Recovery of Poly-Cationic Metal Sulfate from Acid Mine Drainage and its Beneficiation as a Coagulant for Water Treatment

Mamile Belina Mahlohla[1,2], Vhahangwele Masindi[1,2]; Memory Tekere[1], Spyros Foteinis[3]

[1]*Department of Environmental Sciences, College of Agriculture and Environmental Sciences, University of South Africa (UNISA), P. O. Box 392, Florida, 1710, South Africa*

[2]*Magalies Water, Scientific Services, Research & Development Division, Erf 3475, Stoffberg street, Brits, 0250,*

[3]*Research Centre for Carbon Solutions, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom.*

Abstract

Acid mine drainage (AMD) is an acidic effluent enriched with high metal content, posing noteworthy environmental risks. However, AMD treatment can be coupled with resource recovery, promoting circular economy strategies. This study demonstrates the recovery of Fe(III) from AMD using MgO nanoparticles, followed by FeCl_3 synthesis for river water treatment. The optimized conditions (0.2 mL/L FeCl_3, 100 rpm, 5 min contact time) achieved the removal efficacies in the following order: turbidity (99.6%) > Al (99.5%) > Fe (99.4%) > Cr (99.2%) > Ni (98.2%) > Mn (91.5%) > Cu (90.7%) > As (80.5%) > color (46.4%). This study highlights the feasibility of producing $FeCl_3$ from AMD and its effectiveness for drinking water treatment, offering an innovative approach to AMD valorization.

Keywords: Acid mine drainage, resource recovery, ferric chloride, water treatment, circular economy

Introduction

Acid mine drainage (AMD) is a problem in both abandoned and active mines that can greatly affect the ecosystem quality (Simate and Ndlovu, 2014) and particularly surface water and groundwater (Yadollahi *et al.*, 2021). Different technologies have been employed for the treatment of AMD and they include active, passive, and integrated systems (Masindi, 2022). Each approach has different ecological, economic, and social impacts hence there is a need to come up with closed loop systems that seek to omit or minimize the release of waste into the environment. Furthermore, during AMD treatment sludge that is rich in metals and minerals is also produced and this sludge could be beneficiated to produce valuable products that have variety of industrial applications. previous research has demonstrate the feasibility of recovering valuable minerals such as hematite, goethite, magnetite (Akinwekomi *et al.*, 2020) which, among others, can be used to produce Fe-based catalysts (Aslam *et al.*, 2023), as well as gypsum (Masindi *et al.*, 2018a), and clean water (Pino *et al.*, 2020). Recovery is also governed by the dominance of chemical species. Fe and S are the commonly recovered elements, although others valuable elements such as rare earth elements(REE) could also be recovered but in trace concentrations (Mwewa *et al.*, 2022). This study seeks to recover ferric iron (Fe (III)) from AMD using magnesium oxide (MgO) nanoparticles and explore its application to produce ferric chloride ($FeCl_3$) for water treatment.

Methods

Masindi *et al.*, (2018b) confirmed the feasibility of recovering Fe (III) and other elements from AMD using a sequential and fractional approach and this was employed herein for Fe(III) recovery. To this end, AMD was collected from an active coal mine in Mpumalanga, South Africa, using 25 L containers. The samples were pre-filtered using Macherey Nagel (MN 615-Ø125 mm diameter) filter papers and the filtrate was then used for Fe (III) recovery. Surface water samples were collected from the Wilge River Dam, Gauteng Province, South Africa and used to test the efficacy of the AMD-derived FeCl3. Similarly, surface water was collected using 25 L containers. For quality control, sampling containers were rinsed using the same water during the sampling procedure to avoid contamination.

Analysis of AMD and river water

For the characterization of the collected AMD, the river water, and the FeCl3 treated water a multi-parameter probe (Hach Company HD40D) was used to measure the pH and electrical conductivity (EC). Turbidity was recorded using a tungsten lamp turbidimeter (Hach Company TL2350). Metal and non-metal fractions were determined using inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific XSERIES 2 ICP-MS, coupled to ASX-520 auto sampler) and inductively coupled plasma – optical emission spectrometry (ICP-OES) (Agilent Technologies 5110 ICP-OES coupled with SPS 4 auto sampler), as required based in their concentrations.

Recovery of Fe(III) ions and production of ferric chloride

The Fe(III) rich sludge was recovered from AMD by selective precipitation using MgO nanoparticles. Specifically 100 mL of AMD were transferred into a reactor, and a defined dosage of MgO-nanoparticles was added to enact the optimum Fe(III) recovery (Masindi *et al.*, 2018b). After that, the mixture was stirred for 30 minutes at 500 rpm by means of an overhead agitator (stirrer). To separate the sludge from the supernatant, the mixture was allowed to settle for another 30 min. In order to recover valuable minerals, the supernatant was filtered through a Whatman filter. The Fe(III) rich was then dried and stored until utilization for $FeCl_3$ production. The production of $FeCl_3$ solution for this study was achieved by calcining the recovered Fe(III)-rich sludge at 1200 °C in a furnace. The calcination step ensures phase transformation, improved Fe(III) purity, and removal of residual volatiles, enhancing $FeCl_3$ yield. Then, the calcined Fe(III)-rich sludge was reacted with industrial grade hydrochloric acid (HCl) towards $FeCl_3$ synthesis, as described elsewhere (Almeida and Schneider, 2020).

Stock solution preparation, optimization studies, and removal efficiency

The stock solution was prepared by adding 0.7 mL of $FeCl_3$ solution into a 1000 mL volumetric flask, filled with deionised water. The solution was kept in the fridge until utilization for optimization studies.

The removal efficiency (%) was calculated using the subsequent equation (Eq.1):

$$\%\text{Removal} = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100 \qquad (1)$$

Table 1 *The chemical composition of raw mine water.*

Parameter	Units	Real AMD
pH	–	2.1
Sulfate	mg/L	8000
Fe	mg/L	2800
Mn	mg/L	190
Al	mg/L	280
Cr	mg/L	11
Cu	mg/L	0.9
Ni	mg/L	2.1
Zn	mg/L	4.7
Pb	mg/L	1.1
Acidity	mmol $CaCO_3$	26.2

Where, $C_{initial}$ and C_{final} represent initial concentration (level) and final concentration (level), respectively.

For the determination of optimum conditions for contaminants removal from the river water, several operational parameters were optimized, i.e., $FeCl_3$ dosage, mixing speed, and contact time. Batch experiments were conducted in the laboratory using one-factor-at-a-time (OFAT)method to identify those conditions. The experiments were conducted in triplicate, and the obtained results are reported as mean values.

Effect of dosage

Six 1000 mL aliquots of the collected AMD were spiked with different $FeCl_3$ dosages, i.e., 0.1, 0.2. 0.4, 0.6, 0.8 and 1.0 mL. Then, using a jar test stirrer, the mixtures were stirred for 1 min at 200 rpm. Thereafter, the samples were afforded 60 min for the suspended solids to settle. The turbidity was first determined and the supernatant was then filtered using a Whatman gravity filter. After filtration, the pH and EC were measured.

Effect of mixing speed

Similarly, six 1000 mL aliquots of the collected AMD were used, but these were now spiked with different 0.2 mL $FeCl_3$. The mixtures were mixed for 1 min each at different mixing speeds, i.e.,25, 50, 100, 150, 200 and 250 using the jar test stirrer. Thereafter, the samples were afforded 60 min for the suspended solids to settle and the supernatant was filtered using a Whatman gravity filter. The turbidity, pH, and EC were again measured.

Effect of contact time

Congruent to the effect of dosage and mixing speed, six 1000 mL aliquots of the collected AMD were spiked with 02 mL $FeCl_3$ and stirred at 100 rpm for the following durations, i.e., 1, 2.5, 5, 10, 15, 30 min at the jar test stirrer. Similarly, the samples were afforded 60 min to equilibrate and then filtered, while the turbidity, pH, and EC were also measured

Results and discussion

Effect of FeCl3 dosage

The results on the effect of FeCl3 dosages on river water treatment are shown in Fig. 1. As mentioned above, various FeCl3 dosages were examined, i.e., 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mL.

As shown in Fig. 1, there was a variation in the percentage removal of contaminants as a function of dosage. The different chemical species reach equilibrium, in terms of percentage removal, at different FeCl3 dosages. Specifically, turbidity, Al, Fe and Zn, were practically removed at 0.2 mL dosage, at the next dosage (0.4 mL) Fe removal reach equilibrium, while Ni reached equilibrium at 0.6 mL dosage. The overall removal efficacy followed this sequence, Al (100%), Fe (100%), turbidity (99.9%), As (99.8%), Mn (99.4%), Cr (98.6%), Ni (98.5%), Cu (88.2%), Zn (50%) and colour (25%), respectively. There was a decrease in pH with an increase in $FeCl_3$ dosage. Overall, results in Fig. 1 suggest that the optimum dosage is 0.2 mL and this was considered in the subsequent experiments.

Effect of mixing speed

Fig. 2: The effect of mixing speed on the removal of chemical species contained in real river water (conditions: 1 min of mixing, 0.2 mL, and 60 min settling).

The results on the effect of the mixing speed are shown in Fig. 2. As mentioned above, six different mixing speed were considered, i.e., 25, 50, 100, 150, 200, and 250 rpm. Essentially, it was identified that the reduction in contaminants concentration is a function of mixing speed. Specifically, from 0–25 rpm there was a reduction in turbidity, Fe and Al in river water, while Mn, As, and Cu removal increases with increasing mixing speed and at 100 rpm Ni reaches equilibrium. The removal efficacy for the parameters registered the following sequence: As (99.9%), Fe (99.8%), turbidity (99.7%), Al (98.6%), Ni (94.4%), Mn (86.3%), Cr (84.2%), Cu (81.7%), colour (14.3%) removal efficacies. As such, 100 rpm was taken as the optimum mixing speed and will be used in subsequent experiments.

Effect of contact time

The results for the effect of contact time, when using the following durations: 1, 2.5, 5, 10, 15 and 30 min, are shown in Fig. 3.

As illustrated in Fig. 3, increasing the mixing durations are beneficial for the

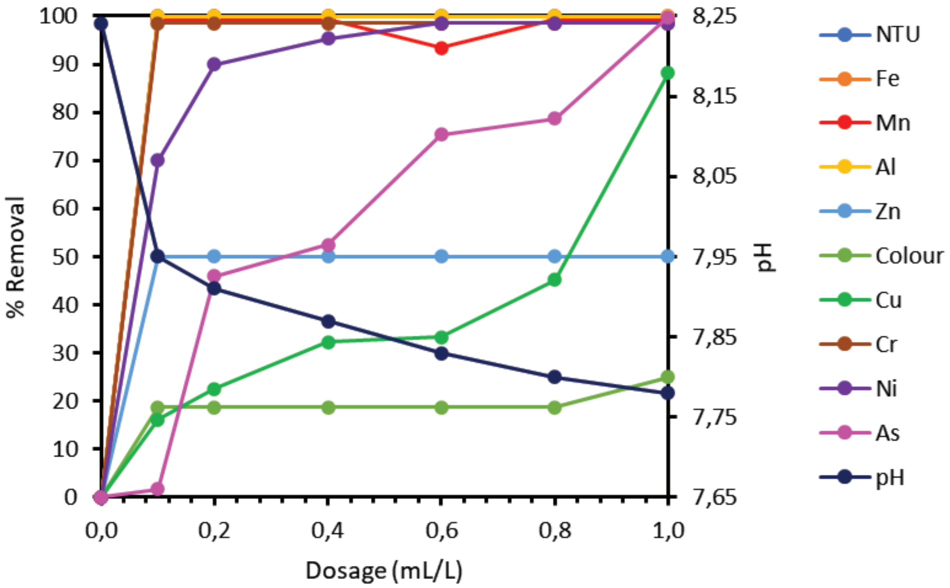

Figure 1 *The effect of $FeCl_3$ dosages on the removal of contaminants contained in real river water (conditions: 1 min of mixing, 200 rpm mixing speed, and 60 min settling).*

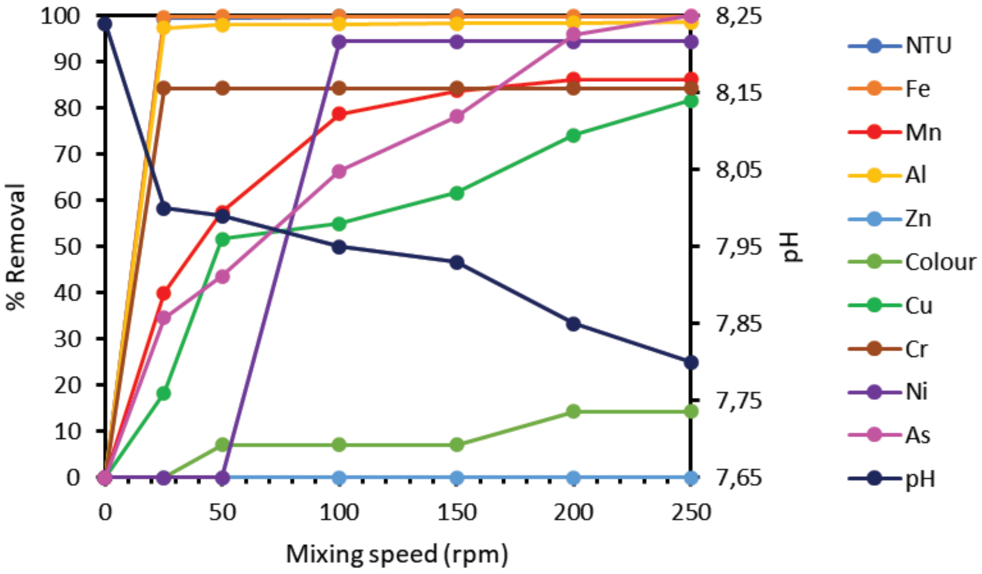

Figure 2 *The effect of mixing speed on the removal of chemical species contained in real river water (conditions: 1 min of mixing, 0.2 mL, and 60 min settling).*

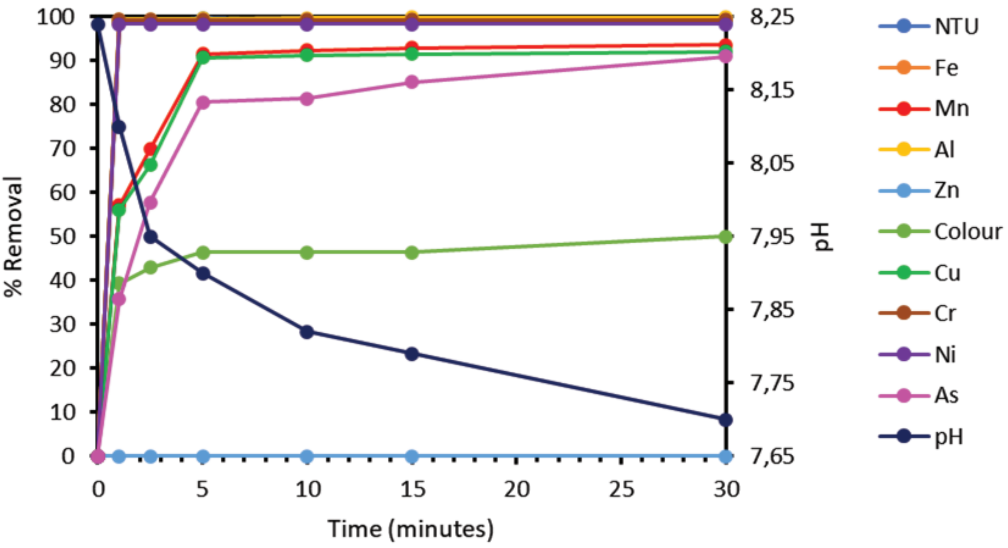

Figure 3 Percentage removal and pH variations in river water when treated for different contact times using FeCl3 synthesized from mine water (Conditions: 0.2 mL: L dosage at 100 rpm mixing speed, followed by 60 min settling time at ambient temperature and pH.)

removal of contaminants, since the percentage removals for all examined contaminants/indicators increase with increasing mixing durations. In more detail, it was observed that turbidity, Fe, Al, Cr and Ni removal plateaus at the first examined mixing duration (1 min), whereas colour removal was observed to reach equilibrium at 5 min mixing duration. The removal percentage efficacies are as follows: turbidity (99.6%), Al (99.5%), Fe (99.4%), Cr (99.2%), Ni (98.2%), Mn (91.5%), Cu (90.7%), As (80.5%) and Colour (46.4%), respectively. The pH also appears to decrease with increasing contact times, and this can be traced back to FeCl3 increasing dissolution with increasing contact times. On the other hand, As removal steeply increase at up to 5 min contact time and then gradually increases until the last examined mixing duration. Based on the aforementioned results 0.2 mL of FeCl3, 100 rpm, and 5 min of mixing are the optimum conditions for river water treatment. Under those conditions the system registered the following sequence in terms of the percentage removal of contaminants; turbidity (99.6%), Al (99.5%), Fe (99.4%), Cr (99.2), Ni (98.2%), Mn (91.5%), Cu (90.7%), As (80.5%) and Colour (46.4%), respectively. These removals render the treated river water within the South African specifications for drinking water quality (SANS 241:2015).

Conclusions

The results from this study illustrate the feasibility of recovering ferric iron (Fe(III)) from acid mine drainage (AMD) and use it for ferric chloride ($FeCl_3$) production. The synthesized $FeCl_3$ was used to treat river water. Its application as a coagulant for treating drinking water was effective at 5 min of contact time, 100 rpm mixing speed, and 0.2 mL/L FeCl3 dosage. The results also highlighted that the AMD-derived $FeCl_3$ can be used for water treatment, as the treated river water was within the South African specifications for drinking water quality (SANS 241:2015).

Acknowledgements

The authors of this study would like to convey their sincere gratitude to the University of South Africa and Magalies Water for extending their facilities towards the accomplishment of the objectives of this project.

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