one described by reference [10], the difference reside in the following: the clinoptilolite size varied from 2.8mm to 5.6mm, it was washed and dried for 24 h, the time allocated to treat it with HCl was of 8 hours and this clinoptilolite was thereafter washed with deionised water and dried at 50°C in the oven for 24 hours. The only similarity resides in the concentration of the HCl used 0.02M and 0.04M.The synthetic solution of copper and cobalt was prepared by dissolving $CuSO_4.5H_2O$ and $(Co (NO_3)_2.6H_2O)$ in deionizer water. The experiments were conducted to determine the effects of pH and mass dosage on the removal % of Cu^{2+} and Co^{2+} by the clinoptilolite. At the end of the treatment period, the clinoptilolite was then separated from solution sample by filtration. A sample solution of 40 ml was taken assayed using atomic adsorption spectroscopy (AAS), (Model Varian Spectra (20/20)) to determine the concentration of Cu^{2+} metals present in the solution. All the experimental analyses where conducted in triplicate and the results reported are the average deviation values of ±0.002. The removal efficiency (%) was calculated as follows:

$$Loading \% = (C_o - C_f) \ x100/C_o \qquad (1)$$

where C_o and C_f are the initial and final ions concentrations of the solution, respectively.

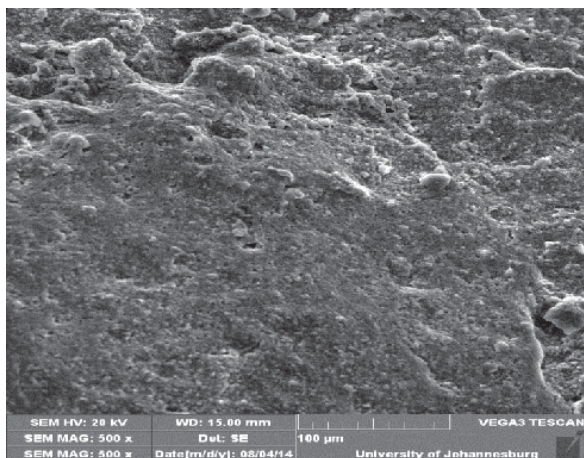## III. RESULTS AND DISCUSSION

Fig. 1 SEM of natural clinoptilolite

Fig. 1 depicts the surface of the clinoptilolite at its natural state, there is presence of the exchangeable ions (Na^+, K^+, Ca^{2+} and Mg^{2+}) on the surface; for the ion-exchange and adsorption happened on the surface of the clinoptilolite. This SEM (Scanning Electron Microscope) analysis was done in order to exhibit the changes of the structure following the conditioning of the clinoptilolite.
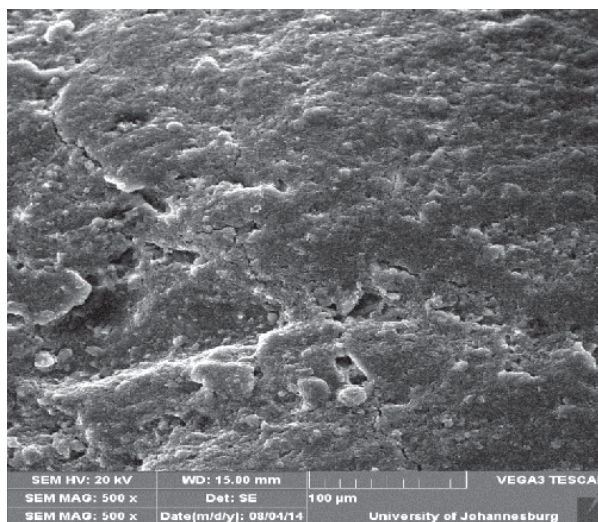

Fig. 2 SEM of 0.02HCl activated clinoptilolite

Fig. 2 shows the presence of holes which looks like craters made on the surface of the clinoptilolite; these craters are pores opening and an indication that the conditioning done on the clinoptilolite was successfully reached. The purpose of this was to increase the ion-exchange capacity on its surface and allow more heavy metal ions to be absorbed and retained onto the clinoptilolite. Figs. 1 and 2 illustrate the surface texture and porosity of clinoptilolite with holes and small opening on the surface which increase the contact area of the adsorbent and consequently lead to the pores diffusion during adsorption [3]. The surface morphology of the modified clinoptilolite as shown in Fig. 2 developed more pores than the natural clinoptilolite; however, the adsorption capacities of the conditioned clinoptilolite were higher than the original clinoptilolite. This can be attributed to the fact that adsorption is a surface phenomenon which is related to the adsorption capacity of the adsorbent. Increase in surface area provides more binding sites for the adsorbate to be adsorbed [3].

The pH of the solution is one of the most important factors affecting the adsorption capacity of the clinoptilolite because the surface zeta potential of the clinoptilolite surfaces and ionization degree of the cations is proportional with the solution pH level [9].
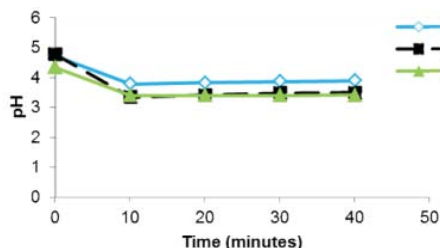
Fig. 3 pH for synthetic solutions with 15 g 0.02M HCl activated
clinoptilolite

Figs. 3 and 4 indicate a slight difference in the results due to mass dosage. As stated earlier the favorable conditions to maximize metal removal are obtained at lower pHs; which still apply for these results in the Figs. 5 and 6. However, by comparing them with Figs. 7 and 6, the 0.04M HCl activated clinoptilolite established an equilibrium value for all the synthetic solutions concentration over a prolonged contact time, while the 0.02M activated clinoptilolite. The equilibrium value for the different concentrations solutions is not easily apparent; there is possibility to be found for a more increase contact time.

Additionally, it is has been found that there is a point limit whereby the activation of the clinoptilolite must not exceed otherwise the adsorption nature of the clinoptilolite would be destroyed. This would imply that something additional had to be done in order to restore that point or to determine a new one where the adsorption capacity of the clinoptilolite would be boundless and unaffected by any change.
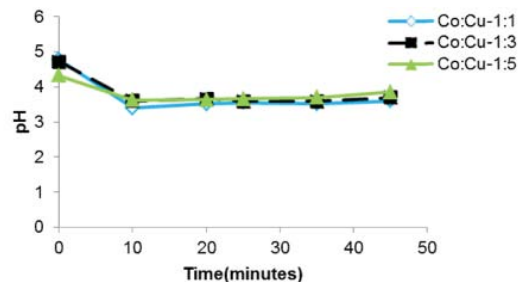

Fig. 4 pH for synthetic solutions with 25g 0.02M HCl activated
clinoptilolite
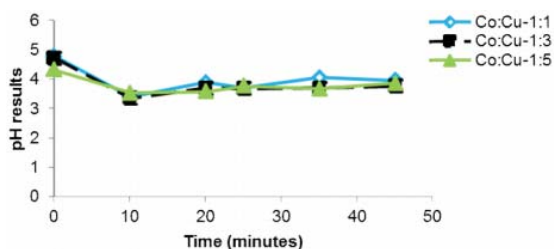
Fig. 5 pH of synthetic solution with 15g 0.04M HCl activated
clinoptilolite

Fig. 6 pH of synthetic solutions with 15g 0.02M H_2SO_4 activated
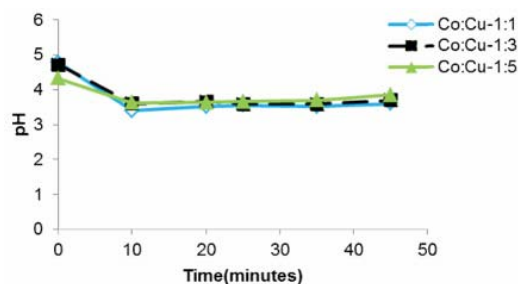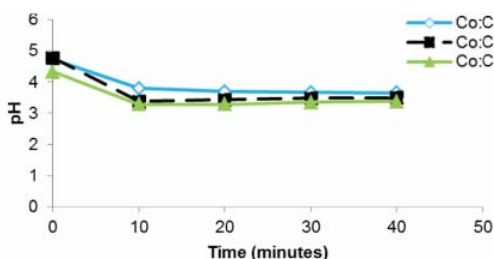clinoptilolite

Fig. 7 pH of synthetic solutions with 25g 0.02M H_2SO_4 activated
clinoptilolite

The corrosive nature of the sulphuric acid is depicted in Figs. 6 and 7 and it is independent on the mass dosage of the clinoptilolite; the same can be said for Figs. 5 and 6. Reference [10] found that the corrosive nature of the HCl is able to eliminate the particles that clog the pores of the zeolites thus improving its adsorption and ion-exchange properties. The study agrees with this by emphasing that the sulphuric acid properties such as strong dehydrating and oxidizing nature are influencing these results as well. As stated earlier, mass dosage does not influence the pH results that much and this can be seen in Figs. 6 and 7. There is a strong influence of the concentration of the acid used for activation of the clinoptilolite. The more the concentration of the acid is the great, the possibility to alter the ion-exchange properties of the clinoptilolite. Therefore it would be advantageous to use high acid concentration to activate clinoptilolite of greater size in order to obtain good results. Reference [11] found that best results for metal removal were obtained with H_2SO_4 activated sample and the highest value reached was 11.5 meq/100g for the +595m size when the activation was done using 2M H_2SO_4.
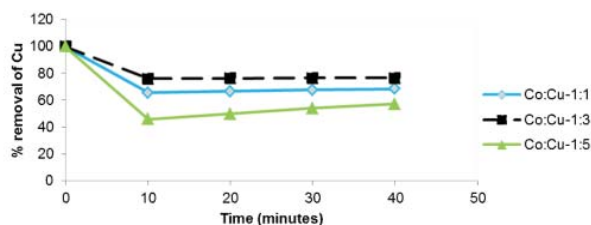

Fig. 8 AAS results of synthetic solutions as per ratio with 15g natural
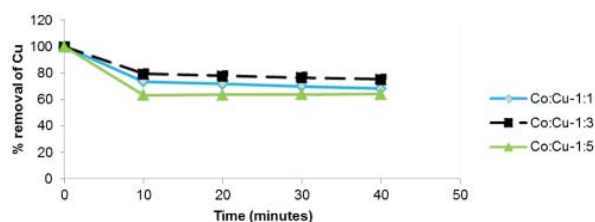clinoptilolite

Fig. 9 AAS results of synthetic solutions as per ratio with 25g natural clinoptilolite

Mass dosage is seen to improve the result in term of copper removal from Figs. 8 and 9; this is due to the presence of more available surface area of the clinoptilolite and the amount of it. These characteristics would favour the ion-exchange. The size of clinoptilolite used in this study is of 1.7mm or 0.0017m and it provided a satisfactory copper removal with a 68% uptake on a same ratio basis 1:1 of copper and cobalt with 15g clinoptilolite and 78% uptake with 25g clinoptilolite for a Co:Cu-1:3 ratios. For this, Reference [10] suggested that the reason being the following the Cu^{2+} ions form stable hydrated complexes with water and some of the Co^{2+} ions in the solution form complexes which are too bulky to move in the zeolite pores.
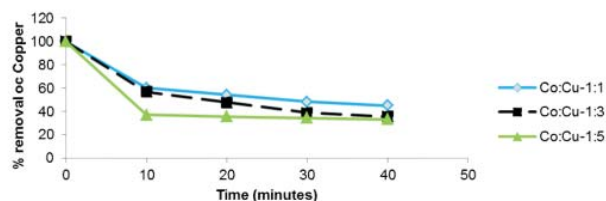

Fig. 10 AAS results of synthetic solutions as per ratio with 25g 0.02M HCl activated clinoptilolite

The activated clinoptilolite results are 60% uptake for the ratio of 1:1. The results shown in Fig. 10 indicate that the removal of copper is slow for the reasons stated in the section under Fig. 10. Reference [10] found that the selectivity of Co^{2+} and Cu^{2+} in the synthetic solutions can be explained in the following manner: for larger anhydrite ions, the charge is more dispersed and the water of hydration is held less strongly by the metal cation and this lead to a situation where the larger the ion, the less hydrated it is and the smaller the relative size of the hydrated ion. They added that the Cu^{2+} ion has valence of +2 and can hold its hydration shell very strongly, while the Co^{2+} ion, a larger divalent cation, hold its hydration shell relatively less strongly; as a result, the Co^{2+} ion can lose its hydration shell readily when it is approaching the clinoptilolite surface and establish a stronger bond with the clinoptilolite than Cu^{2+}, whose approach in the proximity of the clinoptilolite surface is prevented by the bulky surrounding water molecules.

IV. Conclusion

The clinoptilolite use as an ion-exchanger for satisfactory results would have to be done according to the relevant studies. The pH effect on the solution is more acidic due to an increase in H^+ ions in the clinoptilolite structure which results from dissociation of molecules which take place into the solution. The pH decreases steadily for activated clinoptilolite which imply that a control system of the pH can be done at this point to ensure a desired outcome moreover the decrease in pH ensure a great removal of Cu^{2+} and Co^{2+} ions. When it comes to synthetic solutions, there is electron-selectivity; the clinoptilolite prefers the ion with a higher valence when the concentration is lower, which is the copper in this case. This is come into play due to the selectivity nature of the clinoptilolite which according to Reference [10] was shown to be of this order: $Cu^{2+}> Co^{2+}> Fe^{2+}> Mn^{2+}> As^{3+}$. This selectivity behavior does not improve the removal of Copper and cobalt but indicate that the way forward into conquering it would be a greater size in clinoptilolite. The importance of mass dosage lies in that the more available the clinoptilolite the more surface there is to increase the ion exchange and remove as much heavy metals.

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