Recovery of Al(iii) and Fe(iii) from Acid Mine Drainage using CaO and their Subsequent Use in Fluoride Removal from Water

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Abstract—Acid mine drainage (AMD) refers to the drainage of coal mines with heavy sulphur-bearing rocks. The highly acidic nature and higher metal concentration of AMD poses a severe risk to the environment. The purpose of this study was to evaluate the potential of utilising CaO for the recovery of aluminium and iron hydroxides from AMD and their subsequent application in defluoridation. Batch experiments were caried out to determine the rate of neutralization with various CaO dosages and contact time. The results showed that optimum conditions for neutralizing AMD using CaO are 45 min of contact time and 10 g of CaO dosage, where the pH was found to range from 7.23 to 7.40. The EC ranged from 180 to 195 µS/cm, causing a higher formation of insoluble aluminium and ferric hydroxide precipitates, demonstrating that CaO effectively raises the pH of AMD when increasing the dosage. The study revealed that CaO can be used for the recovery of $Al(OH)_3$ and $Fe(OH)_3$. Recovery efficiencies were as high as 99.89 and 97.49% for Fe(iii) and Al(iii) respectively. The defluoridation study using the recovered metal hydroxides proved to be ineffective, as the adsorption capacity was calculated to be 0.45 mg/g. Some new methods and factors can be implemented to obtain acceptable results.
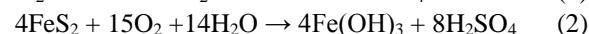
Keywords— acid mine drainage, calcium oxide, defluoridation, neutralisation.

I. INTRODUCTION

Water scarcity is a problem in South Africa. Since the human population is continuing to rise, the economy is developing, and millions of people lack access to basic services, it is believed that the demand for water is already equal to or greater than the supply [1]. Safe and adequate water supply remains the backbone of a healthy economy vital for agriculture, industries, recreation, and domestic uses. Acid mine water discharges typically and pollutes the limited water supplies, posing serious environmental, ecological, and health problems where water users are frequently exposed to high metal concentrations [1]. AMD is a severe environmental issue triggered by mining industries. It is distinguished by elevated levels of dissolved heavy metals and additional contaminants or chemicals [2]. The pH of AMD ranges from 2 to 3. This water's acidity has a very harmful and potentially fatal effects on aquatic life that are sensitive to low pH levels. Acidic waste effluents have severe effects, including toxicity, environmental degradation, and impacts on human health. The oxidation and dissipation of pyrite (FeS_2), and other minerals such as iron and aluminium over extended periods of time are the main causes of the AMD, which pose serious environmental issues that threaten the biodiversity of various ecosystems [3].

AMD is formed when pyrites from the mines, oxygen (from air), and water reacts with each other to produce ferrous hydroxides and sulfuric acids [4]. The chemical reaction involved in the formation of AMD can be represented as follows:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (1)$$

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4 \quad (2)$$

Controlling the acquaintance of pyrite minerals to air and water can prevent or reduce the development of AMD. Engineered solutions like liners, coverings, and drainage systems can be used to accomplish this. Additionally, AMD can be treated and heavy metals and acidity from the water can be eliminated using treatment techniques like neutralization, adsorption, and precipitation [5].

In the absence of better treatment technologies, AMD that is left untreated or treated insufficiently will continue to reduce the advantages of treatment and raise its expenses. It is therefore important to treat the AMD and the effluent before they are discharged to the environment [6]. AMD is treated through a process known as neutralization, in which the AMD interacts with a basic solution like lime (CaO) to change the pH to an acceptable environmental level. Acid neutralization is a crucial step in the treatment of acidic effluent and industrial wastewater. In the process of neutralization, an acid and a base combine chemically to produce salt and water as by-products. Water is made up of hydrogen ions (H^+) and hydroxide ions (OH^-). To neutralise acidic waters, a variety of alkaline solutions are used. But for this study calcium oxide CaO was used.

Lime is widely used as a neutralising agent, and it is justified in removing AMD and other acidic effluents [7]. The process's viability is influenced by several elements, including

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price, the base solution's capacity to increase an acidic solution or sample's pH to a specified level, and availability [8]. Currently, wastewater and water are treated as well as plant effluents, using lime neutralization. Because lime reacts quickly with all acids, including the strongest and weakest of both organic and inorganic types, it is a powerful neutralizing agent [9].

Defluoridation is the process of removing excessive fluoride from water to a safe and acceptable level. Valorisation of AMD sludge for defluoridation is a sustainable and innovative approach to addressing two critical environmental challenges: the management of AMD waste and the provision of safe drinking water to South African economy with water that has high fluoride contamination. The acceptable fluoride level as according to the South African National Standards 241 (SANS 241) is recorded to be 1.5 mg/L. Hazardous fluoride has negative impacts on both human and animals. An important global issue is the contamination of groundwater with fluoride by artificial and natural processes [2].

To remove fluoride from water, several defluoridation methods have been devised such as electrocoagulation, adsorption, and reverse osmosis [10]. Fluorosis problems such as skeletal and dental fluorosis are brought on by drinking water with too much fluoride [11]. Fluoride has harmful impacts on human health, including changes in protein transport, apoptosis, necrosis, and oxidative stress and damage brought on by superoxide anions upon consumption [12]. Hence, it is a necessity to remove fluoride from water.

II. MATERIALS AND METHODS

A. Sampling

The AMD (Fe(iii)-rich water) was collected at Khwezela colliery mine, an open cast thermal coal mining in the Mpumalanga province in South Africa. GPS coordinates: -25.926243, 29.155635.

B. Preparation Of AMD Samples

The AMD sample was diluted by mixing 1 mL of the original sample (AMD) with 99 mL of deionized water (1:100 dilution ratio). Two droplets of concentrated nitric acid were augmented to lower the pH to help prevent the precipitation of certain metals. The sample was filtered to remove suspended solids that may settle during storage and kept at lower temperature (4°C) in the fridge to cool the sample and stop precipitation process.

C. Preparation Of Calcium Oxide (CaO)

Raw calcium hydroxide [Ca(OH)$_2$] was calcined to decompose it into calcium oxide using optimized conditions from [13] (2 hours at 400°C) using a furnace (Carbolite type s30 fitted with 2AU ESF Eurotherm, England). Afterwards it was allowed to cool for 30 minutes at room temperature, then ground into a fine powder using a mortar and pestle.

D. Characterization Studies

E. Characterization Of AMD

The metal content of the AMD was characterized using ICP-MS instrument with the method ME-011 for the determination of metals. A pH or EC indicator (HACH HQ4OD, Aqualytic, South Africa) was used to determine the readings of EC and pH of the AMD sample.

F. Characterization of the neutralizing agent

The AMD sludge containing recovered metal hydroxides was characterized using X-ray Fluorescence (XRF), Fourier transform infrared (FTIR) spectrometry, and Scanning electron microscopy (SEM). A Bruker XRF spectrometer was used to analyze the major and minor elements in the powdered samples (AMD sludge and CaO). FTIR analysis was conducted with the Bruker Alpha-platinum Art equipment to measure the infrared spectra in transmission mode for the prepared powdered calcined calcium oxide and AMD sludge. Then the measurement of bands integrated intensity was made using the OPUS software supplied by the Bruker instrument. SEM analysis was conducted to examine the morphology of the metal hydroxides surface. The type of SEM that was used to analyze metal hydroxides is Zeiss sigma 500 VP scanning electron microscopy, as it provides high resolution images.

G. AMD Neutralization Experiments

H. Neutralization of AMD as a Function of CaO Dosage

500 mL of AMD solution was added into 6, 1000 mL beakers and 1 g, 3 g, 5 g, 10 g, 15g, and 20 g of CaO was added to each beaker. Then the mixtures were agitated for 10 minutes at 200 rpm using a 4-paddle stirrer (Model 1924, Electronics, India). The experiments were carried out in triplicate at room temperature of 25°C.

I. Neutralization of AMD as a Function of Contact Time

500 mL of AMD solution was added to 1000 mL beakers and 10 g of lime dosage was added to each beaker. Then the mixtures were agitated for 10, 30, 45, 60, 90, and 120 minutes at 200 rpm using a 4-paddle stirrer (model 1924, Electronics, India) at room temperature (25°C). The experiments were carried out in triplicate for quality assurance and obtaining accurate results.

J. Calculation Of Metal Hydroxide % Recovery Efficiency Of CaO

The % Recovery efficiency of CaO was computed by the following equation:

% Recovery efficiency = [(C$_0$-C) / C$_0$] ×100 $\qquad$ (3)

Where C$_0$ = initial concentration of Fe^{3+}and Al^{3+} from AMD before neutralization and C = the final concentration of Fe^{3+}and Al^{3+} from AMD after neutralization.

K. Defluoridation Experiments

Optimized conditions of 30 minutes of contact time, 2.5 g of adsorbent dosage, 10 mg/L of initial fluoride concentration established by [14] were applied for the defluoridation of the aqueous solution. 500 mL of 10 mg/L F^- solution was poured in a 1000 mL beaker and mixed with 2.5 g adsorbent dosage (an AMD sludge rich in Al^{3+} and Fe^{3+}). Then the mixture was agitated for 30 minutes at a speed of 200 rpm using the 4-paddle stirrer. Then after stirring the mixture was allowed to sit for 24 hours for the solid residues to settle out. After settling the mixture was filtered using a 0.45 µm filter membrane and pH was measured using the Hanna pH meter instrument, EC using conductivity meter, and fluoride concentration was measured using the HI801 Iris Visible Spectrophotometer.

L. Calculation Of % Adsorption And Adsorption Capacity Of The Sludge

The % fluoride removal by AMD sludge was computed by the following equation:

% Fluoride removal = $[(C_0 - C) / C_0] \times 100$ (4)

Where C_0 = initial concentration of F^- and C = is the final concentration of F^- after treatment with the sludge as an adsorbent.

Then the adsorption capacity of the AMD sludge for fluoride adsorbed per unit mass of adsorbent (q) was calculated using the following equation:

q = $(C_i - C_f / m) \times V$ (5)

where C_i = initial F^- concentration (mg/L), C_f = final F^- concentration after defluoridation (mg/L), V= the volume of F^- solution (mL) and m = mass of AMD sludge (adsorbent dosage) in (g).

III. RESULTS AND DISCUSSIONS

A. Characterization Results

Physicochemical Parameters Of AMD

Table I gives the elemental composition of the AMD.

TABLE I
ICP-MS RESULTS SHOWING THE ELEMENTAL COMPOSITIONS OF AMD BEFORE AND AFTER TREATMENT.

Element composition	Initial (mg/L)	Final (mg/L)
Iron as Fe	169.22	0.327
Aluminium as Al	21.04	0.529
Sulphate as SO_4	471.75	446.76
Magnesium as Mg	18.33	3.88
Manganese Mn	4.19	0.016
Calcium Ca	426.07	406.74

The elemental concentrations show that the AMD sample is rich in Fe, Ca, and SO_4. The recovery of metal hydroxide from AMD was calculated using (3), it was found that the recovery

of $Fe(OH)_3$ from AMD was 99.81% and for $Al(OH)_3$ was calculated to be 97.49%. Therefore, AMD neutralization with lime proved to be effective. Physicochemical characterization of the AMD showed that it has a pH of 2.35, EC of 996.33 µS/cm and a TDS of 697.43 mg/L.

B. XRF Analysis

Table II shows the elemental composition of CaO before and after AMD treatment.

TABLE II
XRF DERIVED CHEMICAL COMPOSITIONS OF ELEMENTS IN CAO AND RECOVERED ELEMENTS EXPRESSED AS OXIDES.

Element Names	Calcium oxide (CaO) %	AMD reacted with CaO sludge %
CaO	51.054	15.767
Fe_2O_3	0.932	16.463
MgO	1.532	2.455
Al_2O_3	1.200	2.696
SiO_2	6.582	6.582
P_2O_5	0.495	0.225
TiO_2	0.130	0.119
MnO	0.028	0.211
S	0	12.744

The chemical composition of the CaO used in this study and AMD sludge sample produced when acid mine water reacted with CaO are presented in Table II. The CaO sample has a higher content of CaO and SiO_2 while the AMD sludge shows a higher Fe_2O_3 content. The CaO content shows a slight variation with the AMD sludge showing a lower value after neutralization meaning that CaO reacted with AMD. Fe, Al, and Mn were found after CaO was contacted with AMD. This suggests that while the CaO is adjusting the pH of the acid water, those elements are precipitating from AMD with a pH increase. Additionally, this suggests that CaO may be utilized to recover metals from AMD in a fractional and sequential manner. The findings also showed that after contacting CaO with AMD, the resultant water was rich in Sulphur (S), therefore the CaO was used to precipitate the sulphate as gypsum.

C. FTIR Analysis

FTIR spectrum of CaO, and a sludge of AMD reacted with CaO are represented in Fig. 1.
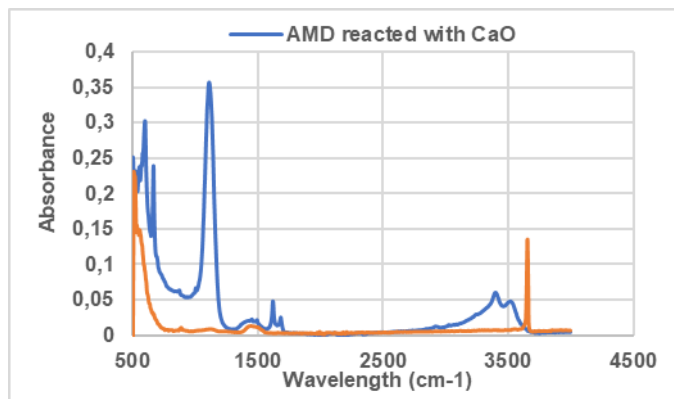
Fig. 1. FTIR scatter graph showing the spectrum of CaO particles and AMD sludge reacted with CaO.

The spectrum of the powdered CaO is presented by Fig. 1 where peaks were observed at 899.65 and 3639.42 cm^{-1} which are strongly associated with the presence of Ca(OH)$_2$. The peak at 899.65 cm $^{-1}$ may be associated with the Ca-O bond. Comparing the results of the calcined Ca(OH)$_2$ and results of Ca(OH)$_2$ and original CaO from other studies [15], [16] it can be said that Ca(OH)$_2$ was completely changed to CaO during synthesis. The spectrum of AMD reacted with CaO sludge peaks were observed at 593.65, 665.05, 1119.98, 1621.83, 1693.23, and 3406.86 cm^{-1}. A study by [17] showed that peaks in the 3200-3600 cm^{-1} range represents O-H stretching vibrations and may be observed due to the formation of hydroxides in the neutralization process. Therefore, the peak at 3406.86 cm^{-1} can be said to be due to the stretching vibration of the O-H bond.

SEM Analysis

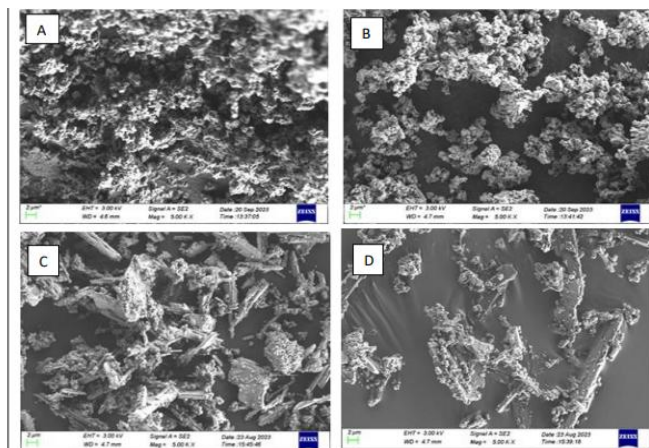Fig. 2 shows the SEM images of raw CaO and AMD sludge

Fig. 2. SEM images showing the surface morphology of the CaO powdered reagent (A) and (B) and image (C) and (D) showing the surface morphology of AMD sludge after treatment.

The image of the raw CaO shows the presence of spherical particles. Following treatment, the material's surface was found to contain a small number of spherical and angular particles. The morphological characteristics show that the

sample's surface characteristics were uniform, proving that a high-quality material was synthesized. Consequently, it demonstrates that CaO totally reacted with AMD, effectively curing it to recover significant metal concentrations.

D. Neutralization Study

Evaluation Of pH On The Neutralization Of AMD Using CaO

Lime (CaO) is currently used by mining industries for the neutralization of AMD. Most commonly, the concentration of hydrogen ions (H$^+$) is used to assess pH and alkalinity by verifying the levels of hydroxyl (OH$^-$), bicarbonate (HCO$_3^-$) and carbonate (CO$_3^{2-}$) ions in water. The acceptable level for pH according to SANS 241 is ≥ 5 to ≤ 9. Fig. 3 represents the variation of pH at different CaO dosages and Fig. 4 represents the variation of pH at different time intervals during the neutralisation experiments.
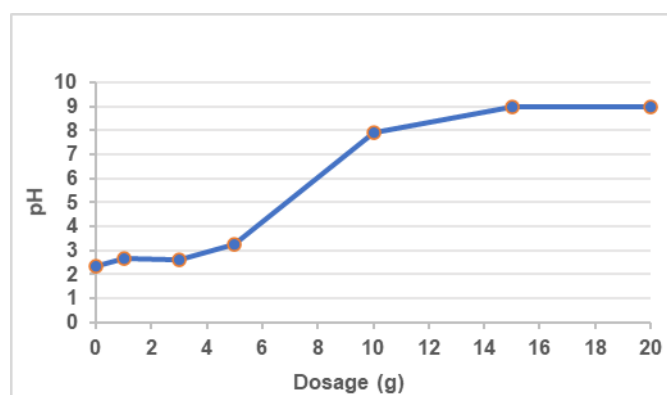

Fig. 3. Variation of pH on neutralization of AMD using CaO at different CaO dosages.
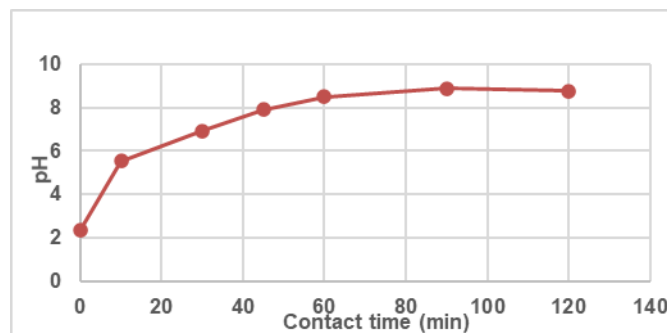

Fig 4. Variation of pH on neutralization of AMD using CaO at different time intervals.

Fig. 3. and Fig. 4. shows the results were CaO was used for Fe^{3+} removal as Fe(OH)$_3$ and Al^{3+} as Al(OH)$_3$. Following the results of the physicochemical parameters before AMD neutralization, it can be said that CaO raises the pH of the AMD to slightly alkaline when increasing the dosages as shown in Fig. 3. The two figures (Fig. 3 and Fig. 4.) show that there was an increase in pH of the solution with an increase in dosage and contact time. The primary mechanism by which AMD is neutralized is through chemical reactions. When calcium oxide (CaO), commonly referred to as quicklime or lime, is added to AMD, it reacts with the acidic components

present in the mine water. The main reactions involved are represented by (5) and (6):

$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O \qquad (5)$$
$$CaO + 2H^+ \rightarrow Ca^{2+} + H_2O \qquad (6)$$
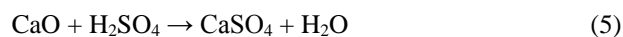
Then these reactions cause an increase in pH of the water during neutralisation. The results shows that there is typically a dose-response relationship between the amount of CaO added and the increase in pH. As it shows that the more CaO is added, the increase in pH becomes more substantial, eventually reaching a point where the pH stabilizes within the desired range from 7.23 to 7.40, which were achieved using optimised conditions of 10 g CaO dosage, at 45 minutes.

E. Evaluation Of EC And TDS On The Neutralization Of AMD Using CaO

One important way to determine the mineralization in water samples is to measure the EC of the water [18]. The presence of ions such as HCO^{3-}, $KHCO_3$, Mg, Ca, Cl and SO_4^{2-} that carry electrical charge in water, makes it more capable to conduct electrical currents. The total amount of dissolved elements in water is measured by TDS. Salinity or conductivity measurements can also be made for the dissolved elements. Fig. 5 and Fig. 6 represent the variation of TDS and EC based on dosage and contact time.
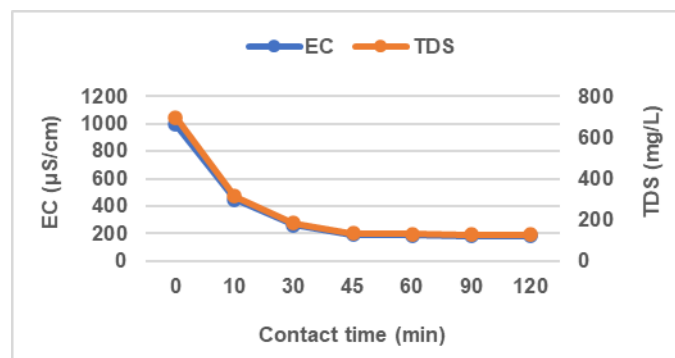

Fig. 5. The responses of EC and TDS on the neutralisation of AMD at different time intervals.
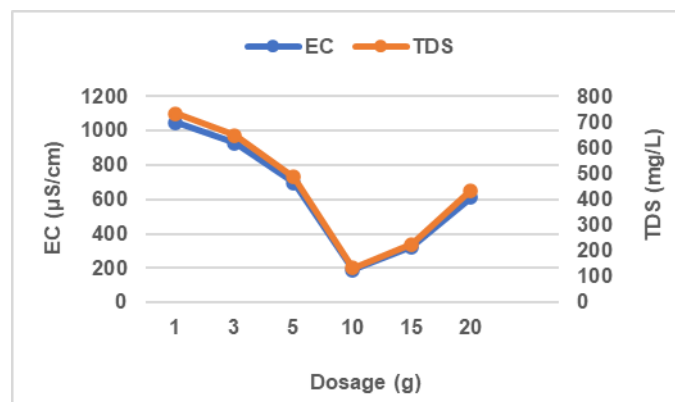

Fig. 6. The responses of EC and TDS on the neutralisation of AMD on different CaO dosages.

The EC ranged from 996.33 to 179.93 µS/cm as shown in

Fig. 5 and Fig. 6. Initially the EC of AMD was high due to the presence of dissolved ions, including metals such as iron and aluminium. The CaO added reacted with the ions present to form insoluble precipitates, reducing the concentration of dissolved ions and consequently decreased the EC in the water. Due to the decrease in EC, it causes a decrease in the TDS of the water, because dissolved ions (sulphate, aluminium, and iron) precipitated. When CaO is added to AMD, it initiates a series of chemical reactions that lead to the precipitation of various ions and the formation of insoluble compounds. For example:

$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O \qquad (5)$$
$$CaO + Fe^{3+} \rightarrow Fe(OH)_3 + Ca^{2+} \qquad (7)$$
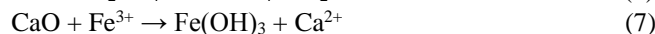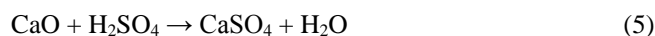
These reactions result in the removal of sulphate ions (SO_4^{2-}) as calcium sulphate ($CaSO_4$) precipitates, and the removal of metal ions as hydroxide or oxide precipitates $Fe(OH)_3$ and $Al(OH)_3$. The solid precipitates were formed because of the reactions that settle at the bottom of the beakers during neutralisation. This removal of solid particles further reduces the TDS in the solution. The decrease in EC and TDS is directly related to the dosage of CaO. As more CaO was added, it led to greater amounts of acid and precipitation of more ions, leading to a more significant reduction in EC and TDS.

F. Defluoridation Study

SANS 241 and WHO states that fluoride concentration in drinking water should be 1.5 mg/L, therefore it is required to determine the effectiveness of the metal hydroxides produced during AMD treatment in helping to bring down the fluoride concentration to an acceptable limit. Defluoridation experiments using metal hydroxides like $Fe(OH)_3$ (iron hydroxide) and $Al(OH)_3$ (aluminium hydroxide) are common methods to reduce the fluoride concentration in drinking water. Table III represents the measured parameters during the defluoridation experiment.

TABLE III
MEASUREMENTS OF WATER QUALITY PARAMETERS FOR THE REMOVAL OF FLUORIDE IN WATER. FIXED VARIABLE (2.5 g OF ADSORBENT DOSAGE, 30 MINUTES OF CONTACT TIME, 200 RPM OF SPEED, AND 25 °C ROOM TEMPERATURE).

Number of tests	Initial fluoride (mg/L)	pH	EC (µS/cm)	Final fluoride (mg/L)
1	9.9	11.82	728	7.76
2	10.5	11.87	800	7.90
3	9.7	11.90	872	7.6

For this study, only 29.03% of the fluoride was removed and then the adsorption capacity of the AMD sludge for fluoride adsorbed per unit mass of adsorbent was calculated to be 0.45 mg/g. The results show that metal hydroxides produced during AMD treatment were ineffective in reducing fluoride levels to within permissible limits. This might have been due to the presence of competing ions in the water such

as sulphate, carbonate, calcium, and magnesium ions found in the adsorbent causing an interference with the adsorption of fluoride ions onto metal hydroxides, reducing the selectivity of the hydroxides for fluoride removal. Due to the high pH range, the metal hydroxides did not perform well.

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