Effective Attenuation of AMD Pollution Potential Using By-product from Municipal Wastewater Treatment

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Abstract

In our concept, the mineral struvite which is a by-product from the treatment of municipal wastewater can be used as an alternative to lime; this by-product was added to AMD of pH 2 and the pH was raised in a stepwise manner giving the opportunity to recover ferric phosphate.

The addition of struvite to AMD resulted in the neutralisation of AMD and the attenuation of inorganic contaminants were ≥98.99% for metals (Al^{3+}, Fe^{3+}, and Mn^{2+}) and ≥30% for SO_4^{2-}. Traces of other metals such as Zn, Cu, Ni, Pb, and Cr were significantly attenuated. Iron phosphate was essentially recovered at pH 3 during the sequential neutralization of AMD.

Our results show that the by-product struvite produced from the treatment of municipal wastewater (MWW) can be successfully applied to increase AMD pH to about neutral and for the removal of metals. This technology offers the benefit of avoiding gypsum fouling.

Keywords: Acid Mine Drainage, Mineral By-Product, Municipal Wastewater, Ferric Phosphate

Introduction

The biodiversity including wildlife and plants is significantly affected on a daily basis by the ineffective management of sewage and effluents [1]. The clogging of conduits and fresh water filters as a result of hypertrophication of water bodies, such as wetlands, rivers and riparian zones, inevitably leads to the killing of a host of organisms including species dependent upon them for survival [2]. The impact of poor management of our effluent is extended to human life which suffers from health issues as well as economic challenges, specifically in less affluent communities. Our municipal sewage systems do not work as per design, but rather contribute to the degradation of our ecosystem. It is estimated that only 60 of our 824 treatment plants are able to operate effectively [3]. The ineffective performance of our sewage systems contributes to the pollution of our dams which are turned green as a result of eutrophication while our rivers have become heavily toxic, harming people who drink the polluted water. The government is faced with the daunting task of ensuring sustainability and improvement of waste management services throughout the country [4].

In South Africa, AMD has been reported in a number of areas, including the Witwatersrand Gold Fields, Mpumalanga and

KwaZulu-Natal Coal Fields, and the O'Kiep Copper District. The Western, Central and Eastern Basins are identified as priority areas requiring immediate action. In Gauteng, 350 ML/d of acid mine water is produced from current and previous mining operations and in Mpumalanga, a volume of 200 ML/d is produced. The situation in other mining regions of the country requires additional information, monitoring and assessments of risk, particularly in vulnerable areas such as the Mpumalanga Coal Fields, where the impact of mining on the freshwater sources in the upper reaches of the Vaal and Olifants River Systems is of serious concern. AMD has increased scrutiny of the practices of mining companies with operations in South Africa and could hold significant regulatory, legal, closure liability, and reputational implications for the industry [5, 6].

These waters need to be treated to drinking water standards before it can be discharged into public streams. A further requirement is that zero waste needs to be left at site. This requires that waste streams be processed in such a way that saleable products can be recovered from the waste streams. Currently, lime is used for pre-treatment which results in the production of a mixture of metal hydroxides and gypsum as a solid waste. The brine from reverse osmosis (RO) plants is stored in evaporation ponds. This practice is not a long-term solution due to the risk of ground water pollution when lined ponds get damaged. It is proposed in this study to achieve selective metals recovery by raising the pH stepwise while treating the AMD. The iron can be recovered as phosphoric complex at pH 3.5 or 4. Ferric phosphate has multiple uses including the use as a human nutritional supplement, as an ingredient in fertilizer, as a snails controller in food crops and an active ingredient of pesticide. Previous studies have shown that iron can preferably react with phosphate in a pH range 4 to 6 forming insoluble iron phosphate species which can precipitate [7].

This innovative study primarily aims at reclamation of valuable minerals from municipal wastewater, and their applications in AMD treatment and ferric phosphate production.

Methods

Samples collection and materials

The municipal wastewater was collected from a plant in Pretoria, South Africa. It was transported in several containers of 25 L capacity and stored in the dark in our laboratory at the Florida Science Campus. Magnesite samples were obtained from a magnesite mine in the Limpopo Province of South Africa and used without further processing. Acid mine drainage (pH 2) was collected from a coal mine in Mpumalanga Province, South Africa. Potassium hydrogen phosphate was purchased from Minema Chemical (PTY) LTD in South Africa.

Treatment of MWW and production of struvite

A fixed mass (15 kg) of the magnesite powder was added to 100 L of MWW in a hopper of 180 L capacity while mixing with a fitted impeller at a speed of 200 rpm for 60 min at room temperature (approximately 25 °C); the pH, electrical conductivity (EC) and redox potential (ORP) were simultaneously recorded using a multi-parameter meter (Hanna Instruments, Johannesburg, South Africa). To determine the effect of phosphate on the crystallization and precipitation of struvite, potassium hydrogen phosphate with the corresponding mass of phosphate of 150 g and 300 g was added to the mixture. See Table 1 for the pH, EC an ORP results. After mixing, the mixture was allowed to settle for about 30 min then the supernatant and the sludge were collected for analyses. The sludge was dried under the sun for two days.

Treatment of AMD

The treatment of AMD was carried out using the sludge with the highest content of struvite which was incrementally added to 5 L AMD in a 10 L bucket such to allow a progressive increase of pH and selective precipitation of ferric phosphate at pH 3 and 4.5. The mixture was mixed at a speed of 300 rpm using an overhead stirring system until a pH of 3 was achieved. The mixing was done for 60 min, at room temperature and the mixture was allowed to settle for 30 min. The supernatant was then collected through

a tap and subsequently treated the same way to achieve a pH of 4.5. The sludge was collected after each step, dried, and stored for further analysis. To assess the effect of mixing time on the treatment of AMD, a specific experiment was conducted during which water samples were collected at 0, 5, 10, 15, 30, 45 and 60 min.

Characterization of solid samples

To ascertain the mineralogy of feed and product minerals, X-ray Diffraction (XRD) was used. Specifically, the PANalytical X'Pert PRO-diffractometer equipped with Philips PW 1710 Diffractometer with graphite secondary monochromatic source with Uniquant software was used for analyses. The morphology, mapping properties, and elemental properties were ascertained using the High Resolution (HR)-Field Emission-Scanning Electron Microscope (FE-SEM) coupled with the Focused-Ion Beam (FIB) and an Energy Dispersive X-ray Spectroscopy (EDX).

Analysis of water samples

The metals in solutions were analysed using the Inductively coupled plasma mass spectrometry (ICP-MS), XSeries 2, ICP-MS, supplied by Thermo scientific, from Hanna-Kunath-Str. 11 28199 Bremen, Germany. The ion chromatography was used to quantify sulphate in solution.

Results and discussion

Treatment of MWW and production of struvite

Characterization of sludge produced during MWW treatment

After addition of magnesite for the treatment of MWW with or without supplementation of potassium hydrogen phosphate (tab. 1), the sludge was collected and analyzed using XRD to determine the mineralogical composition. It was found that five main minerals were dominant in the sludge, including struvite, potassium aluminosilicate, magnetite, dicalcium diphosphate and sillimanite (tab. 2). As shown in Table 2, the highest (36.7%) production of struvite was achieved when there was no supplementation of phosphate; implying that there was enough phosphate in the MWW to react with ammonia and magnesium for the formation of magnesium ammonium phosphate (MAP) also known as struvite [8].

Table 1 *Effect of phosphate concentration on the physico-chemical characteristic of wastewater samples*

[PO4]	pH		EC		ORP	
	Initial	Final	Initial	Final	Initial	Final
No phosphate	7.04	9.28	0.306	0.104	-13	-143
150 mg/L	6.92	8.87	0.341	0.278	-3	-126
300 mg/L	7.11	7.98	0.410	0.240	-9	-70

Table 2 *Mineralogical composition of the sludge produced from MWW treatment*

Minerals	Formula	Content %		
		X_1	X_2	X_3
Struvite	$MgNH_4PO_4(H_2O)_6$	36.7	31	13.2
Potassium aluminosilicate	$K_2Fe_6Si_6Al_2O_20(OH)_2$	25.9	1.96	28.6
Magnetite	Fe_3O_4	7.4	2.6	44
Dicalcium Diphosphate	$Ca_2P_2O_7$	16.4	2.8	3.7
Sillimanite	Al_2SiO_5	13.6	62	10.5

X_1: No PO_4; X_2: 150 g PO_4; X_3: 300 g PO_4

Elemental composition of the MWW sludge

The EDS results (fig. 1) clearly show the abundance (2.6 and 2.8%) of phosphorus in the sludge samples from the reactors supplemented with phosphate, while the sludge sample from the non-supplemented reactor only contains 0.5% phosphorus. The magnesium was relatively high in all the sludge samples as it was mainly derived from magnesite.

AMD treatment using struvite

Neutralization of AMD

The pH, EC, Ca and Mg were recorded over time during the treatment of AMD with the MWW sludge; the results (fig. 2) show that the pH of the solution increases with an increase in time, reaching a pH of 11 after 60 min. The Mg concentration also significantly increased, this was due to the fact that when

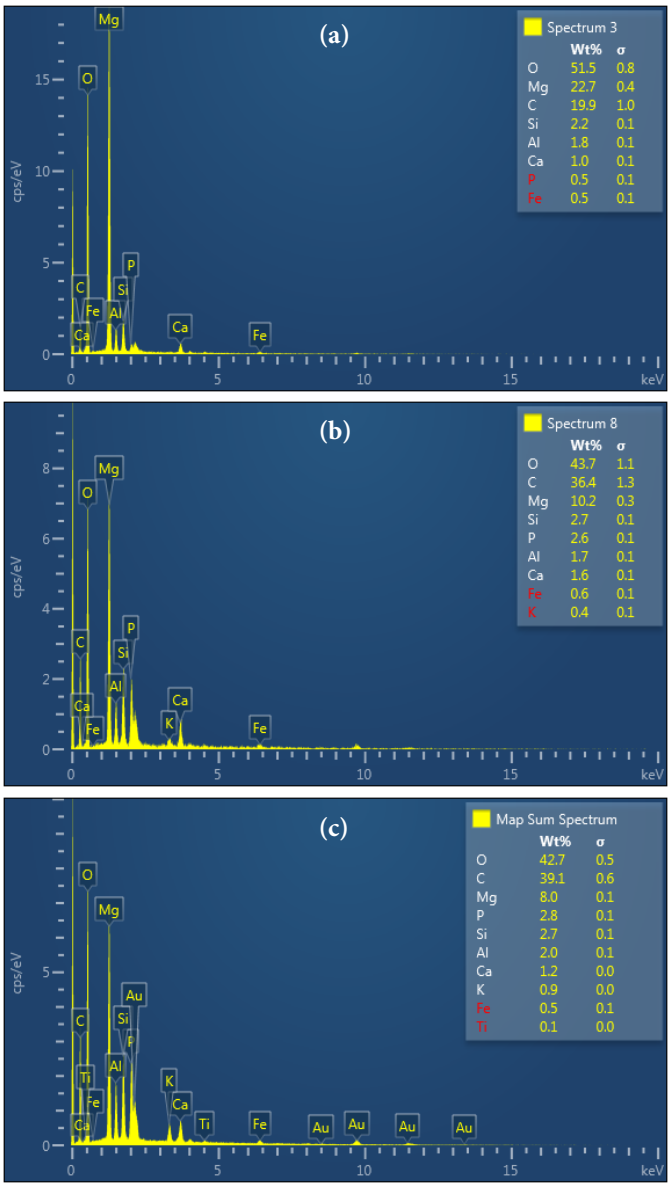

Figure 1 *EDS elemental composition of sludge from MWW treatment (a) no phosphate treatment; (b) 150 g phosphate added and (c) 300 g of phosphate added*

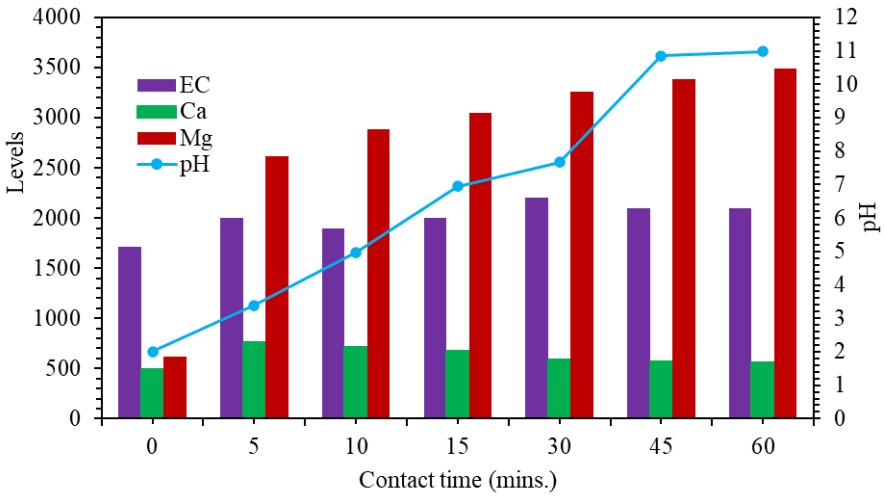

Figure 2 *Variation of physico-chemical parameters during the treatment of AMD*

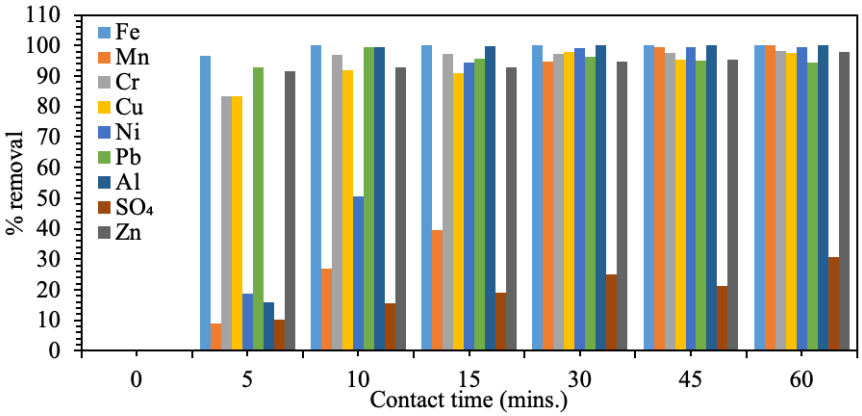

Figure 3 *Effect of mixing time on the removal of metals during the treatment of AMD*

in contact with AMD, Mg from the magnesite mainly forms $MgSO_4$ which is very stable in solution. The EC level and Ca concentration did not vary much after 60 min.

Removal of metals and sulphate from AMD

Most of the metals in solution were almost totally removed (>90% removal) after 30 min (fig. 3). This corresponded to a pH value of 8; a pH at which most of the metal are no longer soluble, forming complexes that precipitate and form the sludge. However, only about 30% of sulphate was removed after 60 min; as explained above, most of the sulphate may have reacted with Mg to form $MgSO_4$ which is highly stable in solution.

Characterization of AMD sludge

Mineralogical composition

The results of the mineralogical analysis (tab. 3) show that about nine minerals including dicalcium diphosphate, aluminum phosphate, iron sulfide, calcium phosphide, silicon oxide, iron phosphate, trimagnesium bis-phosphate, struvite and calcium iron phosphate were prevalent in the AMD sludge. Iron phosphate which is the mineral of interest was mainly recovered (55.78%) at pH 3 (which is the expected pH for the precipitation of ferric iron) while very low recovery (4.56%) was achieved at pH 4.5. The struvite content was very low (1.28%) in the

Table 3 Mineralogical composition of the sludge produced from AMD treatment

Phase name	Formula	Content %	
		pH 3	pH 4.5
Dicalcium Diphosphate	$Ca_2P_2O_7$	10.6	40.03
Aluminum Phosphate	$Al(PO_4)$	20.18	0.26
Iron Sulfide	FexSy	3.71	1.38
Calcium Phosphide	CaP_3	0.34	8.39
Silicon Oxide	SiO_2	0.1	0.076
Iron Phosphate	$Fex(PO_4)y$	55.78	4.56
Trimagnesium bis-phosphate	$Mg_3(PO_4)_2$	0.54	7.32
Struvite	$MgNH_4PO_4(H_2O)_6$	1.28	10.87
Calcium Iron Phosphate	$CaxFey(PO_4)z$	1.06	2.17

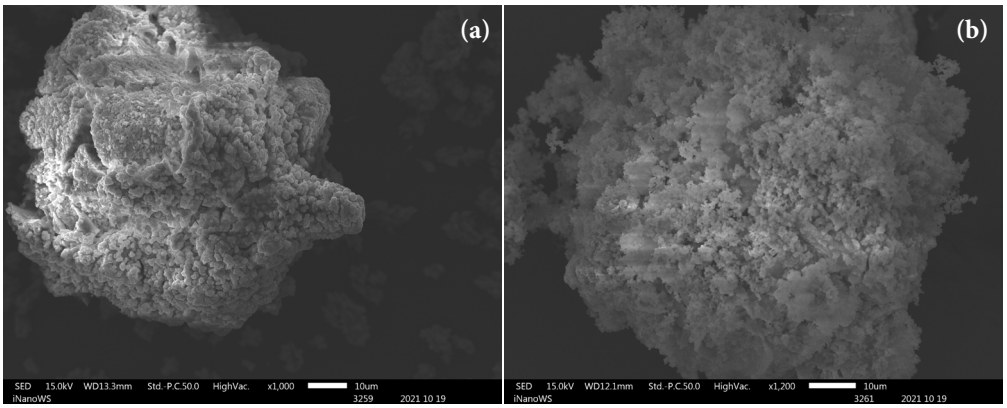

Figure 4 *SEM images of the sludge produced from the treatment of AMD (a) sludge collected at pH 3, (b) sludge collected at pH 4.5*

sludge collected at pH 3 compared (10.87%) to the sludge collected at pH 4.5, because strong acidic conditions contributed to dissolution of struvite into its main constituents which reacted with ions in solution.

SEM images

The SEM images (fig. 4) show that the particles in the sludge collected at pH 3 were coarser than those in sludge collected at pH 4.5. The crystallinity of the latter was more pronounced indicating the purity of the salts formed at pH 4.5. It was evident that at pH 3 some impurities precipitated with the main salts such iron phosphate and aluminium phosphate.

Elemental composition

The EDS results (fig. 5) showing higher content (14.1%) of iron in the sludge collected at pH 3 compared to the sludge collected at pH 4.5, also confirming the preferential precipitation of iron phosphate at pH 3.

Conclusion

The aim of this study was to optimize the production of struvite during the treatment of MWW and assess the potential of struvite for the treatment of AMD and recovery of ferric phosphate. It was found that the supplementation of phosphate during MWW treatment with magnesite does not improve the formation of struvite. Struvite

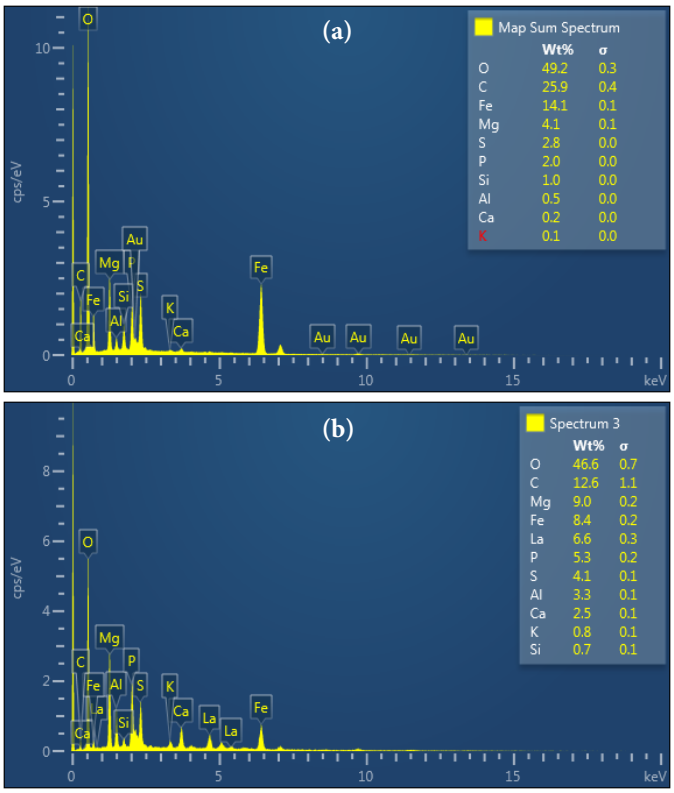

Figure 5 *EDS results of the (a) sludge collected at pH 3, (b) sludge collected at pH 4.5*

was found to effectively increase the pH of AMD and remove almost all the metals from the solution; however, only about 30% of sulphate was removed during the process. Further study is required to improve the purity of ferric phosphate recovered during the treatment of AMD.

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