Adsorptive Removal of Copper (II) Ions from Aqueous Solution using Acid and Thermally Activated Iron Oxide Sand

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Abstract

Heavy metal pollution of water bodies is a common problem in Zambia, whose economy depends on copper mining. Removal of Cu^{2+} ions from the solution via adsorption using iron oxide ore was investigated. The composition of the adsorbent was determined by XRF and ICP-OES. Iron oxide had predominantly Fe_2O_3 at 60 % with less than 3% of SiO_2 and Al_2O_3. The Cu^{2+} ion concentrations were measured before and after adsorption using Atomic Absorption Spectroscopy (AAS). The effects of initial concentration, pH, acid activation, and thermal activation of the adsorbent on adsorption were investigated. A decrease in the adsorption of Cu^{2+} ions with an increase in the initial concentration of adsorbate (Cu^{2+}) was observed. The adsorption of Cu^{2+} ions on acid-activated Iron oxide compared to thermally activated iron oxide ranged from 83-73%, respectively. Adsorption of Cu^{2+} ions was pH dependent with an optimum pH of 7. Acid activation of the adsorbent had better absorptivity since acids cause mineral dissolution, which increases the surface area and porosity of the adsorbent. Iron Oxide adsorbents have the potential to the removal of Cu^{2+} ions from aqueous solutions.

Keywords: Adsorption, Copper ions, Heavy metals, Iron oxide, Pollution.

Introduction

Environmental pollution continues to be a main source of health problems in the world due to the wide uses of chemical materials, chemical detergents, presence of bacteria, and fungi in water bodies [1]. The major sources of these metals in industrial waste-waters include electroplating, mining, fertilizers, pulp and paper, mining and foundry activities, steel production, carbon combustion, solid waste incineration, ceramics, textiles, fertilizers, pigments, batteries, and petroleum industries. Water reservoirs are contaminated by the run-off from these industries [2]. Heavy metals in drinking water pose a threat to human health. Populations are exposed to heavy metals mainly through water consumption, and some heavy metals can bio-accumulate in the human body (e.g., in lipids and the gastrointestinal system) and may induce cancer and other risks [3].

Several methods, such as electrochemical treatment [4], reverse osmosis, adsorption [5], membrane filtration [6], solvent extraction [7], and chemical precipitation [8], have been used to remove heavy metals from contaminated water. Adsorption is a particularly attractive method because of its low cost, high efficiency, and ease of operation [9]. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the use of low-cost adsorbents as alternatives to commercially available activated carbon and zeolites [10]. Inorganic oxides such as iron oxides have large surface areas and chemical and mechanical stability and can sorb heavy metals via adsorption and ion exchange. Iron oxide ore was chosen because it is very abundant in

Zambia, specifically the central province [11]. Furthermore, Iron oxide is one of the metal oxides classified as low-cost adsorbents [12]. Sorption of toxic metals on oxides and clay minerals reduces their concentration and mobility in aqueous solution and natural environment [13]. Zambia largely depends on copper mining. In the process of mining, heavy metal effluents are released into water bodies causing water pollution [14]. One of the major problems Copper Mining has caused in Zambia is water pollution. There is an urgent need to research on cost-effective methods which can be used to remove Copper ions from water in Zambia [15]. In an economy like Zambia that is largely dependent on copper mining [16], the development and engineering of iron oxide as adsorbents for the removal of heavy metals such as copper offers exciting research opportunities in heavy metal mitigation in water.

Experimental Section

Materials

Chemical reagents for the preparation of adsorbate (Cu ions) and other chemicals provided by Mopani Copper Mines Plc included $CuSO_4.5H_2O$ and Amis 0348. Amis 0348 stands for African Mineral Standards 0348 used for certification of copper, cobalt oxide, or sulfides. One adsorbent Iron oxide was collected from Delca Palms Boarding School, Mkushi, Central Province, Zambia. The adsorbent was grounded and sieved to the particle size of 125 μm and dried for 2hrs at 105°C.

Elemental Characterization of the Adsorbents

Elemental composition of the iron oxide ore sample was conducted at Analytical laboratory, Mopani Copper Mines Plc, Kitwe, Zambia.

X-ray Fluorescence (XRF) Analysis

About 0.3g of iron oxide was mixed with of 3g lithium nitrate, 1g lithium tetra borate, 1g lithium bromide, followed by an additional 5g of lithium tetra borate. Afterward, fusion of each

mixture was done at a temperature of 1050 °C. The fused pellets were then analyzed using X-ray Fluorescence (XRF) on a Spectro Xepos spectrometer with the Amis 0348 samples used as quality control standards.

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) Analysis

Acid digestion was used to prepare iron oxide adsorbents for ICP analysis. A 0.25g of adsorbent was mixed with 20 mL of concentrated HNO_3, 10 mL of concentrated $HClO_4$, and 10mL of concentrated HF and heated at 150 °C on a Digi PREP LS heating block. For quality control purposes, Amis 0348 (Laboratory standard) was used as a quality control standard and was prepared by acid digestion in the same way as the adsorbents. The standard was used to verify the entire analytical system and eliminate bias from analytical results by comparing the results of the standard with the values stated on the Certificate of Analysis for Amis 0348.

Thermal and Acid Activation of Adsorbents

For thermal activation, 30g of adsorbent was heated at a temperature of 650°C for 4 hours and then allowed to cool naturally to room temperature. Whereas, for acid activation, 10 g of adsorbent was added to 50 mL of 0.5MHCl solution and stirred at 70° C for 30 min at 140 rpm. Afterward, the activated acid adsorbent was washed with distilled water to achieve neutrality (pH 6.9), thereafter, the adsorbent was oven dried at 120°C for 3 hours and cooled for further use [17].

Stock Solution Preparation Adsorption Experiments

A 1000 mg/L stock solution of Cu^{2+} ions was prepared by dissolving 3.96g of Copper (II) Sulfate pentahydrate ($CuSO_4.5H_2O$)99% in 1000 mL of distilled water. From this stock solution of Cu, working solutions of concentrations ranging from 10, 20, 40, 60, and 80 mg/L were prepared by dilution. In order to study the adsorption of

Cu^{2+} ions onto iron oxide adsorbents, the following factors were investigated:

1. The effect of concentration on the adsorption of metal ions.
2. The effect of pH on the adsorption of metal ions.

The Effect of Concentration on the Adsorption of Metal Ions

In order to investigate the effect of concentration on the adsorption of metal ions, 1.0 g of adsorbent was separately added into 50 ml of metal ion solution of varying concentrations (between 10-100 mg/L), while keeping all other parameters constant (shaker speed= 140 rpm; contact time= 3 hrs.; adsorbent mass=1.0g; temperature= 25℃, pH=7.0). After 3 hours, the mixture was filtered, and the filtrate Cu^{2+} concentrations were measured before and after adsorption using Atomic Absorption Spectroscopy (Anlytikjena, Model novAA 400P). The percentage of Cu^{2+} removal was calculated using Equation 1.

$$Cu^{2+} \text{ removal (\%)} = \frac{\text{Initial } Cu^{2+} - \text{ Final } Cu^{2+} \text{ concentration}}{\text{Initial } Cu^{2+} \text{ concentration.}} \text{ x } 100 \quad \text{Equation 1}$$

The Effect of pH on the Adsorption of Metal Ions

Similarly, the effect of pH on the adsorption capacity of iron oxide was investigated under the same conditions as the effect of concentration. Except in this case, 0.1MNaOH and 0.1MHCl solutions were used to adjust the pH of the metal solution after the addition of the adsorbents to the metal ion solution. After 3 hours, the mixtures were filtered, and the Cu^{2+} concentrations were measured using Atomic Absorption Spectroscopy, and the percentage of Cu^{2+} removal was calculated using Equation 1.

Results and Discussion

Characterization of Adsorbents

X-ray Fluorescence Analysis

The results for the elemental analysis of the adsorbents using XRF are shown in Table 1. Iron oxide sand had predominately a high percentage of iron in relation to silicon and aluminum.

Table 1. Elemental Composition of Raw Inorganic Adsorbent using XRF

Component	Iron oxide (%)
Si	1.18
Al	0.51
Fe	42.57
Ca	0.12
Mg	0.11

In order to express the elemental composition as oxide-based results, the results from Table 1 were multiplied by the stoichiometric oxide conversion factors for SiO_2 (2.1392), Al_2O_3 (1.8895), Fe_2O_3 (1.4297), CaO (1.3992) and MgO (1.6582) [18]. The oxide-based compositions of the two adsorbents are depicted in Table 2. It is evident that iron oxide had up to 18.29% oxygen sites.

Table 2. Oxide-based Composition of Raw Inorganic Adsorbents using XRF

Component	Iron oxide (%) (IO)	Oxide Content (%)
SiO_2	2.53	1.35
Al_2O_3	0.96	0.45
Fe_2O_3	**60.86**	**18.29**

CaO	0.17	0.05
MgO	0.18	0.07

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) Analysis

Elemental composition of the adsorbents was also verified by ICP-OES analysis, however, the use of acid digestion removed silica from the samples. The use of HF during acid digestion makes silica to volatilize before analysis HF breaks up strong Si-O bonds to form SiF_6^{2-} ions in acidic solution. Silicates are converted to volatile SiF_4, which will be lost in open-vessel digestion procedures [19]. Therefore, ICP analysis did not analyze the concentration of silica in the adsorbent. Table 3 shows the ICP-OES results for the major elements in iron oxide being Al and Fe. Using stoichiometric oxide conversion factors, the oxygen content of the individual elements is expressed in Table 4. The results from ICP-OES mirror those from XRF, except that elemental data from ICP is on the lower side.

Adsorption Experiments

The Effect of Concentration on the Adsorption of the Metal Ions

In order to investigate the effect of concentration on the adsorption of metal ions, several adsorption experiments were conducted while varying concentrations between 10-100 mg/L.

Table 3. Elemental Composition of Raw Inorganic Adsorbent using ICP-OES

Component	Iron oxide (%)
Al	0.50
Fe	>31.26
Ca	0.02
Mg	0.07

Table 4. Oxide based composition of inorganic adsorbents using ICP-OES

Component	Iron oxide (%)	Oxide Content (%)
SiO_2	-	-
Al_2O_3	0.95	0.45
Fe_2O_3	>44.69	**13.43**
CaO	0.03	0.01
MgO	0.12	0.07

Table 5. Percent Removal of Cu^{2+} ions using Acid Activated and Thermally Activated Iron Oxide from Different Concentrations of the Ions

Adsorbent	Cu^{2+} initial concentration (mg/L)	Cu^{2+} final concentration (mg/L)	Cu^{2+} removal (%)
Acid Activated			
Iron oxide (IO)	10	1.7	83
Iron oxide (IO)	30	5.4	82
Iron oxide (IO)	80	15.2	81
Iron oxide (IO)	100	20	80
-	-	-	Mean = 82±1
Thermally activated			

Iron oxide (IO)	10	2	80
Iron oxide (IO)	30	6.6	78
Iron oxide (IO)	80	19.2	76
Iron oxide (IO)	100	25	75
-	-	-	Mean = 77±4

The high adsorption of acid-activated adsorbents can be attributed to the fact that acid treatments help in the specific surface area increase, acidic centers, surface functional group modification, and high porosity with solids [17]. Acid activation results in several significant changes in clay adsorbent. Primarily, as most of the clay minerals possess the ion-exchange ability, ion-exchange reactions will occur. The exchangeable cations, usual cations of alkali or alkaline earth elements, e.g., Na^+, K^+, or Ca^{2+} located in the interlayer space of adsorbent, will be substituted for protons resulting from the dissociation of an acid. Protons of the acid easily penetrate into the interlayer space and react mainly with cations of the octahedral sheet. This process is known as "dealumination" as it comprises the substitution of octahedral Al^{3+} or Fe^{2+}/ Fe^{3+} ions by protons and the formation of additional Si-OH groups in the tetrahedral sheet. Consequently, the occurrence of ion exchange and dealumination enhances the surface and structural characteristics of clay minerals towards the adsorption of cations on dangling OH groups [20]. Thermal activation of clay minerals at elevated temperature results in the desorption of adsorbed gases and water molecules and the evolution of the free surface. However, at high pH, the structural integrity of the clay can undergo partial damage or entire structure collapse, followed by a reduction of surface activity [21].

The decrease in percent adsorption of Cu^{2+} on iron oxide as the initial metal concentration increased is apparent as shown in Figure 1. As the concentration of metal ions increased, accessibility of adsorption sites reduced, leading to low adsorption of metal ions. The reduction in the accessibility of adsorption sites by the metal ions was due to the competition of the metal ions for the limited adsorption sites. This may be because at lower concentrations, almost all ions were adsorbed very quickly, but a further increase in initial metal ion concentrations led to saturation of the adsorbent surface [3]. This means that the available binding sites had been saturated, and the adsorbent could no longer bind further ions as the number of sites available on the adsorbent is constant.
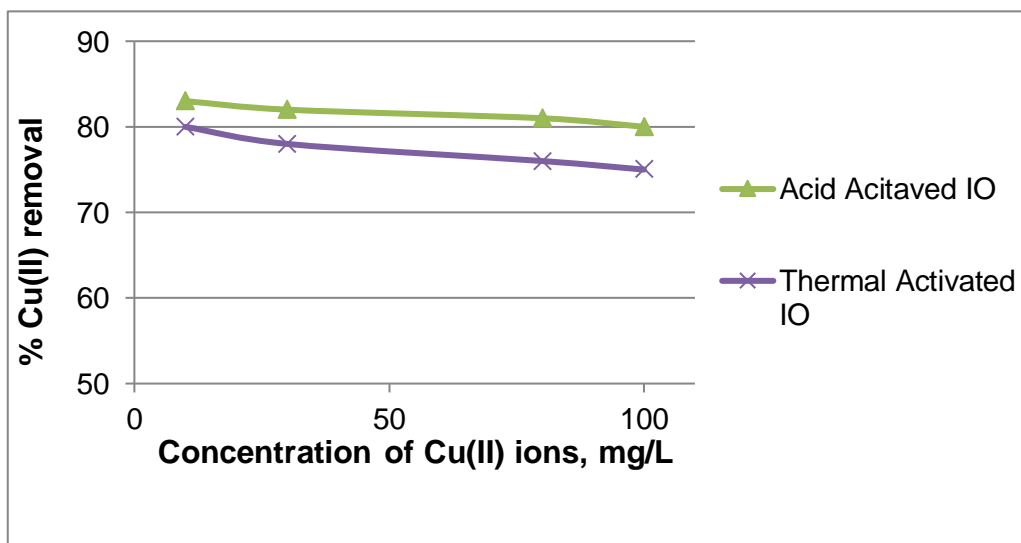

Figure 1. The Effect of Concentration on the Adsorption of Cu^{2+} ions

The Effect of pH on the Adsorption of Metal Ions

In order to investigate the effect of pH on the adsorption of Cu^{2+}, several experiments were conducted at different pH values of 1.0, 4.0, 6.5, 7.0 and 8.5. The impact of pH on the adsorption of Cu^{2+} is shown in Figure 2. As pH increased from 1, the number of adsorbed ions also increased and peaked at pH 7 for Cu ions. The effect of pH on the adsorption of Cu^{2+} using both acid-activated- and thermally activated iron oxide is shown in Figure 2. The amount of Cu^{2+} removed was up to 80-95% at pH 7. It was established that the sorption of Cu^{2+} escalated as the pH increased to an optimum value of 7.

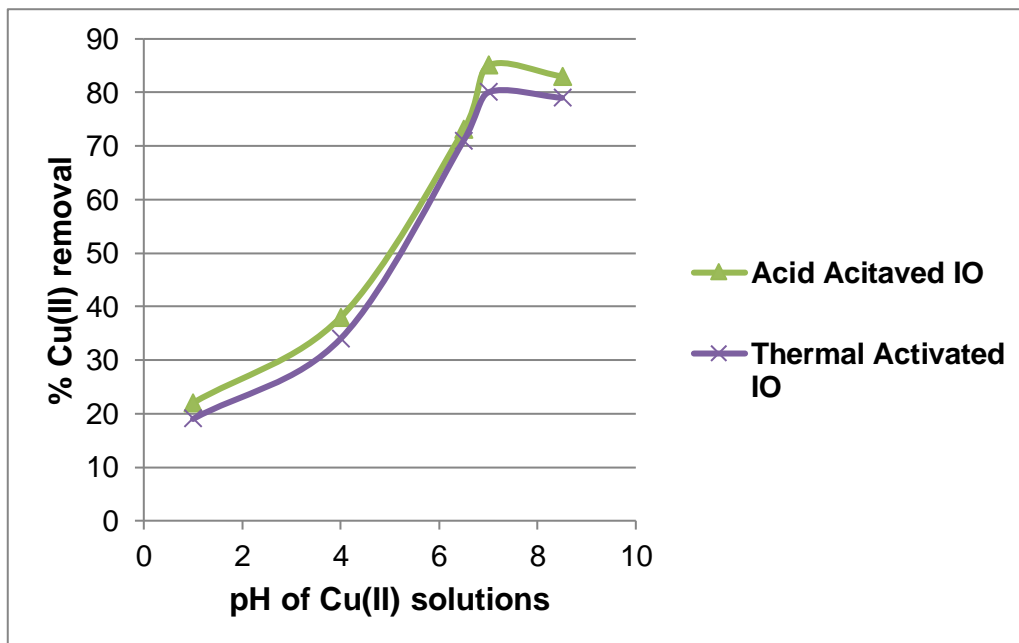This result agrees to that reported by [22]

where a low pH leads to the dissolution of cations such as Fe^{2+} and Al^{3+} that ultimately compete with copper (II) ions for adsorption. As pH increases, more hydroxide (OH^-) sites are generated on the adsorbent leading to electrostatic interaction between the Cu^{2+} ions and the OH^{-1} [22]. In the pH range of 4 to 6, a slight increase in metal removal is observed which might be explained by the fact that the adsorption sites are no more affected by the pH change. An increase in Cu^{2+} as the pH increases can be explained by surface sites and by decreased positive charge, which results in a lower repulsion on the basis of decreased competition between protons and positively charged metal ions during adsorption [23].

Figure 2. Effect of pH on the Adsorption of Copper (II) Ions on Iron oxide (IO)

Additionally, after pH of 7, a decrease of metal removal for Cu^{2+} compared to pH 6 is observed. At a higher pH, copper ions are precipitated in the form of hydroxides, and this reduces the rate of adsorption and, consequently the removal capacity of heavy metals. The precipitation of the metal ions makes them immobile, and this reduces the adsorption of these metal ion. This can also be explained by the increasing amount of Na^+ in the solution (due to pH adjustment), which competes with the

remaining Cu^{2+} on the exchangeable sites [24]. Acid activation proved to be a better method of adsorbent activation than thermal activation. Chemical activation or modification usually provides the strongest effect on the structure and properties of materials because of the chemical interactions of a modifying agent and the surface of the material. Acid treatments help in the specific surface area increase, acidic centers, surface functional group modification, and high porosity with solids [17].

Conclusion

The use of Iron oxide for the removal of copper (II) ions from an aqueous solution via adsorption process has demonstrated the extent to which the metal ions can be removed by these two adsorbents. The results showed that as the initial metal concentration increased, the percentage removal of Cu^{2+} decreased. As the concentration of metal ions increased, accessibility of adsorption sites reduced, which led to low adsorption of metal ions. The reduction in the accessibility of adsorption sites by the metal ions was due to the competition of the metal ions for the limited adsorption sites. This may be because at lower concentrations, almost all ions were adsorbed very quickly, but a further increase in initial metal ion concentrations led to saturation of the adsorbent surface.

Acid activation was found to be a better method of adsorbent activation as compared to thermal activation because the acid treatment causes mineral dissolution, which increases the surface area and porosity of the adsorbent. Firstly, for the concentration with a low pH, the content of H^+ is high, which will lead to mineral dissolution, releasing ions such as Mg (II), Fe (II), and Al (III). These ions compete with copper (II) ions for adsorption sites. At elevated pH, the content of H^+ decreases, leading to many hydroxyl groups on the adsorbents, thus, increasing the rate of adsorption of Cu ions. Secondly, if the pH is low, the surface groups are protonated. Consequently, it will produce a positive surface charge which may weaken the ability to form complexes with Cu^{2+} ions.

Finally, the research has shown that abundant iron oxide can be engineered for the adsorption of metals, and this work prompts an extension to the removal of lead (Pb) ions which has affected the Kabwe Township in Zambian that closed after the depletion of PBS galena ore.

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Disclosure Statement

The authors report there are no competing interests to declare.

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