

Application of a Municipal Waste Byproduct for AMD Treatment: Kinetics and Thermodynamics Predictions

Lumi Mashau, Tshepiso Mpala, Bienvenu Mbuya and Elvis Fosso-Kankeu

Abstract— In this study, the synthesis of struvite from municipal wastewater is evaluated and its application for treating acid mine drainage (AMD). To achieve the goals of this research, batch experiments were conducted to assess the effectiveness of struvite in neutralizing AMD, particularly focusing on raising the pH from an initial value of 1.881 and as a result recovering Fe(III) and Ca. Key parameters evaluated included mixing time, dosage of MgO solution, dosage of struvite, and reactor temperature, with pH closely monitored throughout the process. Aqueous solutions were characterized using Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), while solid samples were analysed using X-ray Fluorescence (XRF), Fourier-Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy (SEM) coupled with energy dispersive spectroscopy (EDS).

The experiment was conducted in two phases. In the first phase, using a magnetic stirrer, the addition of struvite raised the pH of AMD from 1.881 to 8, resulting in a 93.92% removal of iron (Fe) and a 67.78% removal of calcium (Ca). In the second phase, conducted in a reactor, iron removal remained efficient across various temperatures. However, optimizing conditions for calcium recovery required careful management of both time and temperature, particularly avoiding excessively high temperatures that hinder recovery rates. Overall, this study shows that municipal wastewater can be used for the recovery of valuable resources like struvite, contributing to sustainable environmental protection and resource management for future generations.

Keywords— AMD, Municipal Waste Byproduct, Effects Of Temperature And Oxygen, Struvite.

I. INTRODUCTION

The foundation of our economy is water. Water supplies that are safe and sufficient are essential for household, industrial, recreational, and agricultural purposes [1]. South Africa, which is predominately a dry nation, is quickly running out of water, endangering its supply both in terms of quantity and quality [2]. Historically, the construction of dams has served as a primary method to secure sufficient water supplies for irrigation, hydroelectric power generation, and domestic consumption [3].

One of the sectors that power South Africa's economy is mining; nonetheless, in its quest for expansion, this sector jeopardizes ecological and water quality [4]. Acid mine

drainage (AMD) is the most notable type of environmental contamination that mining operations in South Africa and across the world cause. AMD is identified by elevated sulfate concentrations, low pH, high salinity and heavy metal toxicity [5-8]. The likelihood of a mine producing acid and discharging pollutants relies on various factors and is specific to the particular site.

Acid mine drainage (AMD) occurs due to the breakdown of minerals rich in sulfide, particularly in the coal mining sector where pyrite (FeS_2) is the predominant mineral. Geological formations containing substantial pyrite deposits are frequently situated both above and below coal seams earmarked for extraction [9]. When exposed to water and atmospheric oxygen, pyrite undergoes oxidation, leading to the generation of acid mine drainage. Through a mixture of non-living and living reactions, the oxidation of pyrite results in the creation of ferrous iron, sulfate, and hydrogen ions. This process can result in pH levels dropping as low as 2, alongside elevated levels of acidity and dissolved metals. As a consequence, acid mine drainage (AMD) has the potential to significantly degrade receiving waters [10].

Municipal sewage systems often fail to operate as intended, instead, they actively contribute to the deterioration of our ecosystem [11]. The inefficiency of our sewage systems leads to the contamination of our dams, causing them to exhibit green discoloration due to eutrophication. Similarly, our rivers have become highly toxic, posing a threat to individuals who consume the polluted water [12]. For recycling purposes, it is crucial to treat mine drainage and wastewater. Reducing sulfur in diverse industrial processes frequently requires the utilization of carbon sources to interact with sulfur compounds. Municipal waste by-products have the potential to function as carbon sources in the process of sulfur reduction [13].

Over time, there has been a growing focus on researching treatment strategies instead of preventive measures, as the ineffectiveness of prevention strategies has become evident. Various active and passive remedial solutions have been studied, developed, and commissioned to address this pollution concern. Despite the success of numerous treatment options, additional factors like cost and the generation of toxic waste

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must be carefully evaluated before selection. These considerations can lead to higher disposal costs, ultimately limiting the practicality of implementing many of these methods [14].

This study is motivated by the potential benefits of repurposing municipal waste by-products in the treatment of acid mine drainage (AMD). AMD poses environmental risks due to its high acidity, dissolved metals, and sulfate content, and traditional treatment methods are costly and resource intensive. Exploring how municipal waste by-products could help treat AMD is crucial, as current knowledge on the practicality and eco-friendliness of this approach is limited [15]. Research is needed to determine the most effective ways to use these materials. If successful, this method could not only treat AMD but also support the smart reuse of waste, promoting a more environmentally friendly and cost-effective approach. Understanding the right conditions, potential risks, and long-term effects is important to ensure this method complies with environmental regulations while providing a sustainable alternative to traditional treatments.

When exploring methods for treating AMD generation with a municipal waste by-product, it is essential to consider various critical factors, including temperature, bacterial activity, iron sulfide content in AMD, the impact of time, chemical dosage applied to generate the municipal waste by-product, and the chemical composition of the waste by-product. This investigation specifically focuses on the chemical dosage utilized in producing the municipal waste by-product, the chemical composition of the waste by-product, and the factor of time.

This study aims to evaluate the feasibility of using a municipal waste by-product for the treatment of AMD.

II. METHODOLOGY

A. Water sample collection

Acid mine drainage was collected from a coal mine in Mpumalanga, South Africa, and municipal wastewater (MWW) was collected from a plant in Tshwane, South Africa. Magnesium oxide (MgO) was purchased from Minema Chemicals, Gauteng, South Africa.

B. AMD and MWW analysis

The chemical and physical properties of AMD and MWW were determined through measuring the pH and electrical conductivity (EC), using a portable multimeter while atomic absorption spectroscopy (AAS) was used for positive ions analysis, and ion chromatography (IC) for negative ions analysis.

C. Treatment of municipal wastewater and production of byproduct (struvite)

To produce the MWW by-product, a solution of 1 g/L MgO was prepared and mixed for 30 minutes on a magnetic stirrer at 200 rpm and 25°C. The MWW was filtered with filter paper, and the solids were discarded. Different ratios of MWW to MgO solution (1:0.5, 1:1, 1:1.5, and 1:2) were tested for struvite

production, keeping the MWW volume constant at 200 mL while varying the MgO volume. The sludge was allowed to settle for 30 minutes, excess water was discarded, and the sludge was dried in an oven at 100°C for 2 hours, ground into fine powder, and taken for scanning electron microscopy (SEM) analysis. Phosphate and ammonia concentrations were monitored during the struvite synthesis process, for assessing the optimum conditions required for recovery. Phosphate and ammonia monitoring was done before and after MgO addition was done. Since the 1:0.5 ratio was found to be optimal, at a pH of 9.30, the experiments going forward continued with the 1:0.5 ratio, stirring for 30 minutes at 200 rpm and 25°C, followed by another 30-minute settling period. Excess water was discarded, and the sludge was dried and ground into a fine powder to maintain consistency. This process was repeated in each run until enough struvite was produced for analysis and AMD treatment.

D. Characterization of struvite

Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the functional groups present in the struvite, while scanning electron microscopy (SEM) coupled with Energy Dispersive x-ray Spectroscopy (EDS) was used to examine the physical characteristics of the sludge crystals, such as size, shape, surface features and the elemental composition of the struvite crystals. X-ray fluorescence (XRF) was also used to examine the mineral composition of the struvite crystals.

E. Treatment of AMD using a magnetic stirrer

Different masses of struvite (0.5 g, 0.75 g, 1 g, and 1.5 g) were tested in 50 mL of AMD to adjust the pH from 1.96 to 8. The 1.5 g of struvite successfully raised the pH to 8, so the experiment proceeded with that amount. The treatment was carried out for 90 minutes at 300 rpm and 25°C. Afterward, the mixtures were allowed to settle for 30 minutes, and the excess water was collected for Atomic Absorption Spectrometry (AAS) while the struvite was dried. Half of the sludge from each treatment time was heated at 100°C to produce goethite, while the other half was heated at 850°C to produce hematite, both for a duration of 24 hours. The samples were then analysed using XRF and SEM-EDS.

F. Treatment of acid mine drainage using a reactor

Using the same approach, 1.5 g of struvite was added to 50 mL of AMD, and once the pH reached 8, the mixture was transferred into a reactor. The experiment was conducted at varying times and temperatures: for 20, 40, and 60 minutes at 25°C, and at 35°C, 45°C, and 55°C. The mixtures were filtered using filter paper, and the excess water was collected for analysis.

III. RESULTS AND DISCUSSION

A. Physical and chemical properties of MWW and AMD collected from Tshwane, South Africa and Mpumalanga, South Africa.

Table 1 highlights the physical and chemical properties of municipal wastewater (MWW) and acid mine drainage (AMD), showing clear differences in their composition. The MWW is

alkaline, with a pH of 8.2, while the AMD is highly acidic, with a pH of 1.881, indicating its corrosive nature. MWW is also rich in phosphate (113.9 mg/L) and ammonia (120 mg/L), which are typical in municipal wastewater. On the other hand, AMD contains significantly elevated levels of heavy metals, including iron (5530 mg/L) and calcium (133.2 mg/L), presenting major environmental concerns. Additionally, both samples contain calcium and magnesium, with AMD having much higher concentrations of these cations.

TABLE I: PHYSICAL AND CHEMICAL PROPERTIES OF THE MWW AND AMD

Parameter		MWW	AMD
Turbidity	NTU	80.0	-
pH		8.2	1.881
EC	mS/m	-	17.1
P	mg/L	113.9	-
Fe	mg/L	0.245	5530
Mn	mg/L	0.262	133.2
Ca	mg/L	210	739
Mg	mg/L	140	631.8
NH ₃	mg/L	120	-

B. Struvite synthesis: Phosphate and ammonia recovery from MWW at various ratios

The synthesis of the MWW byproduct struvite was assessed by measuring phosphate and ammonia uptake from the solution, in the presence of MgO. In Table 2, it is evident that with the MgO:MWW ratio of 0.5, the recovery of phosphate and ammonia from the MWW was the highest, indicating that nearly all the phosphate and ammonia precipitated, leaving minimal residual content in the MWW. However, as the ratio increased, the recovery of these components decreased, possibly due to the elevated pH caused by the addition of more MgO [11]. Struvite synthesis has been reported to be optimal at pH 8.5 – 9.5. This trend implies that at higher MgO ratios, the system becomes less efficient for struvite formation. As discussed in the introduction, recovering struvite from MWW is critical because of the inefficiency of our sewage systems that leads to the contamination of our dams, causing them to exhibit green discoloration due to eutrophication. Ecological imbalances further result, leading to a harm to ecosystems.

TABLE II: RECOVERY OF PHOSPHATE AND AMMONIA FROM MWW IN FORMING STRUVITE.

Ratio of MWW to MgO Solution	Phosphate (%)	Ammonia (%)
1:0.5	99.2	84.5
1:1	98.0	80.0
1:1.5	96.2	45.2
1:2	45.1	39.2

C. Characterization of struvite using XRF

After the addition of an MgO solution for the treatment of municipal wastewater (MWW), experiments were conducted at 30 mins, using four different ratios. The resulting sludge

(struvite) was collected and analyzed using XRF to determine mineral composition. As shown in Table 3, following struvite production at 30 mins, 18.6% magnesium in the form of MgO and 44.7% phosphorus as P₂O₅ were obtained, signifying successful recovery, results closely similar to Fosso-Kankeu et al [11], confirming the mineral's identity.

TABLE III: XRF RESULTS FOR STRUVITE AT 30 MINUTES.

Component	Mass (%)
Mg	18,57%
Al	6,97%
P	44,71%

D. The chemical functional groups of the struvite

An analysis of the differing functional groups present within struvite at various ratios was conducted using FTIR, shown in Figure 4. The peaks observed at 2907 cm⁻¹ and 3013 cm⁻¹ correspond to the stretching vibration of H-O-H and the anti-symmetric and symmetric stretching of N-H functional groups. Additionally, the absorption peak at 1047 cm⁻¹ represents the vibration of PO₄, while the peaks at 1436 cm⁻¹ and 1403 cm⁻¹ indicate the bending vibration of N-H in NH₄⁺. Furthermore, the hydrogen bonding between water and phosphate is represented by the peak at 2144 cm⁻¹, similar to the journal published by [16].

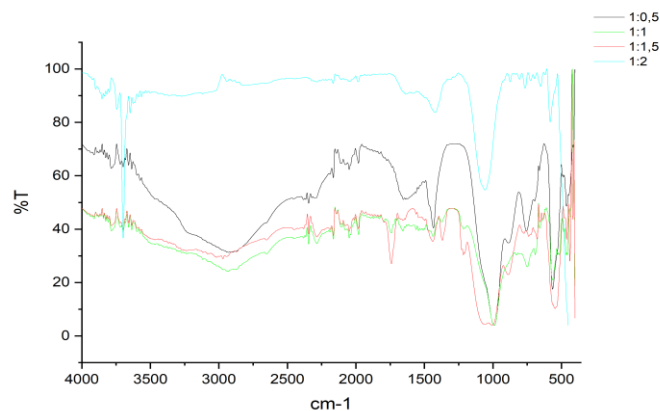


Fig. 1: FTIR graph for Struvite synthesis.

E. Treatment of acid mine drainage

Following AMD treatment with struvite, the water samples were analyzed before and after treatment and results are shown in Table 4. The results in table 4 demonstrate the effectiveness of the neutralizing capacity of struvite in treating acid mine drainage (AMD). After reacting with struvite, the pH of the AMD increased from an acidic 1.881 to a neutral 8, The oxidation-reduction potential (ORP) decreased significantly as well from 665.8 mV to 183.5 mV, reflecting a reduction in the oxidative nature of the solution. The concentrations of key metals, such as iron and calcium, showed significant reductions: iron decreased from 5530 mg/L to 336.3 mg/L, and calcium dropped from 739 mg/L to 238.1 mg/L. Magnesium levels also fell dramatically from 631.8 mg/L to 2.41 mg/L. Overall, these changes confirm that struvite efficiently neutralizes acidity and removes harmful metals, improving the quality of the treated AMD.

TABLE IV: PHYSIOCHEMICAL PROPERTIES OF AMD BEFORE AND AFTER REACTION WITH STRUVITE.

	AMD	Struvite-treated AMD	%Recovery
pH	1.881	8	
ORP	665.8	183.5	
EC(mS/m)	17.1	14.1	
Fe (mg/L)	5530	336.3	93.92%
Ca (mg/L)	739	238.1	67.78%
Mg (mg/L)	631.8	2.41	99,62%

F. Characterization of the AMD treatment sludge

Following AMD treatment with struvite, the sludge produced was further treated at 100°C and 850°C. The SEM-EDS results on Figure 5 indicate a difference in the composition of the sludge treated at 100°C and 850°C, suggesting visible mineral formations at each temperature. The higher phosphorus and sulfur content at 100°C, along with lower iron concentration, pointed to the formation of goethite, which often forms under moderate temperatures and contains more hydrated iron oxide phases. While the significant increase in iron content and reduced phosphorus and sulfur levels at 850°C pointed to the transformation of the material into hematite, a more stable iron oxide that forms at higher temperatures. These findings being consistent with the typical thermal behavior of iron oxides, where goethite transforms into hematite as the temperature increases, confirming the formation of goethite at 100°C and hematite at 850°C [17].

In terms of SEM imagery, the 100°C sample showed round rod-like structures that merge into larger particles, characteristic of goethite's needle-like crystals [18]. On the other hand, the 850°C sample displayed a denser, more compact structure, showing hematite's plate-like, crystalline formations similar to a paper published by Liu et al [19].

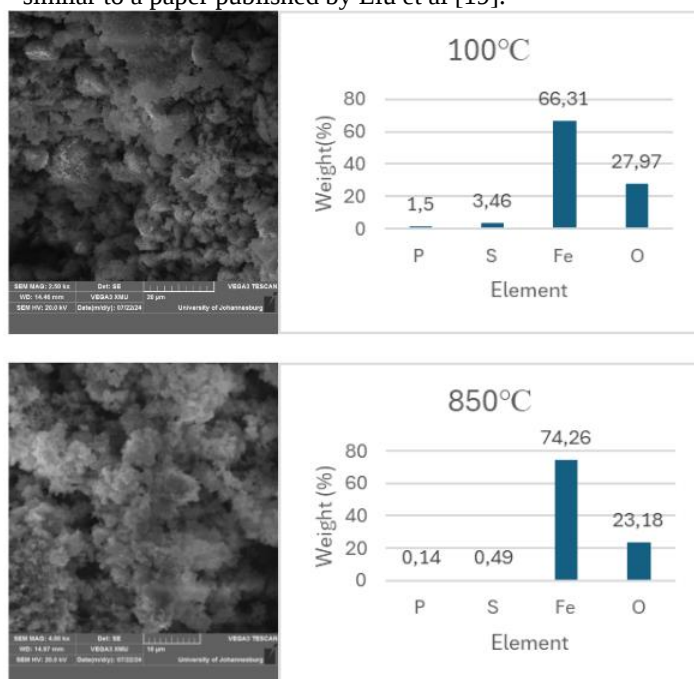


Fig. 2: SEM-EDS of AMD byproduct at varying temperatures.

G. Mineral composition of the struvite-treated AMD sludges at varying temperatures

The XRF results show changes in the mineral composition of struvite-treated AMD sludges that were treated at 90 minutes and then heated at two temperatures (100°C and 850°C) for 24 hours. The content of Fe_2O_3 was increasingly high, reaching 79.71% after 90 minutes at 100°C and peaking at 92.78% after 90 minutes at 850°C. This increase in iron oxide suggests that the sludges are forming iron-rich minerals like goethite at the lower temperature and hematite at the higher temperature. Phosphorus (as P_2O_5) appeared only in specific samples, with higher levels found at 850°C, indicating that the heat enhanced phosphorus retention. In summary, the results indicate that higher temperatures enhance the concentration of iron and promote the formation of specific minerals while also affecting the stability of magnesium and phosphorus in the treated sludge.

TABLE V: XRF DATA OF AMD BYPRODUCT NEUTRALISED WITH STRUVITE

Mineral	100°C	850°C
Time (min)	90	90
Fe_2O_3	79,71%	92.78%
P_2O_5	-	0,75%
MgO	1,60%	1,33%
CaO	0,80%	1,28%

H. Iron and calcium recovery following AMD reactor treatment

Following AMD treatment with struvite in a reactor, iron and calcium concentrations were monitored and are shown in Figure 7. At 25°C, calcium recovery improved over time, peaking at 67.01% after 60 minutes, while iron recovery remained consistently high at 100%. In contrast, at 35°C, calcium recovery showed an initial increase but slightly declined at 60 minutes, suggesting a potential optimal treatment duration around 40 minutes, with iron recovery also maintaining high levels. The 45°C treatment indicated a marked decrease in calcium recovery, especially at 60 minutes, where it dropped to 26.43%, although iron recovery remained at 100%. Notably, at 55°C, calcium recovery significantly declined, with values as low as 3.18% after 60 minutes, indicating that higher temperatures negatively impacted calcium recovery. Throughout all temperatures, iron recovery was consistently high, demonstrating that struvite treatment effectively removes iron from AMD under various conditions. Overall, these findings suggest that while iron removal is efficient across different temperatures, optimizing conditions for calcium recovery requires careful consideration of both time and temperature, particularly avoiding excessively high temperatures that hinder recovery rates.

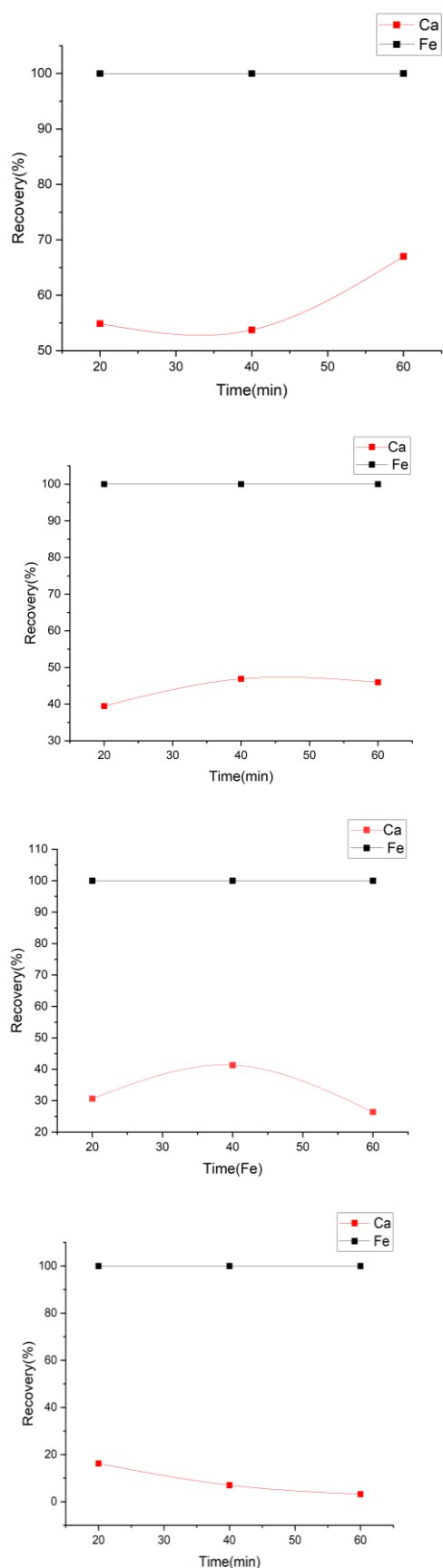


Fig. 3: Recovery of Iron and Calcium after AMD reactor treatment

IV. CONCLUSION

AMD poses environmental risks due to its high acidity, dissolved metals, and sulfate content. Exploring how municipal waste by-products could help treat AMD is crucial, as current knowledge on the practicality and eco-friendliness of this approach is limited. The aim of this work was to recover struvite as a byproduct from municipal wastewater using MgO and assess its application in the treatment of acid mine drainage (AMD). The recovery of struvite was successful, with SEM-EDS showing images of characteristic morphology while XRF data revealed the optimal presence of phosphate as P_2O_5 . An optimal uptake of phosphate and ammonia was also noticed, confirming synthesis. Following the application of struvite in AMD neutralization, the pH was raised to 8, indicating effective treatment, while the recovery of iron sludge was notably enhanced. The conversion of this iron sludge into iron-rich minerals such as goethite and hematite was successful, with the presence of these minerals corroborated by FTIR, XRF, and SEM coupled with EDS analyses.

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