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Witwatersrand Basin Acid Mine Drainage (AMD) Softening via Urea Hydrolysis: Part 1 Experimental

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South Africa is a water scarce country with a semi-arid climate. The pollution of freshwater resources by the acid mine drainage (AMD), which is mostly acidic and hard, has exacerbated the problem. This research focuses on the treatment of AMD from the three goldfields (Eastern - EB, Central - CB and Western - WB basins) of the Witwatersrand basin, Gauteng, South Africa with the aim of recovering water (fit-for-purpose) and marketable mineral(s) for industrial use. In this preliminary study, the AMD water samples from these three basins were subjected to urea hydrolysis at varying urea concentrations (urea to total metal [U]/[M] ratios ranging from 3.3 to 10), constant reaction times (3 h) and temperature (80 °C). This resulted in the pH of the AMD water samples of the three basins (EB, CB and WB) being increased to an average of approximately 8.8, and the softening of water, with more than 98% removal of calcium. The sulphate removal ranged between 38 to 50%, while the method also displayed a positive impact in the reduction of magnesium (up to 34%) and the monovalent cations (sodium up to 33% and potassium up to 44%) from the polluted AMD water samples. In addition, calcium carbonate (aragonite polymorph), a mineral with vast industrial applications, was recovered in the process. The significance of the findings is that, firstly an environmentally benign method has been demonstrated to effectively soften and remove the AMD pollutants. Secondly, the AMD pollutants were converted to a valuable industrial product without generating any waste in the process.

1. Introduction

The increasing emissions of greenhouse gas (GHG) has a devastating impact on climate change, so is the acid mine drainage (AMD) in polluting freshwater resources and the environment. The impact of AMD, mine wastewater characterized by low pH and high in concentration of toxic heavy metal sulphate salts, has been felt world over where there are mining activities, especially for coal and gold mining (Zhang et al., 2023). This is mainly because these minerals are found in ores containing sulphide minerals (e.g. Pyrite or "fool's gold") which when exposed to water, oxygen and microorganisms, oxidizes resulting in sulphate formation, reduced pH, this then dissolves the other heavy metals present in the ore (Rodrigues-Galan et al., 2019). This wastewater then leaches, polluting the ground and surface freshwater resources as well as degrading the environment in the vicinity of the mining operations, especially the disused or abandoned ones (Mhlongo & Amponsah-Dacosta, 2016). In South Africa, this has been amplified by the fact that it is a water stressed country due to its semi-arid climate with rainfall of 490 mm/annum, well below the global average of 860 mm/annum (Roffe et al., 2019). The pollution of both fresh and ground water systems, environmental degradation and negative socio-economic impact by the AMD is well documented, especially in the Witwatersrand, which is the focus area of this study (Durand, 2012). The South African government and mining houses have tried to mitigate the situation by setting up treatment plants in the three Witwatersrand basin (Digby Wells Environmental, 2012). However, the current intervention implemented in the Witwatersrand basins only partially addresses the AMD problem as the technology deployed, High Density Sludge (HDS) process, has several challenges, namely (i) it is costly to run, (ii) it generates waste that needs to be disposed of, and (iii) the resulting water that is discharged to the receiving bodies is still high on sulphates (Hobbs, 2017).

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Lorio and co-workers (2022), used an Analytical Hierarchy Process in the selection of the optimum AMD treatment technology in the Philippines context and alluded that the HDS process is the most stable alternative, regardless of the above-mentioned shortcomings. Admittedly, AMD has presented a formidable challenge due to its complex nature and associated costs, where there is no one solution to the problem that can be deployed universally (Wibowo et al., 2021). That is, each mine, region and geography need to be researched for an appropriate and best solution to be implemented (Naidu et al., 2019). This has been demonstrated by the continued research interest on the AMD remediation/treatment strategies, and the focus has shifted to the development of sustainable technologies where there is zero waste generated and the process can be self-funding based on the resulting water and mineral(s) recovered being of commercial value (Moodley et al., 2018). In this paper, a circular economy approach model is proposed as shown in Figure 1. That is, to develop an AMD treatment technology that is environmentally friendly to produce water and mineral(s) that can be used for agricultural and industrial purpose, respectively, thus generating revenue to sustain the AMD remediation process and zero waste (Kefeni et al., 2017). In this study, a homogeneous precipitation of AMD pollutants via urea hydrolysis is proposed based on its advantages that includes highly crystalline materials with uniform particle sizes being synthesized as well as the resulting solution containing ammonium salts that can be used as fertilizer in agricultural applications (Subrt, 2012). For the samples of interest, it was established that calcium carbonate (aragonite polymorph) was the predominant mineral recovered (Khumalo & Chirwa, n.d.). However, this is beyond the scope of this paper.

Figure 1: Circular economic approach for AMD treatment.

2. Materials and methods

2.1 Materials

AMD water samples from the three basins in Gauteng (South Africa), Eastern (EB) Springs, Central (CB) Germiston and Western (WB) Randfontein, were collected at the pumps from the mine shafts before entering the treatment plants into 50 Lt High Density Polyethylene (HDPE) containers. Urea ($CO(NH_2)_2$), analytical grade with purity >99.9%, was purchased from Sigma-Aldrich South Africa. The water samples and reagent were used as is without any pre-treatment.

2.2 AMD treatment and characterization

The AMD water samples were transferred into a 1 Lt round bottom two-neck flask fitted with a condenser and digital thermometer. Urea granules were added so that the final concentration of the mixture (total urea to metal ratio [U]/[M]) ranged between 3,3; 4 and 10, based on the composition of each basin, to see if any minerals could be recovered. That is, three reactions for each basin (EB 1 - 3, CB 1 - 3 and WB 1 - 3). The mixtures were then heated to 80 °C under reflux on a heating mantle and continuous stirring using a magnetic stirrer at 50 rpm for 3 h. The reaction mixtures were then removed from the heat source and stirring to be air cooled. The precipitates were then collected qualitatively by vacuum filtration using the Whatman No. 1 filter paper, the precipitates were washed once with deionized water and then air dried in the fume hood overnight. The dry powders were then collected and kept in sealable plastic bags to avoid any contamination for characterization. The supernates were collected during the first filtration, before the washing of the precipitates with deionized water in to 500 ml HDPE bottles for later characterization. The AMD water samples, prior and post urea hydrolysis, were conditioned to 25 °C for 24 h before testing. The pH of the samples was determined using a Thermo Fisher Scientific Orion STAR pH/conductivity meter (United States). The concentrations of the dissolved metals (cations) were analysed using the Agilent Technologies 700 Series ICP-OES (United States) after filtering the solutions through a 0.45 μm Millipore filter and preserved with 1% (w/w) nitric acid. The sulphate (anion) content of the samples was determined using a Thermo Fisher Scientific Aquakem 200 Photometric Analyzer (United States) after precipitating the anions with barium chloride and measuring the turbidity at 405 nm. All the results are reported as averages of five determinations as they were analyzed at an ISO17025 laboratory.

3. Results and discussions

The physical and chemical properties of the AMD samples as received are presented in Table 1. It should be noted that the average uncertainties for all the measured parameters are below 5% except for sodium content (7.7%). The results of the AMD samples from the three basins after being exposed to urea hydrolysis at different urea concentrations are summarized graphically in Figure 2.

Table 1: Physical and chemical properties of the samples from the three goldfields in the Witwatersrand basin as received.

Parameter	EB	CB	WB	Units
pH @25°C	7,95	2,26	3,86	pH units
Element				
Calcium (Ca)	319	550	547	mg/L
Potassium (K)	16,8	23,8	22,7	mg/L
Magnesium (Mg)	134	299	136	mg/L
Sodium (Na)	191	214	164	mg/L
Sulphate (SO_4^{2-})	1320	2995	1872	mg/L

The results of the AMD water samples showed that the physical and chemical properties of the three basins (EB, CB and WB) are different. As expected, the AMD sample with the lowest pH, CB, had the highest concentration of pollutants followed by the WB and EB. In all the untreated samples, calcium, magnesium, sodium and sulphate are above the limits of the South African National Standard (SANS) for portable water, SANS 241:2015, which are 150 mg/L, 70 mg/L, 200 mg/L and 250-500 mg/L, respectively.

On the pH, only the EB sample is within the limit, 5,0-9,7 pH units and the other samples are very acidic. The pH of all the samples were adjusted to within the standard limits at the lowest urea concentration, [U]/[M] ratio of 3.3, indicating the efficiency of the method in neutralizing the AMD. Beyond this concentration, the increase in the pH of the AMD from the three basins with increasing urea concentration was marginal, averaging at 8.8 pH units as shown in Figure 2A. It was interesting to observe the decrease in the sulphate concentration with increasing urea concentration (Figure 2B). The EB sample displayed the highest decrease, 50% closest to the 500 mg/L standard limit, at the highest urea concentration, [U]/[M] of 10, while the CB and WB samples displayed 42% and 38% reduction, respectively. The current technology employed at the three basins, HDS, removes the sulphate as gypsum ($CaSO_4 \cdot 2H_2O$) and magnesium sulphate ($MgSO_4$). However, the process still leaves high levels of sulphate in the final discharge, necessitating additional treatment technology to remove it to acceptable levels (Lourenco & Curtis, 2021).

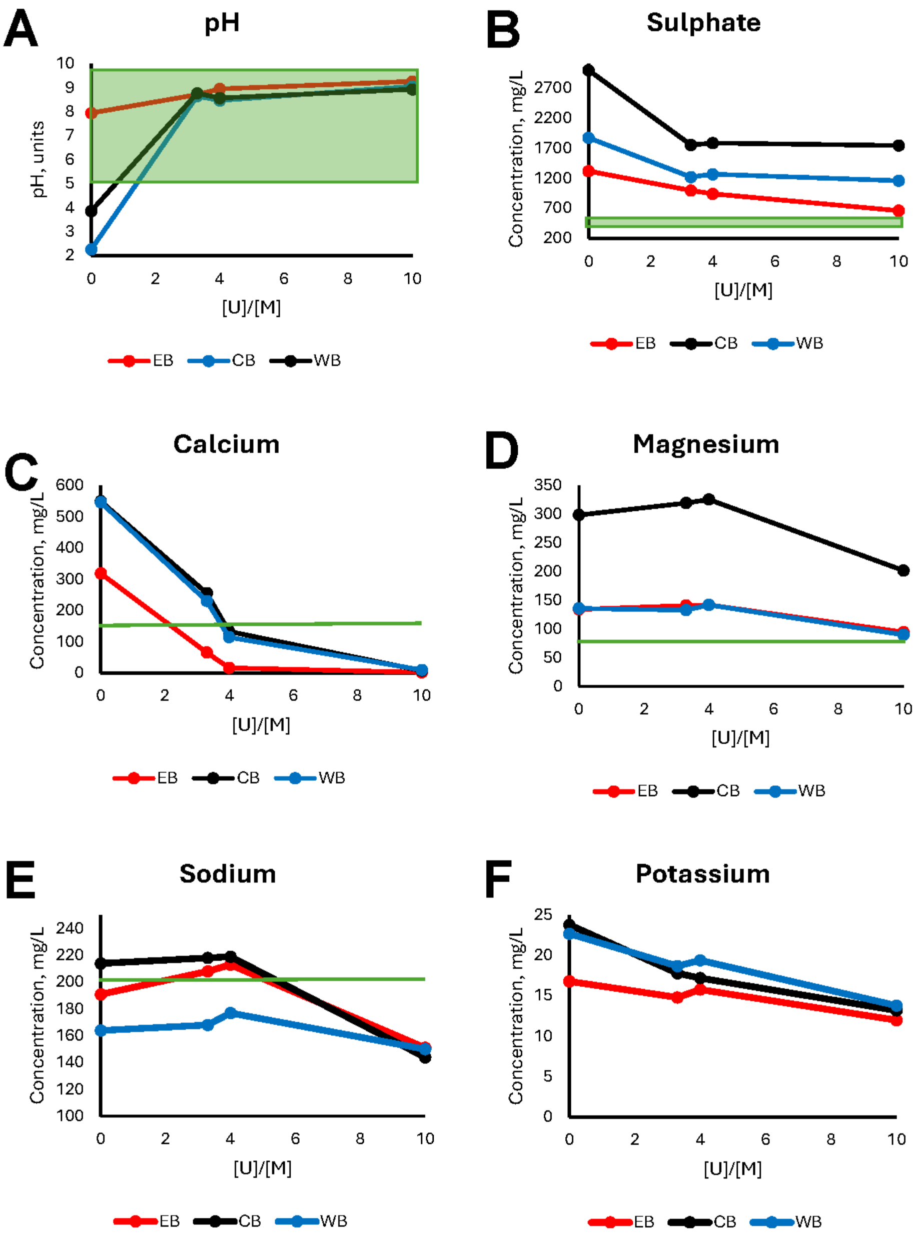

Figure 2: AMD results of the three Witwatersrand basins with the SANS 241:2015 limits.

Several potential technologies have been proposed to address the sulphate removal, with majority of them only being at a laboratory investigation stage, with both advantages and disadvantages (Ashane et al., 2018). On the positive side, the Rhodes BioSURE process has been promoted to the pilot plant stage, removing sulphates to levels below 100 mg/L and its disadvantages being the generated sludge and sulphide gas as well as the limited availability of biomass to achieve these results (Rose, 2013). On the circular economy approach, sulphate can be removed as sulphuric acid via several processes which are a subject of research as one example (Naidu et al., 2019). For this work, the results showed a promising trend, within a reasonable reaction time (3 h), on the removal of sulphate anions. However, the method needs to be optimized to reduce the sulphate to acceptable levels for targeted applications, e.g., agricultural uses (Chen et al., 2021).

Of all the contaminants, the method displayed the highest efficiency in removing calcium at an average of 98.7%, well below the standard limit, for the three basins (Figure 2C). Calcium, together with magnesium are responsible for the hardness of water, with the major problem of its manifestation being the scale formation, which is a costly menace on infrastructure, both domestically and industrially (Lethea, 2017). For agricultural applications, the South African Water Quality Guidelines does not specify the amount of calcium for irrigation but specify the Target Water Quality Range (TWQR) of 0 - 1000 mg/L for livestock watering (Department of Water Affairs and Forestry, 1996a). Similarly, with magnesium, 0 – 500 mg/L, which in all the treated AMD samples comply to TWQR but does not meet the SANS 241:2015 standard (Figure 2D). On sodium, the results comply to SANS 241:2015 as it is below 200 mg/L for all three samples at [U]/[M] of 10 (Figure 2E). The potassium in all the samples is below the standard's limit, 50 mg/L (Figure 2F), even for the untreated water. However, it is interesting to observe that the potassium decreases with increasing urea concentration. The results also highlight the urgent need for a rapid and vigorous update of the South African legislative framework to eliminate these inconsistencies and ambiguities with regards to standards and guidelines for wastewater treatment intended for re-use (Grewar, 2019).

4. Conclusions

In this study, an environmentally benign urea hydrolysis approach was developed for the treatment of acid mine drainage from the three Witwatersrand basins. The method demonstrated to be effective in softening and removing the AMD pollutants, namely, divalent and monovalent cations as well as the sulphate anion. The effectiveness of the method can be rated in the following order $\mathrm{Ca}^{2+} \gg SO_4^{2-} > \mathrm{K}^{1+} > \mathrm{Mg}^{2+} > \mathrm{Na}^{1+}$. That is, more than 98% removal of calcium, up to 50% of sulphate anion, as well as reduction of monovalent cations from the acid mine drainage of the three Witwatersrand basins in Gauteng, South Africa. The resulting water from all the three basins can be of use for the agricultural irrigation as it within the South African Target Water Quality Range for this application. This paper proposes an environmentally benign and self-sustaining method of AMD treatment as no waste is generated in the process, since only fit-for-purpose water was produced with a potential to generate revenue.

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