The synthesis of calcium phosphate from municipal wastewater and its application for the removal of metals from acidic effluents

By

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DECLARATION

I, **Nepfumbada Collen (14014248)**, hereby declare that this dissertation ``The synthesis of calcium phosphate from municipal wastewater and its application for the removal of metals from acidic effluents`` submitted for the Master of Sciences in Chemistry at the University of Venda by me is my own work, that it has not been submitted for any degree or examination at this or any other institution, and that all the sources I have used or quoted have been indicated and duly acknowledged by complete references.

Signature: Date: 24/04/2021

LIST OF PUBLICATIONS

The following papers are linked to this study:

I. **Synthesis of calcium phosphate from stimulated municipal wastewater using calcium hydroxide: Experimental and geochemical modelling approach.**

Authors: Collen Nepfumbada, Vhahangwele Masindi & Nikita Tawanda Tavengwa

Manuscript Under review – Journal of Desalination and Water Treatment.

II. **Utilization of the synthesized calcium phosphate from municipal wastewater for the removal of metals from acidic effluents.**

Authors: Collen Nepfumbada, Vhahangwele Masindi & Nikita Tawanda Tavengwa

Manuscript under review – Journal of Environmental Chemical Engineering.

LIST OF RELATED PUBLICATIONS

I. **Removal of phosphate from wastewater using geogenic calcium carbonate: A column study.**

Authors: Collen Nepfumbada, Vhahangwele Masindi & Nikita Tawanda Tavengwa

Manuscript Under review – Journal of Water Science and Technology.

II. **The use of calcium phosphate for the treatment of acid mine drainage.**

Inventors: Collen Nepfumbada, Vhahangwele Masindi & Nikita Tawanda Tavengwa

Patent status – Draft for provisional patent under development.

COMMITMENT OF THE AUTHORS

Paper I. Primary author, engaged in designing, carrying out the feedstock preparation and characterization, precipitation experiments, evaluation of the results and writing of the article. Co-authors reviewed the draft manuscript and made suggestions for improvement. Furthermore, the co-authors supervised the project and reinforced the technical aspects of the projects.

Paper II. Primary author, engaged in designing, carrying out the feedstock preparation and characterization, precipitation experiments, evaluation of the results and writing of the article. Co-authors reviewed the draft manuscript and made suggestions for improvement. Furthermore, the co-authors supervised the project and reinforced the technical aspects of the projects.

ABSTRACT

The contamination of the environment with wastewaters emanating from different operations and industrial activities has been an issue of prime concern to national and international research communities. Grossly, acid mine drainage (AMD) and municipal wastewater (MWW) are the most common waste streams that pose major environmental threats to surface and ground waters if left untreated. Specifically, trivalent (e.g., Fe^{3+} and Al^{3+}) and divalent (e.g., Mg^{2+}, Ca^{2+}, and Mn^{2+}) ions including rare earth metals contained in acid mine drainage (AMD) have strong affinity to phosphate contained in municipal wastewater (MWW). Therefore, their sequential treatment could be feasible, particularly when viewed under reuse, recycle, and resource recovery paradigm in wastewater management. Due to stringent environmental regulation, contaminants embodied in AMD and MWW exceed the prescribed limits for different defined uses hence they need to be managed prior discharge into the environment. In this study, the recovery of phosphate as calcium phosphate from municipal wastewater using hydrated lime was explored. The generated sludge, known as calcium phosphate, was used for the removal of heavy metals from acidic effluents. In light of subsequent stages, it is crystally clear that this study is stratified into two-phases, of which, phase one is the synthesis if calcium phosphate from MWW using lime, and phase two is the employment of calcium phosphate for the removal of metals from acidic effluents. To fulfil the goals of this study, the one factor-at-a-time (OFAAT) parameters were explored, and they include the effect of contact time, feedstock dosage, concentration and pH. The resultant sludge was ascertained using different state of art analytical techniques and equipment such as the X-ray diffraction (XRD), Focused ion beam (FIB) and high-resolution (HR) field emission scanning electron microscopy (FE-SEM), coupled with Electron Dispersion Spectroscopy (EDS) capabilities. Thenceforth, the PH REdox EQuilibrium (PHREEQC) (in C language) was used to substantiate the experimental results. The aqueous samples were characterised using Atomic Absorption Spectrometer (AAS) and anions were ascertained using Ion chromatography (IC). All experiments were done in triplicates and the results were reported as mean values. Findings from this study revealed the following: (a) In the first part of the study, MWW was reacted with calcium hydroxide to synthesize calcium phosphate. Approximately 99% and 30% removal efficacy for phosphate and nitrate, respectively, were observed from municipal wastewater using hydrated lime. The optimum conditions were observed to be solid: liquid ratio of 0.06 g: 100 mL and contact time of 60 min, pH of 10. An increase in feedstock dosage resulted in pH increase, this could be attributed to the neutralisation process followed by nucleation and precipitation of phosphate as calcium phosphate ($Ca_3(PO_4)_2$), hence decreasing phosphate concentration in the product water. The sludge obtained from this phase of the project was used for the subsequent stage which is the removal of heavy metals from acidic effluents.

(b) In the second part of this study, calcium phosphate was reacted with simulated and real acidic effluents rich in heavy metals for their attenuation. The interaction of AMD with calcium phosphate led to an increase in pH and a significant reduction in concentrations of metal species. The optimum conditions were observed to be 60 min of mixing, and 1.0 g feedstock dosage and pH 9.0. The removal of metals was observed to be dependent on pH. The metals removal efficiency obeyed the sequence: Fe (99%) > Mn (95%) > Al (80%). The pH of reacted AMD was (≥ 10). The removal of metals from aqueous solution was independent of chemical species concentration. The PHREEQC geochemical model also confirm that the species existed as divalent, trivalent and oxyanions in aqueous solutions. Furthermore, metals were predicted to precipitate as metal hydroxides. Specifically, the geochemical model explicitly showed that Al was removed as $Al(OH)_3$, Fe as $Fe(OH)_3$. Al and Fe precipitated as iron (oxy)-hydroxides and aluminium (oxy)-hydroxides. Mn precipitated as rhodochrosite and manganite. This would explain the reduction of metal species in product water. The XRD confirmed the formation of new mineral phases although most of it were amorphous in nature hence they could not be detected under the XRD. Thenceforth, phosphate was removed to below the SANS 241-2: 2015 specifications, WHO standards, EPA guidelines and DWS water quality guidelines. In conclusion, calcium phosphate was successfully synthesized from MWW using hydrated lime. This denotes that Ca in hydrated lime scavenged the phosphate in MWW to form calcium phosphate. Furthermore, the synthesized mineral phase proved to have strong neutralisation capacity. Calcium phosphate has neutralised AMD and attenuated high levels of metal species from acidic mine effluents. This study verified that the concept of circular economy and waste beneficiation via the recovery of valuable minerals that could be valorised for secondary application such as metals removal is feasible. This will go a long way in minimizing ecological footprints associated with acid mine drainage and municipal wastewater discharge.

Keywords: Acid mine drainage, municipal wastewater, pollution, calcium phosphate, metals, batch experiments; precipitation, geochemical modelling.

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DEDICATION

To my mother, thank you for being so humble and patient. Your support brought me this far and I say thank you once again. I also want to thank my wife for always encouraging me to work hard to reach this far.

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LIST OF ABBREVIATION AND ACCRONYMS

AMD	Acid mine drainage
BET	Brunauer–Emmett–Teller
DW	Domestic water
DWAF	Department of Water Affair Standard
EC	Electrical conductivity
EDS	Energy-dispersive spectroscopy
EPA	Environmental Protection Agency
FTIR	Fourier-transform infrared spectroscopy
GFAAS	Graphite furnace atomic absorption spectroscopy
HR	High Resolution
ICP-OES	Inductively coupled plasma atomic emission spectroscopy
MAP	Magnesium, ammonium, and phosphate
MWW	Municipal wastewater
MWWTP	Municipal wastewater treatment plant
NEMA	National Environmental Management Act
NIST	National Institute Standards and Technology
SANS	South African National Standard
SEM	Scanning electron microscopy
TDS	Total dissolved solids
WHO	World Health Organisation
XRD	X-ray powder diffraction
XRF	X-ray fluorescence

NB: Elements could be found on the periodic table.

CHAPTER ONE

INTRODUCTION

This chapter gives the background to the study with specific focus on the objectives of the study, problem statement, motivation, and hypothesis. It concludes by giving the dissertation outline or structure of the dissertation (First to last chapter).

1.1 Background information

Ecological contamination with variety of wastewater streams emanating from anthropogenic and geogenic activities has been a topical issue of prime concern to national, regional and international scientific communities. This is crystally compounded by the magnitude of ecological impacts posed by these wastewater streams. As such, custodians of the receiving environment have developed stringent regulatory frameworks to ensure maximum protection of the receiving environment and curtail potential impacts. Specifically, municipal wastewater (MWW) and acid mine drainage (AMD) are commonly occurring waste streams in the environment and their treatment is of great concern to preserve the quality of water resource (Makhathini et al., 2020). AMD is an acidic and metalliferous drainage which is generated from myriads of mining and industrial operations (Idaszkin et al., 2017; Jones and Cetin, 2017). This effluent stream is generated from the oxidation of sulphide bearing minerals such as pyrite (FeS_2) and other reactive sulphide-bearing minerals when exposed to air and water releasing acid, sulphate and metal ions into the environment.

Acidification of the water typically increases the solubility, mobility and bio-availability of metals, raising the concentration of these to unacceptable and often toxic levels. Physico-chemically, AMD comprise a yellowish to reddish colour, primarily due high concentration of Fe which turns red post oxidation. The deposition of Fe as iron hydroxide lead to the smoothening of the floor. Chemically, AMD constitute Fe, Al, Mn and sulphate as major elements, Mg and Ca as intermediate, and As, Cr, Zn, Pb, Cu, Co, Mo as trace elements. The embodied chemical species have been reported to pose numerous toxicological effects to living organisms and afield (Azimi et al., 2017; Yadav et al., 2019). Depending in the host geology and geological strata, radionuclides and rare earth metals can be prevalent in AMD and deposits thereof. According to Masindi et al. (2019), the levels of contaminants in AMD could be Al (200 mg L^{-1}), Fe (2000 mg L^{-1}), Mn (100 mg L^{-1}), and sulphate (6000 mg L^{-1}). These elements are way above the prescribed limits for discharge and need to be removed prior the discharge of these effluents to different receiving environments. Various passive, active, and hybrid technologies have been employed for the treatment of acid mine drainage (AMD). Passive treatment process rely on natural energy such as gravity and self-purification whereby a neutralising agent or plants with affinity with certain contaminants are used (Vasquez et al., 2016). Active treatment process rely on the use of neutralising agents (Skousen et al., 2019), filtration (Qin et al., 2019), adsorption (Lee et al., 2015) and desalination (Lopez et al., 2018). Of which, their hybrid generation is the combination of those two approaches in whichever algorithm. The commonly used neutralisation agents include lime (Balladares et al., 2018; Wang et al., 2019; Liu et al., 2015), soda ash (Masindi et al., 2017; Gorakhki and Bareither, 2015), and magnesite (Ngulube et al., 2018; Sadik et al., 2016), amongst others. The use of alkaline agents for AMD treatment has been very popular and alternative sources of neutralising agents should be considered to avoid their potential depletion and foster their sustainability.

According to literature, real municipal wastewater comprise elevated levels of phosphate and ammonia (Mavhungu et al., 2020) in addition to microbiological fractions (Ebrahim et al., 2018) and organic substances (Assress et al., 2019). These elements have been posing devastating effects to different receiving environments and compartments (Mavhungu et al., 2019). They enrich the waterbodies with nutrients hence fostering the rapid growth of aquatic plants (Masindi et al. 2021). A vicious cycle ensue when these plants dies since they consume the water dissolved oxygen during aerobic decomposition hence devoiding the aquatic ecosystem of life (Peña-Guzmán et al., 2019). The United Nation has a firm advocacy towards circular economy and wastewater valorisation (Campanari et al., 2019). This could potentially be explored in this context since phosphate enriched in municipal wastewater has strong affinity to Al and Fe included in acid mine drainage (AMD). Latest studies have been exploring the recovery of phosphate and ammonia in real municipal wastewater for the synthesis of struvite and calcium phosphate (Mavhungu et al., 2020) but their secondary applications have been merely explored.

In light of the above, these two wastewater streams [acid mine drainage (AMD) and real municipal wastewater (RMWW)] could potentially be benefited specifically considering them under the concept of circular economy, wastewater beneficiation and valorisation (Muhmood et al., 2019). Stringent environmental regulations require these wastewater streams to be treated prior discharge to different environments (Gebreeyessus et al., 2019). Conventionally, lime is used in the removal of lime as calcium phosphate and it is mainly disposed into the landfill (Monballiu et al., 2020). Recent innovation has been focusing on the valorisation of calcium phosphate, Masindi et al. (2021) explored the use of calcium phosphate for the production of phosphoric acid. However, to the best of our knowledge, the application for neutralisation of acidic and metalliferous wastewater has never been explored. This study intends to developed a closed-loop and synergistic effect towards the management of AMD and MWW. This will go a long way in conserving virgin and pristine materials through the use of recovered valuable minerals.

1.2 Problem statement

The release of effluents rich in toxic and hazardous elements has been an issue of prime concern to different ecological systems and end-users (Hembrom et al., 2020). Specifically, AMD comprise heavy metals, oxyanions, metalloids, rare earth metals and radionuclides such as Al, Fe, Mn, Zn, Cu, Pb, Ni, As, Cr, Mo and U, amongst others. According to toxicological and epidemiological studies, chemical embodied in AMD could lead to numerous disorders in living organisms. They can contribute to a number of eco-toxicological effects can be seen and they include skin irritation to several cancers, kidney, gastric and liver damage, pulmonary congestion, oedema, and other impairments to living organisms (Oberholster et al., 2021; Castaño-Sánchez et al., 2020). On the other hand, municipal wastewater comprise nutrients, microbial components, and organic matter amongst suspended solids (Roychand et al., 2020; Yu et al., 2020; Sorokina, et al., 2020). Of prime concern, is the discharge of effluents rich in nitrate and phosphate into the receiving environment (Wan et al., 2020). This enriches the receiving ecosystem with nutrients hence accelerating the growth of aquatic plant (Banu et al., 2020; Dong et al., 2020; He et al., 2020). When these plants dies, they deplete the water dissolved oxygen due to aerobic decomposition leaving the water devoid of oxygen (Wu et al., 2019). This will reduce the aesthetic value of the area and kills aquatic organisms (Bhagowati and Ahamad, 2019; Karpowicz et al., 2020; Longley et al., 2019). Ingestion of high level of nitrite could lead to blue baby syndrome and this affects the haemoglobin which is the carrier of oxygen to the body systems (Pelaz et al., 2018; Ward et al., 2018; Wang et al., 2018). Different water quality guidelines, specifications, and standards require these compounds to be removed from final water before water could be discharged into the environment (Edition, 2011; SANS 241 – 1, 2015). In light of their toxicological effects, the wastewater streams need to be managed prior discharge into the environment. This study was therefore developed with the aim of recovering phosphate from real municipal wastewater using hydrated lime and explore its potential application in the removal of metals from acidic effluents from a mining house or any industrial application such as metallurgical process. This will go a long way in curtailing ecological footprints and catastrophes associated with municipal wastewater and acid mine drainage (AMD). This will also foster the concept of circular economy by demonstrating the feasibility of recovering valuable minerals from wastewater and employ it for the treatment of another wastewater in a circular economy fashion.

1.3 Objectives

1.3.1 Main objective

The overall aim of this study is recover phosphate from real municipal wastewater and explore its potential application in the removal of metals from acidic and metalliferous mine effluents.

1.3.2 Specific objectives

To fulfil the overarching goal of this novel study, the following specific objectives will be pursued:

- Investigation of the physico-chemical properties of municipal effluents and acid mine drainage (AMD) using different analytical techniques
- Determination of the chemical and the mineralogical properties of the feed and product minerals during the treatment process
- Optimisation of the conditions that are suitable for the recovery of phosphate from municipal effluents using hydrated lime as the feedstock
- Optimisation of the conditions that are suitable for the treatment of acidic and metalliferous mine effluent using the synthesized product mineral (calcium phosphate).
- Employing the PH REdox EQuilibrium (in C language) (PHREEQC) geochemical model to substantiate mechanisms that governs the removal of pollutants from aqueous solutions
- Comparing the quality of product water with different water quality guidelines, specifications, and standards

1.4 Research questions

In order to address the main and specific objectives of this project, specific questions were formulated. These led to tasks that had to be accomplished to achieve the objectives of this project. The research questions were as follows:

- What are the physico-chemical properties of municipal effluents and acid mine drainage (AMD) from Mpumalanga coal mine
- What are the physicochemical and mineralogical properties of calcium hydroxide and calcium phosphate?
- What are the optimum conditions that are suitable for the synthesis of calcium phosphate from municipal effluents using hydrated lime as the feedstock?
- What are the optimum conditions that are suitable for the treatment of acidic and metalliferous mine effluent using the synthesized calcium phosphate as feedstock?
- What is the chemistry of processed water and the resultant solid residues after interacting municipal wastewater with the calcium hydroxide?
- What is the chemistry of the processed water and the resultant solid residues after interacting AMD with calcium phosphate?
- How does the quality of treated water compare with the South African water quality guidelines?

1.5 The dissertation outline

This dissertation is divided into six chapters, each explaining different aspects of the investigation in relation to the identified objectives and purpose of the study. A summary of each chapter is given below.

Chapter one: Introduction

This chapter gives a brief background of the areas of study and its principal focus. It also discuss the problem to be investigated, objectives that will be used to address the identified problem of the study, and ultimately the structure of the dissertation.

Chapter two: Literature review

This chapter will give an in-depth review on the sources of pollution (acid mine drainage and municipal wastewater), their ecological impacts in relation to toxicity, technologies that have been used for their removal, geochemical models for their attenuation and a summary of the literature survey.

Chapter three: General materials and methods

This chapter will give detailed information on the materials and methods that were used to achieve the outlined objectives of this study. Quality control measures will also be emphasized in this section.

Chapter four: Recovery of phosphate using hydrated lime

This chapter pointed out the optimum conditions that were used for treatment of MWWTPs using calcium hydroxide. The analytes of interest were NO_3^- and PO_4^{3-}. The chemistry of the product residues and the fate of chemical species in MWW after the treatment process are explained. Mechanisms of the precipitation process occurred were also reported in this section. This chapter will explicitly discuss routes which were used to optimize the removal of phosphate from wastewater using hydrated lime. The state-of-art and advanced analytical techniques such as HR-SEM coupled with EDS, FTIR, XRF, XRD, and PHREEQC geochemical model which were used to determine the composition of the Feed and product materials will also be unpacked.

Chapter five: Removal of metals from acidic effluents using the synthesized calcium phosphate

This chapter will meticulously elucidate routes which were used to optimize the removal of metals from acidic effluents using the synthesized calcium phosphate. The state-of-art and advanced analytical techniques such as HR-SEM coupled with EDS, FTIR, XRF, XRD, and PHREEQC geochemical model which were used to determine the composition of the Feed and product materials will also be unpacked.

Chapter six: General conclusion and recommendation

This chapter will infer an overarching conclusion towards the identified objectives of this study and their success. It will also enumerate research gaps and potential research avenues that could possibly be investigated in relation to the findings of this study.

REFERENCES

REFERENCES

Assress, H.A., Nyoni, H., Mamba, B.B. and Msagati, T.A., 2019. Target quantification of azole antifungals and retrospective screening of other emerging pollutants in wastewater effluent using UHPLC–QTOF-MS. Environmental Pollution, 253, pp.655-666.

Azimi, A., Azari, A., Rezakazemi, M. and Ansarpour, M., 2017. Removal of heavy metals from industrial wastewaters: a review. Chemical and Biological Engineering Reviews, 4(1), pp.37-59.

Balladares, E., Jerez, O., Parada, F., Baltierra, L., Hernández, C., Araneda, E. and Parra, V., 2018. Neutralization and co-precipitation of heavy metals by lime addition to effluent from acid plant in a copper smelter. Minerals Engineering, 122, pp.122-129.

Banu, H.A.T., Karthikeyan, P., Vigneshwaran, S. and Meenakshi, S., 2020. Adsorptive performance of lanthanum encapsulated biopolymer chitosan-kaolin clay hybrid composite for the recovery of nitrate and phosphate from water. International journal of biological macromolecules, 154, pp.188-197.

Bhagowati, B. and Ahamad, K.U., 2019. A review on lake Eutrophication dynamics and recent developments in lake modeling. Ecohydrology & Hydrobiology, 19(1), pp.155-166.

Campanari, S., Augelletti, F., Rossetti, S., Sciubba, F., Villano, M. and Majone, M., 2017. Enhancing a multi-stage process for olive oil mill wastewater valorization towards polyhydroxyalkanoates and biogas production. Chemical Engineering Journal, 317, pp.280-289.

Castaño-Sánchez, A., Hose, G.C. and Reboleira, A.S.P., 2020. Ecotoxicological effects of anthropogenic stressors in subterranean organisms: A review. Chemosphere, 244, p.125422.

Dong, H., Shepsko, C.S., German, M. and SenGupta, A.K., 2020. Hybrid nitrate selective resin (NSR-NanoZr) for simultaneous selective removal of nitrate and phosphate (or fluoride) from impaired water sources. Journal of Environmental Chemical Engineering, 8(4), p.103846.

Ebrahimi, A., Kebria, D.Y. and Najafpour, G.D., 2018. Co-treatment of septage and municipal wastewater in a quadripartite microbial desalination cell. Chemical Engineering Journal, 354, pp.1092-1099.

Edition, F., 2011. Guidelines for drinking-water quality. WHO chronicle, 38(4), pp.104-108.

Gebreeyessus, G.D., Mekonnen, A. and Alemayehu, E., 2019. A review on progresses and performances in distillery stillage management. Journal of Cleaner Production, 232, pp.295-307.

Gorakhki, M.H. and Bareither, C.A., 2015. Salinity effects on sedimentation behavior of kaolin, bentonite, and soda ash mine tailings. Applied Clay Science, 114, pp.593-602.

He, H., Huang, Y., Yan, M., Xie, Y. and Li, Y., 2020. Synergistic effect of electrostatic adsorption and ion exchange for efficient removal of nitrate. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 584, pp.123973.

Hembrom, S., Singh, B., Gupta, S.K. and Nema, A.K., 2020. A comprehensive evaluation of heavy metal contamination in foodstuff and associated human health risk: a global perspective. In Contemporary environmental issues and challenges in era of climate change (pp. 33-63). Springer, Singapore.

Idaszkin, Y.L., Carol, E. and Del Pilar, A.M., 2017. Mechanism of removal and retention of heavy metals from the acid mine drainage to coastal wetland in the Patagonian marsh. Chemosphere, 183, pp.361-370.

Jones, S.N. and Cetin, B., 2017. Evaluation of waste materials for acid mine drainage remediation. Fuel, 188, pp.294-309.

Karpowicz, M., Zieliński, P., Grabowska, M., Ejsmont-Karabin, J., Kozłowska, J. and Feniova, I., 2020. Effect of eutrophication and humification on nutrient cycles and transfer efficiency of matter in freshwater food webs. Hydrobiologia, 847(11), pp.2521-2540.

Lee, H., Kim, D., Kim, J., Ji, M.K., Han, Y.S., Park, Y.T., Yun, H.S. and Choi, J., 2015. As (III) and As (V) removal from the aqueous phase via adsorption onto acid mine drainage sludge (AMDS) alginate beads and goethite alginate beads. Journal of Hazardous Materials, 292, pp.146-154.

Liu, F., Zhou, J., Zhou, L., Zhang, S., Liu, L. and Wang, M., 2015. Effect of neutralized solid waste generated in lime neutralization on the ferrous ion bio-oxidation process during acid mine drainage treatment. Journal of hazardous materials, 299, pp.404-411.

Longley, K.R., Huang, W., Clark, C. and Johnson, E., 2019. Effects of nutrient load from St. Jones River on water quality and eutrophication in Lake George, Florida. Limnologica, 77, p.125687.

Lopez, J., Reig, M., Gibert, O., Valderrama, C. and Cortina, J.L., 2018. Evaluation of NF membranes as treatment technology of acid mine drainage: metals and sulfate removal. Desalination, 440, pp.122-134.

Makhathini, T.P., Mulopo, J. and Bakare, B.F., 2020. Possibilities for acid mine drainage co-treatment with other waste streams: A review. Mine Water and the Environment, 39(1), pp.13-26.

Masindi, V., Osman, M.S. and Abu-Mahfouz, A.M., 2017. Integrated treatment of acid mine drainage using BOF slag, lime/soda ash and reverse osmosis (RO): Implication for the production of drinking water. Desalination, 424, pp.45-52.

Monballiu, A., Ghyselbrecht, K., Pinoy, L. and Meesschaert, B., 2020. Phosphorus reclamation by end-of-pipe recovery as calcium phosphate from effluent of wastewater treatment plants of agroindustry. Journal of Environmental Chemical Engineering, 8(5), p.104280.

Muhmood, A., Lu, J., Dong, R. and Wu, S., 2019. Formation of struvite from agricultural wastewaters and its reuse on farmlands: Status and hindrances to closing the nutrient loop. Journal of environmental management, 230, pp.1-13.

Ngulube, T., Gumbo, J.R., Masindi, V. and Maity, A., 2018. Calcined magnesite as an adsorbent for cationic and anionic dyes: characterization, adsorption parameters, isotherms and kinetics study. Heliyon, 4(10), p.e00838.

Oberholster, P.F., Goldin, J., Xu, Y., Kanyerere, T., Oberholster, P.J. and Botha, A.M., 2021. Assessing the adverse effects of a mixture of AMD and sewage effluent on a sub-tropical dam situated in a nature conservation area using a modified pollution index. International Journal of Environmental Research, 15(2), pp.321-333.

Park, I., Tabelin, C.B., Seno, K., Jeon, S., Ito, M. and Hiroyoshi, N., 2018. Simultaneous suppression of acid mine drainage formation and arsenic release by carrier-microencapsulation using aluminum-catecholate complexes. Chemosphere, 205, pp.414-425.

Pelaz, L., Gómez, A., Letona, A., Garralón, G. and Fdz-Polanco, M., 2018. Nitrogen removal in domestic wastewater. Effect of nitrate recycling and COD/N ratio. Chemosphere, 212, pp.8-14.

Peña-Guzmán, C., Ulloa-Sánchez, S., Mora, K., Helena-Bustos, R., Lopez-Barrera, E., Alvarez, J. and Rodriguez-Pinzón, M., 2019. Emerging pollutants in the urban water cycle in Latin America: A review of the current literature. Journal of Environmental Management, 237, pp.408-423.

Qin, J., Cui, X., Yan, H., Lu, W. and Lin, C., 2019. Active treatment of acidic mine water to minimize environmental impacts in a densely populated downstream area. Journal of Cleaner Production, 210, pp.309-316.

Roychand, R., Pramanik, B.K., Zhang, G. and Setunge, S., 2020. Recycling steel slag from municipal wastewater treatment plants into concrete applications–A step towards circular economy. Resources, Conservation and Recycling, 152, p.104533.

Sadik, C., Moudden, O., El Bouari, A. and El Amrani, I.E., 2016. Review on the elaboration and characterization of ceramics refractories based on magnesite and dolomite. Journal of Asian Ceramic Societies, 4(3), pp.219-233.

Skousen, J.G., Ziemkiewicz, P.F. and McDonald, L.M., 2019. Acid mine drainage formation, control and treatment: Approaches and strategies. The Extractive Industries and Society, 6(1), pp.241-249.

Sorokina, K.N., Samoylova, Y.V. and Parmon, V.N., 2020. Comparative analysis of microalgae metabolism on BBM and municipal wastewater during salt induced lipid accumulation. Bioresource Technology Reports, 11, p.100548.

Vasquez, Y., Escobar, M.C., Neculita, C.M., Arbeli, Z. and Roldan, F., 2016. Selection of reactive mixture for biochemical passive treatment of acid mine drainage. Environmental Earth Sciences, 75(7), pp.576.

Wan, J., Wu, B. and Lo, I.M., 2020. Development of Fe^0/Fe_3O_4 composites with tunable properties facilitated by Fe^{2+} for phosphate removal from river water. Chemical Engineering Journal, 388, pp.124242.

Wan, Z., Zhang, Y., Lu, S., Zhang, X., Liu, X. and Yang, Y., 2020. Effect of packing substrates on the purification of municipal wastewater treatment plant effluent. Environmental Science and Pollution Research, 27(13), pp.15259-15266.

Wang, H., Gu, H., Lan, S., Wang, M. and Chi, B., 2018. Human health risk assessment and sources analysis of nitrate in shallow groundwater of the Liujiang basin, China. Human and Ecological Risk Assessment: An International Journal, 24(6), pp.1515-1531.

Wang, X., Jiang, H., Fang, D., Liang, J. and Zhou, L., 2019. A novel approach to rapidly purify acid mine drainage through chemically forming schwertmannite followed by lime neutralization. Water research, 151, pp.515-522.

Ward, M.H., Jones, R.R., Brender, J.D., De Kok, T.M., Weyer, P.J., Nolan, B.T., Villanueva, C.M. and Van Breda, S.G., 2018. Drinking water nitrate and human health: an updated review. International journal of environmental research and public health, 15(7), p.1557.

Wu, K., Li, Y., Liu, T., Huang, Q., Yang, S., Wang, W. and Jin, P., 2019. The simultaneous adsorption of nitrate and phosphate by an organic-modified aluminum-manganese bimetal oxide: Adsorption properties and mechanisms. Applied Surface Science, 478, pp.539-551.

Yadav, V.B., Gadi, R. and Kalra, S., 2019. Clay based nanocomposites for removal of heavy metals from water: a review. Journal of Environmental Management, 232, pp.803-817.

Yu, M., Liu, S., Li, G., Zhang, H., Xi, B., Tian, Z., Zhang, Y. and He, X., 2020. Municipal wastewater effluent influences dissolved organic matter quality and microbial community composition in an urbanized stream. Science of The Total Environment, 705, p.135952.

CHAPTER TWO

LITERATURE REVIEW

This chapter will give the general review on the sources of pollution (acid mine drainage (AMD) and municipal wastewater), their ecological impacts in relation to toxicity, technologies that have been used for their removal, geochemical model for their attenuation, and a summary of the literature survey.

2.1 Water pollution

South Africa is a water scarce country and the presence of MWW and AMD effluents in water streams threatens the safety of this resource. Water is polluted if some substances or effluents are present in water to such a way that the water cannot be utilized for the intended purpose. Water contaminated by MWW and AMD poses detrimental threat to living organism, especially when the water is used as a source of drinking and for domestic purposes. For example, polluted waters are potent agents of diseases such as cholera, typhoid fever, and tuberculosis in the life of a human (Owa, 2014). Water pollution by mining operations and municipal wastewater effluents is of a major concern in South Africa. Spills or leakage of effluents from mining and MWWTPs result in degradation of water quality due to toxic chemicals, nutrients and heavy metals which are discharged from these operation (Jhariya et al., 2016). Controlling and reducing water pollution is a significant concern to our society.

2.2 Municipal wastewater treatment plants as a source of water pollution

The human population in South Africa has been increasing at a high rate since the development of science and technology. This indicates that waste which are being released are in large amount that may surpass the capacity that the municipal wastewater treatments plants can handle primarily due to an increase on the demands for food. However, the output of effluents from MWWTPs and the removal of nutrients such as phosphate, nitrate and ammonia becomes compromised. Phosphate and nitrate are among the most problematic pollutants in MWWTPs and are highly affecting the surface and the groundwater globally.

Phosphorus in MWW is present mainly in the form of orthophosphate, polyphosphates, and organic phosphorus (Ebbers, et al., 2015; Nejad, et al., 2013; Zamani et al., 2012). Polyphosphates and organic phosphorus are converted to orthophosphate by hydrolysis/or microbial mobilisation (Weiner, 2008). Orthophosphate is a soluble inorganic phosphate, and remains the only form of phosphorus, which is directly assimilated by most plants, including algae (Hussain et al., 2011; Paleka and Deliyanni, 2009; Xu et al., 2010). The collective form of the element in water usually alters continually due to the process of decomposition and synthesis between organically bound forms and oxidized inorganic forms. Phosphate can also be considered as a pollutant when discharged into water bodies if its concentration is higher than the permissible limit in water (Duan et al., 2020).

Nitrate (NO_3^-) is the major form of nitrogen that originate in natural waters and remains one of the most frequent contaminants in surface water (Jagessar and Sooknundun, 2011). Ammonia, ammonium, and ammonia hydroxides are another form of nitrogen which are present in natural waters. Nitrate is a stable and highly soluble ion with low potential for co-precipitation or adsorption (Tyagi et al., 2018). These properties make it difficult to be removed from the water. Nitrate in water sources is related to nitrogen fertilizer and domestic wastewater. However, the pollution of water resources by nitrate has become of great concern worldwide in recent years (Ahmad et al., 2016).

2.3 Sources of nutrients contamination in MWWTPs

Phosphate and nitrate are a major nutrient contaminant and contribute significantly to water pollution. Phosphate and nitrate commonly originate from human activities, animal wastes, food-processing effluents, commercial fertilisers, agricultural land runoffs and household detergents (Weiner, 2008; Shrimali and Singh, 2001; Alshameri et al., 2014; Zamparas and Zacharias, 2014). Other sources include leached or weathered soils from igneous rocks and mining. Phosphate rocks and ores are the main sources for phosphorus fertilizer production. The inorganic phosphorus, which is the soluble part, is available for plants to be absorbed. By the plant uptake, phosphorus ends in the food chain and is returned to the environment via animal manure and human excreta (Ronteltap, 2009). Industries like plastic, metal treatment, textile, plywood, household cleaning and pharmaceutical industrial effluents further increase the level of nitrate contamination in the groundwater (Singh et al., 2006; Flyammer, 1995). The underlying factors that influence nitrate increase in soil and water are industrial, stock breeding and agricultural activities (Mikhak et al., 2017).

2.4 Environmental implication of MWW effluents

2.4.1 Impacts of MWW effluents on agriculture

Phosphorus and nitrate are essential nutrients to sustain life. Nitrate (NO_3^-) is found naturally in the environment and is an important plant nutrient. However, phosphorus plays a key role in energy metabolism, structural strength, genetic components, and photosynthesis processes (Cong et al., 2020; Moriyama et al., 2020). In an agricultural point of view, the optimum range of phosphorus concentration is vital to sustaining soil fertility and food crops production (Pierzynski et al., 2005). Therefore, lack of phosphorus along with its low solubility causes growth limit for plants. Phosphorus is one of the most important components of biochemical processes in a living organism, this is since phosphorus occurs in enzymes which catalyse chemical reactions of biosynthesis and energy transfer in plants. Phosphorus is also a component of nucleic acid, phytin, and phospholipids of plant cells (Karunanithi et al., 2015). Phosphorus is also a very important microelement for plant growth including algal growth in water (Abowei et al., 2010). Phosphates are absorbed by aquatic plants and algae and it constitutes an integral part of their body component (Zamparas and Zacharias, 2014).

2.4.2 Impact of MWW effluents on human health

Phosphate is an essential nutrient for plants to live and is the limiting factor for plant growth in many freshwater ecosystems. However the health problem associated with excessive use of phosphate is not known. Like phosphate, nitrate (NO_3^-) is found naturally in the environment and is an important plant nutrient. However, nitrate exposure to human has several negative health effects in such as goitre, thyroid disorder, stomach cancer, cytogenetic defects, and birth defects (Ayyasamy et al., 2007; Song et al., 2012). Nitrate in drinking water is significantly associated with methemoglobinemia, which is also known as "blue-baby syndrome." Baby formula mixed with nitrate-contaminated water exposes infants to nitrate. Nitrates in drinking water can also affect certain adults and small children. Pregnant women can pass methaemoglobin on to developing fetuses and low birth weights have been attributed to high nitrates exposure in women (Chen, 1996; Shih et al., 1997)

2.4.3 Impact of MWW effluent on water

Environmental concerns associated with the discharge of nutrients such as phosphorus and nitrate mainly involve its impact on water bodies which results in eutrophication (Nodeh et al., 2017). Eutrophication is the process in which nutrient is enriched and the associated excessive plant growth in water bodies (Du et al., 2019). It is part of the natural ageing process of lakes and is increased by human impacts (Van Ginkel, 2011). Eutrophication limits the growth and diversity of aquatic biota, and under extreme conditions, can causes fish to die. In this phenomenon, high turbidity prevents the penetration of light into lower depths of water bodies which reduce the growth of submerged aquatic vegetation and benthic organisms. Phosphorus and nitrogen are the major causes of eutrophication in rivers and lakes (Pierzynski et al., 2005; Syers et al., 2011). Large amounts of phosphate in the aquatic environments may cause abnormal algae and aquatic plants growth which result in water quality reduction and depletion of dissolved oxygen in the water bodies with negative impacts on the aquatic organisms and the changes in taste, colour and loss of biodiversity (Barca et al., 2012). Therefore, the use of nutrients especially phosphorus in excessive amount should be considered as an important environmental concern that causes eutrophication and it needs to be reduced and to be controlled by means of severe measurements. As shown in Table 2.1, MWWTPs effluents are mostly dominated by PO_4^{3-}, NO_3^- and NH_4^+. The concentrations of these pollutants are far above the legal requirements.

Table 2. 1. Comparison of the physiochemical characteristic of wastewater from different studies and legal requirement in accordance to WHO

	Parameters						
Streams	pH	TDS (mg L^{-1})	TSS (mg L^{-1})	PO$_4^{3-}$ (mg L^{-1})	NO$_3^-$ (mg L^{-1})	NH$_4^+$ (mg L^{-1})	References
WWTP	5.6	740	-	7.4	20.5	-	Daneshvar et al., (2019)
PCWW♦	8.0	163	39	1.8	25	28.7	Hodges et al., (2017)
MWW	8.9	60	-	1.3	1.8	42.0	Mujtaba and Lee.,(2017)
Wastewater	7.2	52	-	9.3	10.5	26.5	Almomani et al., (2019)
Wastewater	6.8	180	-	0.9	11.3	7.8	Pham and Bui, (2020)
Wastewater	7.5	29.0	-	5.9	37.3	61.68	Rosli et al., (2020)
DW¤	7.3	171	-	11.73	4.87	50	Medhi and Thakur, (2018)
MWW	-	257	184	2.8	1.2	37.8	Foladori et al., (2018)
DW	-	446.3	-	7.42	16.6	56	Silambarasan et al., (2021)
Wastewater	6.7	4611	-	68	64	-	Kotowska et al., (2018)
DS☺	8	250	190	19	0.9	-	Sengar et al., (2018)
WHO	6.5– 9.0	≤ 450	≤60	≤5	≤4	≤20	WHO, 1999

♦PCWW-Petrochemical wastewater, ¤DW-Domestic wastewater, DS☺- Domestic sewage

2.5 Mining

Mining is the extraction of minerals and other geological materials of economic value from deposits on the earth. Mining industries plays a huge role in national economic development, and on the other hand, it undesirably impacts our environment in several ways. Since the the development of large-scale mines, mining industry has been increasing rapidly. The issue of mining disturbs large areas of land and water. The environmental problems associated with mining activities are natural land degradation, air and water pollution with heavy metals, organic and inorganic waste, negative impact on terrestrial and aquatic ecosystems, human health and socio-economic (Ugya et al., 2018). Mining of coals, gold and metals produces excess amount of solid and liquid wastes that are potentially hazardous to the environment and water bodies (Jamal et al., 2015).

2.5.1 Mining and water pollution

Water is essential to sustain life on Earth. A prerequisite of sustainable development to monitor uncontaminated water bodies such as streams, rivers, lakes, and oceans must be measured to ensure good quality water. Mining operations can affect the health of living organism through water.

2.6 Types of water pollution from mining operations

There are four main types of mining impacts on water quality including heavy metal contamination and leaching, processing chemicals pollution, erosion, and sedimentation as well as mine drainage. Variety of mine drainages have been studied in the literature. Mine water can be divided into three main categories based on their acid/base properties (Iakovleva and Sillanpää, 2013) such as acid mine drainage (AMD), neutral mine drainage (NMD) and saline mine drainage (SMD). The pH values of these drainages vary depending on the elements being mined and conditions at the mining sites (Rakotonimaro et al., 2017). AMD is regarded as the major problem associated with the mining industry due to its toxicity (Moodley et al., 2018).

2.6.1 Acid mine drainage

Working and closed mines are continuously discharging mine water onto the surface and groundwater bodies. These mining effluents are characterized of high concentration of heavy metals and acidity (Westholm et al., 2014; Park et al., 2019). AMD is the most significant environmental pollution problem which is associated with mining industries (Naidu et al., 2019). Specifically, AMD is generated from gold, coal, and copper mining amongst other mining activities and it is characterised by low pH content ($\leq 2 - 3.5$) and high levels of heavy metals, particularly Fe, Mn, Ni, Co, Zn and Cu (Foudhaili et al., 2019) which pose serious threats to humans, plants, and aquatic organisms (Mativenga and Marnewick, 2018; Zhang et al., 2019; Wu et al., 2020). According to Mulopo (2015), AMD is also characterised by high content of total dissolved solids (TDS), high sulphates and heavy metals. The degree of pollution by AMD to the environment is reliant on its composition and pH, which in turn may differ depending on the geology of the mine sites or sources (Kefeni et al., 2017).

2.6.2 Sources of acid mine drainage

The main source of AMD is the oxidation of sulphide mineral ores, which are firstly exposed to the environment through mining activities or natural weathering processes. AMD is mostly formed in mine workings, waste-rock dumps, and tailings storage facilities where metal sulphide minerals such as pyrite (FeS_2), pyrrhotite ($Fe_{(1-x)}S$), chalcopyrite ($CuFeS_2$) and marcasite (FeS_2) are exposed to oxygen, water and microorganisms during the mining of minerals (Tutu et al., 2008; Costello, 2003; Diz, 1997; Bigham and Cravotta, 2016; Nleya et al., 2016; Tomiyama et al., 2019; Rodríguez-Galán et al., 2019; Kebede et al., 2017). The minerals and mining industries produce two sources of AMD generation which are primary and secondary.

2.6.2.1 Primary sources include (Qiao et al., 2020):

- Mine rock dumps
- Tailings ponds
- Underground and open pit mine workings
- Underground pumped water
- Diffuse seeps from replaced overburden in rehabilitated areas
- Construction rock used in railway
- Haulage roadways and dams

2.6.2.2 Secondary sources are mainly (Liu et al., 2018):

- Mineral processing sludge pounds
- Rock chips
- Concentrated load-out

- Stockpiles
- concentrate spills along roads
- emergency ponds

2.6.3 Prevention of AMD generation

The prevention of AMD formation at sources is regarded as the preferred option to control AMD (Li et al., 2018). Generally, prevention is the reduction of factors that promotes the generation of AMD such as oxygen supply, water penetration, leaching, sulfide mineral disposal and bacteria (Win et al., 2020). AMD prevention comprises of several methods such as special handling, segregation, encapsulation, dry and water cover (Kefeni et al., 2017). Moreover, increasing the availability of minerals which neutralize acidity in AMD or increasing the insinuated water pH could also be considered as an alternative option (Kotsiopoulos and Harrison, 2017).

2.6.4 Formation and constituents of AMD

AMD is formed during the mining of mineral ores and waste materials with sulphide minerals such as pyrite when exposed to water and oxygen. Acid generation and metals dissolution are the primary problems associated with pollution from mining activities. It is also responsible for the generation of acid and metals dissolution in coal and hard rocks (Joseph, 2018; Park et al., 2019; Pak et al., 2016). Generally, pyrite is relatively stable under both acidic and alkaline conditions in the presence of oxidants such as oxygen (O_2) and ferric ion (Fe^{3+}) where it rapidly dissolved as indicated by equation (2.1) to (2.4).

$$2FeS_{2(s)} + 7O_{2(g)} + 2H_2O \xrightarrow{\text{bacteria}} 2Fe^{2+}_{(aq)} + 4H^{+}_{(aq)} + 4SO^{2-}_{4(aq)} \tag{2.1}$$

$$4Fe^{2+}_{(aq)} + O_{2(g)} + 4H^{+}_{(aq)} \rightarrow 4Fe^{3+}_{(aq)} + 2H_2O_l \tag{2.2}$$

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO^{2-}_{4(l)} + 16H^{+} \tag{2.3}$$

$$Fe^{3+}_{(aq)} + 3H_2O_l \rightarrow Fe(OH)_{3(s)} + 3H^{+}_{(aq)} \tag{2.4}$$

Equation (2.1) indicate that as pyrite gets exposed to oxygen and water, it then oxidized which result in the release of hydrogen ion (H^+), sulphate ions (SO_4^{2-}) and ferrous iron (Fe^{3+}). This reaction of oxidation takes place in a very slow rate in undisturbed rock and the acid generated during this course of reaction is buffered by water (Park et al., 2018). The exposed surface area of these sulphur-bearing rocks is increased by mining activities which allows excess generation of acid to be beyond the water's natural buffering capabilities (Masindi et al., 2018). Further oxidation of Fe^{2+} (ferrous iron) to Fe^{3+} (ferric iron) occurs in the presence of excess oxygen and atmospheric oxygen which is precipitated as either ferric hydroxide ($Fe(OH)_3$) (Eq. (2.3)) or consumed to dissolve more pyrite (Eq. (2.4)) depending on the pH of the system. These reactions from (2.1) to (2.4) briefly summarizes the formation of AMD from storm water and oxygen weathering pyrite (Johnson and Hallberg, 2005; Tabelin et al., 2017).

2.7 Environmental implication of AMD

The general impact of AMD relies on local environmental conditions and differs significantly depending on the geomorphology, climate, and post mining management of the affected surroundings (McCarthy, 2011; Swer and Singh, 2004). As mentioned earlier, AMD introduces sulphuric acid and toxic heavy metals into the environment (Minnaar, 2020; Dutta et al., 2020). These toxic heavy metals are non-biodegradable and may contaminate drinking water which is ingested by humans causing detrimental health problem (Rai et al., 2019; Ali et al., 2019). Water pollution, deterioration of the ecosystem, and degradation of agricultural lands are some of the visible environmental outcomes of AMD (Suh et al., 2017; Olías et al., 2017). This section gives a detailed discussion of the impacts of AMD components on plant, water, aquatic life, and animal life.

2.7.1 Impacts of AMD on agriculture

Mining activities can result in soil contamination over a large area (Alekseenko et al., 2018). Pollution of soils by AMD poses adverse effects for plant growth and crop development. Plants suffer oxidative stress upon exposure to heavy metals, leading to cellular damage and disturbance of cellular ionic homeostasis, disturbing the physiology and morphology of plants (Simate and Ndlovu, 2014). Most plants cannot tolerate low pH water because the high hydrogen content causes inactivation of enzymes, restricting respiration and root uptake of mineral salts and water (Bell et al., 2010). Agricultural activities which are close to the mining projects are usually affected. Erosion of exposed soils extracted mineral ores, tailings, and fine material in waste rock piles can result in substantial sediment loading to surface waters and drainage ways. In addition, spills and leaks of hazardous materials and the deposition of contaminated windblown dust can lead to soil degradation (Ugya et al., 2018). AMD can also be toxic to vegetation; however, toxicity depends on discharged volume, pH, total acidity, and concentration of dissolved chemical species (Qian et al., 2018). When rainwater fills the mines, it creates acid drainage causing contamination to the groundwater and local rivers. Consequently, the aquatic life is potentially at risk, the vegetation on the surroundings are being damaged, the soil is contaminated (Water, 2016). The pH is the most critical with respect to aquatic life (Abdel-Satar et al., 2017). Acid mine drainage (AMD) can also cause a reduction in diversity and a total number of macro-invertebrates and changes in community structure (Gitari et al., 2006). Low pH of mine discharge results in solubility of heavy metals in water and its high concentration causes toxicological effects on aquatic ecosystems (Rakotondrabe et al., 2018).

2.7.2 Impact of AMD on human health

AMD is a unique pollutant because acid generation and discharge continue to occur even after and when the mining process has closed or ceased. AMD pose a serious threat to the health of humankind and ecological systems because it contains trace elements such as Cu, Cd, Pb, Ni, As, and Zn which are not-biodegradable and thus tend to accumulate in living organisms causing various diseases and disorders (Moreno et al., 2001; Carlson et al., 2002; Tepanosyan et al., 2018). People may be exposed to AMD pollutants through indirect exposure by eating food crops that are irrigated with AMD contaminated water. Explicitly, exposure to toxic and hazardous metals, metalloids and oxyanions in AMD could lead to the following conditions, skin irritation to several cancers, kidney, gastric and liver damage, pulmonary congestion, oedema, and other impairments to living organisms (Machado et al., 2017). This is solely based on the eco-toxicological and epidemiological reports (Andjelkovic et al., 2019).

2.7.3 Impact of AMD on water quality

Water pollution is one of the major problems associated with mining operations. AMD has become a serious environmental concern for the long-term sustainability of the country’s fresh water supply (McCarthy and Humphries, 2013). AMD is responsible for depositing a large amount of acid to many streams throughout the coal producing regions. Mine water effluent that contains toxic chemicals or heavy metals can escape, or be discharged, to local water bodies causing contamination of surface and groundwater to the levels that can result in degradation of water quality (Wright et al., 2018). Most of waste/dumps which are generated from mining operation are radioactive, toxic, and carcinogens and their primary health effects occur when consumed in water (Fungaro et al., 2012). The problem of AMD is not restricted to the local area where mining operation is being practiced but may extend to distances if the affected water can get discharged into the main water stream (Rezaie and Anderson, 2020).

AMD impacts more frequently on the quality of ground water than that of surface water. Therefore, mining activities poses a serious risk/threat for people accessing surface and groundwater for drinking (Mativenga and Marnewick, 2018), as a result this could cause several diseases which is harmful to human health when used for drinking. Meticulously, the AMD introduce acidity in the receiving ecosystem hence altering the pH of a given ecosystem, thenceforth, toxic metals gets introduced hence increasing the concentration of metals in water (Skousen et al., 2019). The shift in the physico-chemical properties of the water will cause species to die or migrate hence reducing the biodiversity of given area (Moodley et al., 2018). Deposition of metals and their precipitation covers the floor of the river hence affecting benthic organisms (Kaur et al., 2018).

2.7.4 Impact of AMD on aquatic life

The ecological health effects of AMD are most clearly seen in aquatic environments, such as streams, lakes, and rivers where it can be harmful to fish and other species. Low pH of mine water can result in the solubility of heavy metals in water when discharged into water bodies. Acute exposure of high concentration of metals can kill organisms directly, while long term exposure to lower pH can cause mortality or other effects, such as stunted growth, lower reproduction rates, deformities, and lesions (Vyawahre, and Rai, 2016). Aquatic organisms, such as fish, accumulate heavy metals from AMD directly from contaminated water and indirectly via the food chain (Simate and Ndlovu, 2014). The toxicity and acidity of AMD contaminated water have been found to result in severe oxidative stress, which impairs the osmotic balance of fish by interfering with the uptake of salts through the gills (Chadwick, et al., 2013; Simate and Ndlovu, 2014). Acute exposure to the metals may result in death whilst chronic exposure may result in mortality or stunted growth, reduced growth, reduced reproduction, deformities, or lesions. The primary cause of death in acid water is the loss of sodium ions from the blood. Less availability of oxygen to the cells and tissue leads to anoxia and death as acid water increases the permeability of fish gills to water adversely affecting the gills function (Vyawahre and Rai, 2016).

2.8 Effect of high level of sulphate

Metal sulphides contribute greatly to the formation of AMD. Sulphides produce sulphates and consequently acidify the medium by converting to sulphuric acid. Oxidation of metal sulphides is the main sources for the deposition of the sulphates into waterways (Fernando et al., 2018). Generally, most of waters which are affected by AMD also contain some levels of the sulphate ion. The high sulphate ion content is a serious challenge which can even occur after AMD has been treated, particularly by neutralization using limestone. The presence of sulphates ion in water is considered not to be toxic in low concentration but can negatively affect the taste of water. However, the presence of sulphate ions in water at concentration higher than 600 mg L^{-1} results in a laxative effect. Sulphate produced from sulphide rocks at anaerobic condition have negative effects in the aquatic environment causing lack of oxygen resulting fish, plant and plankton deaths. Scaling of pipes and corrosion are also major problems in the industrial level due to high concentrations of sulphate (Luptáková et al., 2016). Table 2.2 list the maximum allowable limit of sulphate in water as per different regulatory organisation.

Table 2. 2. Recommended maximum sulphate levels

Regulatory body	Maximum sulphate level (mg L^{-1})
US EPA	≤ 250
WHO	≤ 500
EU guide limit	≤ 1000
DWAF	≤ 600
Australia	≤ 1000
SANS	≤ 25

(DWAF, 1993; WHO, 1996, US EPA, 1999)

2.9 Heavy metal from AMD

The rapid industrialization and intensive agricultural activities over the last few years have resulted in the deposition of various pollutants in the environment, mainly in soil and water, which has led to the accumulation of heavy metals (Edao, 2017). Heavy metals are natural occurring elements from the earth's crust, and some of them (e.g., Cu and Zn) are essential for normal metabolic functions in plants, animals, and humans (Sun et al., 2018). Heavy metals, or potentially toxic elements, form a specific group of pollutants which are then discharged into the environment because of industrial activities, such as the mining. The operational processes of the mining industry involve a series of steps during extraction and purification processes which result in the release of metals into waterways through AMD (Monge-Amaya et al., 2015). Contamination of soil by heavy metal is one of the most environmental problems throughout the world. The toxicity of heavy metal towards biological systems such as humans, animals, microorganisms, and plants has been reported by several researchers (Wuana et al., 2010).

2.9.1 Impact of dissolve heavy metals from AMD

AMD comprises of various number of dissolved metals as indicated earlier, which are toxic by nature. The environmental effects of these metals will be discussed in this section.

2.9.1.1 In soil and plant

Pollution of soil by heavy metal due to anthropogenic activities, such as mining activities, industrial production, traffic, wastewater irrigation, sludge or municipal compost, pesticides, and fertilizers, has become a problematic to the environment in many developing countries (Chaoua et al., 2019). This is ascribed by the fact that, these metals do not degrade biologically as a result their total concentrations last for a long time after being released to the environment resulting soil degradation (Sun et al., 2018). Accumulation of heavy metals from AMD in soil can reduce its quality, reduce crop production and the quality of agricultural products (Ibrahim et al., 2015). Soil is known as the major sink for anthropogenic heavy metal discharge through various pathways. Generally, plants show signs of stress when they accumulate excess amount of heavy metals. Therefore, stressed plants resemble a sign of metal contamination. However, some plant species can be able to accumulate large amounts of heavy metals without showing any stress which can pose a potential risk to animals and humans (Edao, 2017). All heavy metals at high concentrations can show strong toxic effects and are considered as environmental pollutants. Excess amount of heavy metals in soils can cause the disruption of natural terrestrial ecosystem (Ezeabara et al., 2014).

2.9.1.2 In human

Heavy metals pose a serious risk to humans and animals through ingestion of plants that have bio-accumulated toxic metals from contaminated soil (Ogunkunle and Fatoba, 2013). AMD also contains dissolved lead which poses a threat to plants, animals, and human. In humans and other animals, lead acts as a central nervous system toxin. High levels of contact may cause brain damage (Hsieh et al., 2017). Lead exposure is also associated with blood disorders, kidney damage, miscarriages, and reproductive disorders (Wang et al., 2019). In addition, the presence of heavy metals in the environment, particularly above their acceptable levels, results in the pollution of environment which can causes serious health problems to humans and animals (Sedibe et al., 2017).

2.9.1.3 Water quality

Dissolved heavy metals do not only elevate toxicity of AMD but also act as metabolic poisons (Engwa et al., 2019). Apart from all other pollutants, heavy metals have become of a great interest to environmental chemists because of the nature and extent of their toxicity (Jain and Gauba, 2017). Generally, heavy metals in natural water resources are mainly present in trace amounts but most of them are toxic even at a very low concentration. Metals such as As, Pb, Cd, Ni, Hg, Cr, Co, and Zn are highly toxic even in small amounts (Masindi and Muedi, 2018). Even though when there are many other sources of water contamination mining, industrialisation, and urbanisation are major sources for increase in high level of heavy metal in water (Khan et al., 2019). These heavy metals can act together to suppress algal growth and affect fish and benthos. Heavy metals are deposited in water resources by runoff from industries, municipalities, and urban areas. Most of these metals end up accumulating in the soil and sediments of water bodies (Musilova et al., 2016). Table 2.3 list the acceptable limits of specific metal ion in drinking water as regulated by different bodies.

Table 2. 3. Permissible limits of different heavy metals in drinking water

Heavy metals	Acceptable limit (mg L^{-1})			
	WHO	USEPA	ISI	SANS
Fe	0.1	-	0.3	300
Al	-	-	-	200
Mn	0.01	0.05	0.1	100
Co	0.05	-	-	-
Zn	5.0	-	5.0	3
Pb	0.05	0.05	0.10	10
Cu	1.0	1.3	0.05	1000

WHO: World Health Organization, USEPA: United States Environmental Protection Agency, ISI: Indian Standard Institution and SANS: South African National Standards

2.9.1.4 Impact of solid precipitate from AMD

Neutralisation of AMD by the precipitation process of iron hydroxide and iron oxide can lead to the formation of an orange-brown precipitate known as ochre. The ochre precipitate can be extremely toxic to aquatic environment (Rezaie, and Anderson, 2020). This precipitate is deposited on the bottom of river or stream beds and forbids bottom feeding organisms from obtaining food by reducing the food sources available for animals at the top of the marine food chain, e.g. fish and sharks (Simate and Ndlovu, 2014). Ochre also comprises of toxic metals such as copper, cadmium and zinc whose precipitate may hide the surface of the steam sediments damaging habitat, reducing availability of clean gravels used for spawning, and reducing fish food items such as benthic macroinvertebrates. Figure 2.1 shows a picture of water affected by AMD, taken from the Western Basin, Johannesburg, South Africa.

Figure 2. 1. An image of water affected by AMD in Western Basin (Gonah, 2017)

It is clearly visible that the water is orange-brown in colour. This might have been due to be presence of dissolved iron and other metals in the water. It can be also observed that the orange-brown precipitate is settling at the bottom of the water hence confirming the occurrence of ochre precipitate. Despite the toxic effects that ochre pose, deterioration of the ecosystem is the obvious impact of AMD observed in this image (Correia et al., 2017). Therefore, essential measures to deal with the AMD issue to minimize its harmful impact on the receiving environment is required.

2.10 Management strategies

2.10.1 Management strategies of MWW effluents

Different methods which involve physical, biological, and chemical approaches have been investigated for the removal of phosphorus and nitrate from wastewater, these include chemical precipitation, crystallization, adsorption and ion exchange processes, membrane processes, electrochemical processes, and biological processes (Hutnik et al., 2013; Loganathan et al., 2014; Luo et al., 2015; Tarayre et al., 2016; Ichihashi and Hirooka, 2012). Most of these approaches are not useful because their high costs or are operationally complex. However, crystallization and chemical precipitation are extensively used approaches that produce a relatively high recovery rate and considerable economic efficiency; they produce valuable products with few environmental risks (Tarayre et al., 2016; Dai et al., 2016; Dai et al., 2017). Phosphorus removal from wastewater is done by the transfer of phosphate from the liquid form to solid form, this is followed by solid-liquid separation and at the end phosphorus is removed in sludge form (Melidis, 2012).

2.10.1.1 Removal techniques for MWW pollutant

2.10.1.1.1 Ion exchange

Ion exchange is mainly used for the softening of water during drinking water treatment and demineralization of ions such as removal of $Ca^{2+,}$ $Mg^{2+,}$ Na^+, Cl^-, SO_4^{2-}, and NO_3^-. Due to the rapid growth on the health effects which are brought by other anions contaminant such as ammonia, sulphate, fluoride, nitrate and phosphate, the application of ion exchange in water treatment has been amplified. Ion exchange is a well-established physicochemical process which involve exchanging of ions in water with ions within the solid phase of a resin (Hardwick et al., 2016). The solid phase or ion exchanger must be insoluble and can be of natural resin or synthetic material such as polymeric resin. These exchangers have immobile charged functional groups situated on their external or internal surface and linked with these groups are ions of opposite charge called counter ions. These mobile counter ions are connected by electrostatic attraction to each of the charged functional groups to indulge the condition that electron neutrality is sustained at all times within the exchange material as well as in the bulk aqueous solution. The counter ion can either be a cation or an anion contingent to the functional group of the exchanger and can exchange with another counter ion in the aqueous phase. This technique has been traditionally utilized for the purification of water and the removal of metal contaminants from wastewaters streams (Sole et al., 2017). Ion exchange is the most used method for nitrate removal from the municipal water treatment plant. Several researchers has investigated the effectiveness of this approach on the removal of nitrate from drinking water (Richard, 1989; Fletcher et al., 1991; Rogalla et al., 1991; Ruppenthal, 2004, 2007; Wang et al., 2007). A conventional ion exchange process involves the exchange of nitrate ions in the source water with chloride ions on the resin material (Clifford, 1999; Wachinski, 2006).

2.10.1.1.2 Crystallization

During the recovery of nutrients through struvite crystallization, solution chemistry plays an important role in crystal formation, which affect the overall removal/recovery of the nutrients from wastewater. Magnesium ammonium phosphate ($MgNH_4PO_4•6H_2O$), commonly known as struvite, is a white crystalline substance, formed by the reaction of free magnesium, ammonium and phosphate. It is formed when the ion activity of magnesium, ammonium and phosphate exceeds the solubility product of struvite. The simplified form of the reaction involving the struvite formation is illustrated in Equation (2.5) (Rahaman et al., 2014):

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \tag{2.5}$$

Similar to any other reactions involving crystallization processes, struvite precipitation also depends on supersaturation of solution, while, the generation of supersaturation depends on the constituent species concentration, as well as the solution pH and ionic strength (Munch and Barr, 2001; Suthar and Chokshi, 2011). Solution containing struvite species: Mg, NH4 and PO4, once mixed, undergoes chemical transformation and based on species concentration and solution pH, can form different compounds and complexes. However during the formation of struvite, phosphate get adsorbed by Mg to form $MgPO_4$ which then attract NH_4 to form struvite complex mineral. The formed struvite is slightly soluble in water but soluble in acid solution (Liu et al., 2013). Struvite precipitation has been considered as an innovative and profitable physico-chemical treatment method for recovery of recyclable constituents from nutrient-laden industrial discharges (Kaan et al., 2018). The recovered struvite hardly contains any toxic substance and can be sold to fertilizer companies as a fertilizer raw material (Jabr et al., 2019; Muhmood et al., 2019). The formation of struvite crystals is a method which converts hazardous waste into a non-hazardous useful nutritious resource (Pramod et al., 2011). Struvite precipitation occurs under alkaline conditions (Liu et al., 2019).

2.10.1.1.3 Adsorption

Adsorption is a physico-chemical process in which a solid, called adsorbent, retains a certain kind of molecules, called adsorbates that are contained in a gas or liquid (Birbas, 2011). Adsorption process involves mass transfer process in which substances present in a liquid phase are adsorbed or accumulated on a solid phase and thus removed from the liquid. Adsorption of phosphorus and nitrate is the most widely used method in wastewater treatment plants using different adsorbents. In this method, it is possible to use low-cost materials such as industrial by-products and naturally occurring materials (Loganathan et al., 2013). The application of adsorption is limited by its high operation costs and removal efficiency. Adsorption of phosphorus and nitrate depends on several factors such as the type of adsorbent used, its surface area, pH, and contact time. There are several adsorbents which have been investigated by previous researchers to remove nitrate and phosphate from different wastewater streams. These include carbon-based compounds (Alagha et al., 2020; Jiao et al., 2021; Karthikeyan and Meenakshi, 2019), naturally occurring minerals (Sellner et al., 2019; Manikam et al., 2019), agricultural wastes (Qiao et al., 2019; Banu et al., 2019), zeolites (He et al., 2017; Gouran-Orimi et al., 2018), metal oxides and hydroxides (Wu et al., 2019; Yu et al., 2019), layered double hydroxides (LDHs) (Yang et al., 2019; Zhang et al., 2021), biosorbents and other synthetic organic and inorganic compounds (Yin et al., 2017; An et al., 2019; Sahu et al., 2020). However, the selectively of these adsorbents must be employed to effectively remove these anions. Sayadi et al. (2016) used microalgae spirulina platensis and chlorella vulgaris for the removal of phosphate and nitrate in aqueous solution. According to Mitrogiannis et al. (2017), phosphate was removed from aqueous solution by means of adsorption onto $Ca(OH)_2$ treated natural clinoptilolite. El-Shazly et al. (2011) used batch electrocoagulation unit with vertical monopolar aluminium electrodes for the removal of nitrate from wastewater. Theresa et al. (2013), investigated the removal of metals and acidity from acid mine drainage using MWW and activated sludge. Mohan and Chander. (2006) used lignite-A low-cost sorbent for the removal and recovery of metal ions from acid mine drainage.

2.10.1.1.4 Chemical Precipitation

Chemical precipitation method in wastewater treatment refers to the variation in the form of materials dissolved in water to form solid particles. This method is mostly used to remove ionic constituents from water bodies by the addition of metal salts to reduce the solubility. It is mainly used for the removal of metallic cations (Yadav et al., 2019) and anions such as fluoride, cyanide, and phosphate, as well as organic molecules such as phenols and aromatic amines by enzymes and detergents (Zueva, 2018). Nevertheless, the widespread utilization of chemical precipitation as the conventional treatment method for phosphate removal from wastewaters, the excessive production of sludge at higher phosphate concentrations is unbearable, which demands proper sludge handling facilities (Yan et al., 2019; Ojovan et al., 2019) with slower rate of metal precipitation. In addition, the settling characteristics of generated sludge requires separate sedimentation and filtration units for effective solid–liquid separation (Sarode et al., 2019). Chemical precipitation is a very flexible approach to phosphate removal and can be useful at several stages during wastewater treatment. Chemical precipitation of phosphate works by converting phosphorus to form a solid substance such as sludge. This is done by the addition of metal salts which react with the soluble phosphorus and form solid precipitates as phosphate removed by means of separating solids from liquids such as clarification and filtration. The phosphate precipitation is achieved by the addition of metal salts which form insoluble phosphate compounds as illustrated by equation (2.6 and 2.7) (Melidis, 2012).

$$3\ Ca(OH)_2 + 2\ H_3PO_4 \rightarrow 6\ H_2O + Ca_3(PO4)_2. \qquad (2.6)$$

$$5\ Ca(OH)_2 + 3\ H_3(PO_4) \rightarrow Ca_5(PO_4)_3\ (OH)_2 + 9H_2O \qquad (2.7)$$

Like any other reactions involving chemical precipitation, calcium phosphate precipitation also depends on constituent species concentration, as well as the solution pH and ionic strength. Once Ca and PO4 interact, they undergoes chemical reaction and based on species concentration, molar ratio and solution pH, different compounds and complexes could be formed. However during the formation of calcium phosphate, phosphate get adsorbed by Ca to form $\mathrm{Ca_nPO_4}$complex mineral. Chemical precipitation is the main commercial method used for the removal of phosphate using aluminium, calcium, magnesium, or iron as a coagulant (Chimenos et al., 2003; Uludag-Demirer and Othman, 2009; Ben Amor 2008). This approach is usually favoured due to wide spread of its application, although there is production of tertiary sludge. Chemical precipitation typically produces phosphorus bound as a metal salt within the wasted sludge. It therefore has potential value in agricultural activities. Recovery of phosphorus from phosphorus containing wastewater is essential for developing an alternative source of phosphorus to overcome its global scarcity. Chemical precipitation helps to remove phosphate from wastewater to generate reusable compounds such as Tricalcium phosphate (Eq. 2.6) and hydroxyapatite (Eq. 2.7), which have gained interest as they can be utilized as fertilisers. Li et al., 2019 uses magnesium and iron ions to precipitate phosphorus. Guan et al., 2020 also recovers phosphate from urine using usable magnetic Fe_3O_4@ ZrO_2 nanoparticles.

2.10.2 Management strategies of AMD effluents

AMD generation can be controlled by checking chemical reactions that generate acid and microbial reaction. Because water is considered to be the transport medium for contaminants, therefore, AMD migration can be controlled by managing the flow of water, diverting the surface water flowing towards the site of pollution, preventing hydrological water seepage into the affected area and proper management of acid-generating waste (Akcil and Koldas, 2006).

2.10.2.1 Method for the treatment of AMD effluents

Because of the difficulties which are found in controlling the AMD at source, it is rather a best approach to collect and treat AMD, thereby minimizing the impact of AMD on receiving streams, river, and other environmental components. There are number of methods which are available for the treatment of mine water. These technologies involve one or a combination of chemical, physical, and biological processes. Treatment of AMD is generally categorised into active and passive treatment although there is an emerging approach that firmly rely on the synergy of their hybrid arrangements or integration of different processes and mechanisms to acquire water that comply to different standards (Orden et al., 20121), specifications (Ali et al., 2019), and guidelines (Jouini et al., 2020).

2.10.2.1.1 Active treatment

The most widely used treatment to remidiate AMD is active treatment that includes various processes such as aeration, addition of neutralizing agents, reverse osmosis, ion exchange, electro dialysis and natural zeolites (Saha and Sinha, 2018). Active treatment technologies for the treatment of AMD involve the utilization of alkaline substance to increase its pH, counteract acidity and to precipitate metals (Qin et al., 2019). In active treatment method, addition of various chemicals as neutralising agents to the source of AMD or directly to the receiving stream that has been polluted is involved. Active treatments have been found to be more successful. Chemicals such as $CaCO_3$ (calcium carbonate), CaO (calcium oxide), $Ca(OH)_2$ (calcium hydroxide), NH_3 (ammonia), NaOH (sodium hydroxide), MgO, Mg(OH)2, $MgCO_3$, magnesium bicarbonate and Na_2CO_3 (sodium carbonate) are successfully used in active treatment (Jamal et al., 2015; Kirk Nordstrom, 2020; Kalombe et al., 2020; Rey et al., 2020; Sulaiman et al., 2018; Retka et al., 2020). Neutralizing the acidity of AMD by limestone and to remove the metals by forming their insoluble hydroxide precipitates is the commonly used treatment method for AMD (Nleya et al., 2016) as indicated in equation (2.8):

$$Me^{n+} + 2\ OH^{-}_{(aq)} \rightarrow Me(OH)_{n} \qquad (2.8)$$

Although this method is an effective method for AMD treatment, the main disadvantage of this method is based on a large amount of sludge production that has costly disposal requirements (Nleya et al., 2016, Wang et al., 2013). The active treatment system is more complex and requires more unit processes and constant maintenance. Its operational cost is higher as compared to the easiest and uncomplicated passive treatment system (Yadav and Jamal, 2016; Hallberg and Johnson, 2003).

2.10.2.1.2 Passive treatment

Since the early 1970s, passive treatment systems which depend on the use of biological, geochemical, and physical processes have been developed to treat mine water to improve water quality (Skousen et al., 2017). Passive treatment technologies for AMD are categorized into primary passive treatment and secondary passive treatment processes. Primary passive treatment is generally divided into biological processes and geochemical processes that contain inorganic materials, such as carbonates. The biological processes include aerobic and anaerobic wetlands, vertical flow reactor/wetlands, and bioreactors. The geochemical processes include anoxic limestone drains, open limestone channels, limestone leach beds, steel slag leach beds, limestone diversion wells, and limestone sandstones. Some of the processes which have been have classified as biological also use geochemical processes (Humphries et al., 2017; Jamalet al., 2015; Skousen et al., 2017; Vikram et al., 2017).

2.10.2.1.4 Integrated approaches

In recent years, several researchers had been dealing with nutrients removal from municipal water treatment plant and acid mine drainage using a single method approach. However, the use of integrated approaches (Figure 2.2) for chemical species in wastewater is more profitable than using a single approach. Williams et al. (2015) used ion exchange-precipitation for nutrient recovery from dilute wastewater. Rasalingam et al. (2014) also use TiO -SiO mixed oxide materials for the removal of hazardous pollutants from wastewaters. Holloway et al. (2014), Holloway et al. (2015) have coupled forward osmosis with a membrane bioreactor for wastewater nutrient recovery. A generic schematic presentation of a integrated approach is demonstrated in Figure 2.2.

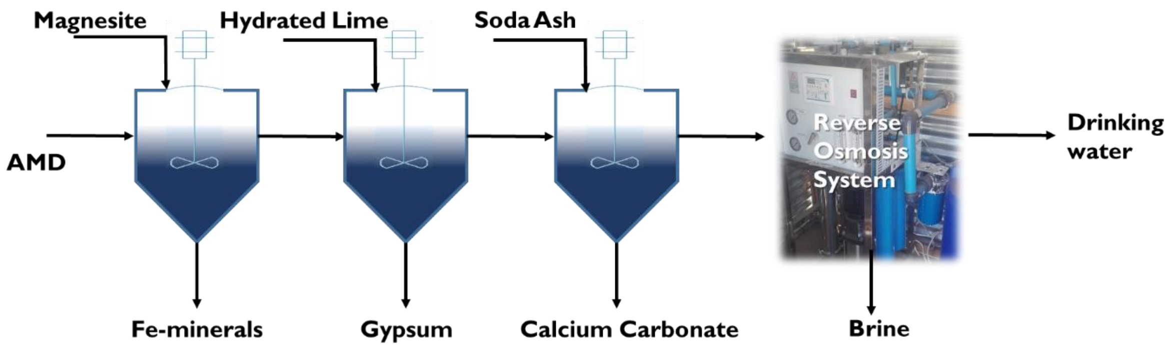

Figure 2. 2: Schematic presentation of an integrated approach for AMD treatment (Modified from Mavhungu et al. 2020).

2.11 Water quality guidelines

2.11.1 Water quality guidelines for MWW effluents

Water quality guidelines of different classification have been documented by different health agencies (Lester, 1969). Some of such type of agencies include United State Public Health Service Drinking Water Standards (USPHS) (1962), Indian Council of Medical Research (ICMR) (1962) and World Health Organisation (1992). Water standards guidelines are imperative since the quality of water directly affects the health of living organism (Umar, 2000). The recommended value of phosphorous in drinking water according to EPA is 5 mg L^{-1}. Although, in the permissible limit, it can be essential for human health, however, beyond a permissible limit it may cause several diseases to the human body (Bricker et al., 1971). According to the USEPA (1986), phosphate discharge into water bodies should be within 0.05 mg L^{-1} so that eutrophication cannot take place and for the prevention of algal bloom it should be maintained in the range between 0.01 and 0.03 mg L^{-1}. Phosphate can be found as a free ion in water bodies and as salt in terrestrial environments used in detergents as water softeners (Atobatele and Olutona 2013).

2.11.2 Water quality guidelines for AMD

The National Environmental Management Act (NEMA) of South Africa 108 of 1998, specifies that everyone has the right to live in an environment which is safe and unlikely to cause any serious effects to their health. The legislative requirements for industrial effluents are primarily governed by the Department of Water Affairs Standards (Masindi and Muedi, 2018). This purpose demand that everyone who uses water for industrial purposes shall purify or otherwise treat such water in accordance with requirements of DWAF and SANS (Van der Linde and Feris, 2010; Biswas et al., 2014; Madzivire et al., 2014). As shown in Table 2.4, mine effluents in South Africa are dominated by dissolved Al, Fe and Mn. These concentrations exceed the legal requirements of that element in water for AMD and few in ND exceeds.

Table 2. 4. The related criteria for discharge of acidic water as compared to DWS and SANS water quality guidelines

Parameter	Acid mine drainage	Neutral drainage	DWAF	SANS
pH	< 1.4 to > 3.5	> 6	5.0-10.0	6.5-9.4
Al	350	0.01	0.5	0.3
Fe	6.75	0.07	1	0.2
Mn	5.29	25.0	0.2	0.5
Cu	17.3	-	1	2
Zn	2.53	0.16	5	5

Coal and gold mining AMD (Wan Zuhairi et al., 2009; Feng et al., 2004)

Neutral drainage water (Masindi V and Muedi, 2018)

2.12 Geochemical modelling

Modelling and computer validation are the vital tool that can be utilized to escalate knowledge into geochemical processes both to understand laboratory experiments and field data as well as to make assumptions of long-term performance of chemical components in a system under study. Increasing expertise of the potential environmental threats instigated by activities such as mining, disposal of wastes, and chemical spillage, have disputed attention in the competence to foresee pollution situations and fabricate management strategies to reduce environmental impact. Due to the issues of complication and the time-scales involved, it is often challenging to operate sufficiently realistic laboratory experiments to perceive the long-term behaviour of most environmental systems. However, geochemical models can be utilized to interpret and predict the processes that may occurs over time-scales that are not attainable in experiments hence modelling becomes the most significant tool that is necessary from long term experiments. Furthermore, geochemical modelling can be useful to optimization process to distinguish influential parameters during wastewater treatment and help in fabricating effective technologies to avoid the discharge of hazardous substances in the environment. Though it cannot replace experimental effort, modelling is a useful analytical tool that can be engaged to connect the gap between laboratory experiments, field observations, and the long-term behaviour of geochemical systems (Parkhurst, 1995, Parkhurst and Appelo, 1999, Halim et al., 2005, Zhang and Luo, 2007, Martens et al., 2008, Tiruta-Barna, 2008, Wissmeier and Barry, 2010, Charlton and Parkhurst, 2011, Van Den Akker and Ahn, 2011, Chidambaram et al., 2012, Van Pham et al., 2012, Zhao et al., 2012). In this work, PHREEQC Geochemical Modelling Code will be used to model the processes involving the interaction of the feedstock and the contaminant-containing solutions.

2.13 Summary of the literature review

Based on the literature review, the undermentioned areas of interest related to the subject of the current study were discovered. Traditional methods for the treatment of MWWTPs and AMD have been fabricated, however, factors such as operational cost, handling processes and production of secondary sludge which is detrimental and necessitates special disposal facilities which are costly to sustain has become of emerging problem. For this reason, several legislative concerns and stringency of environmental regulations has increased. Calcium based materials have been successfully used for the treatment of both MWWTPs and AMD but the production costs in case of calcite becomes a restrictive factor when is being applied in large-scale process because cost is regarded as limiting factor in all the treatment technologies. Calcium phosphate has never been used for the treatment of AMD as such there is a need to assess the efficiency of amorphous calcium phosphate to treat AMD. Calcite have been utilized for neutralization and removal of metals from AMD, but it has shown poor potential on attenuation of inorganic pollutants. To counter to the challenges that are being posed by current technologies, government, mining houses, and scientific communities requires an innovative and locally available technologies for treating MWWTPs and AMD. Furthermore, to overcome the over exploitation of resources and to reduce the utilization of the virgin and raw materials as well as the modified calcium based as feedstock, the feedstock can be prepared in a composite form with some metal oxides and carbonates. The present study was designed to address those challenges by synthesizing the composite with high removal and neutralisation capabilities. Calcium phosphate which is synthesized from municipal wastewater during phosphate recovery with hydrated lime has never been used for the treatment of AMD, instead, has been used for agricultural soil amendment. This literature review revealed the need to use hydrated lime individually and calcium phosphate for treatment of MWW and AMD, respectively. The synthesized calcium phosphate has never been used for acid mine drainage treatment. This will be the first study to explore the potential application of calcium phosphate for neutralisation and attenuation of metal ions from metalliferous and acidic mine effluents.

REFERENCES

REFERENCES

Abdel-Satar, A.M., Ali, M.H. and Goher, M.E., 2017. Indices of water quality and metal pollution of Nile River, Egypt. The Egyptian Journal of Aquatic Research, 43(1), pp.21-29.

Abowei, J.F.N., 2010. Salinity, dissolved oxygen, pH and surface water temperature conditions in Nkoro River, Niger Delta, Nigeria. Advance Journal of Food Science and Technology, 2(1), pp.36-40.

Abowei, J.F.N., Davies, O.A. and Eli, A., 2010. Physicochemistry, morphology and abundance of fin fish of Nkoro River, Niger Delta, Nigeria. International Journal of Pharma and Bio Sciences, 6(2), pp.1-11.

Agboola, O., 2019. The role of membrane technology in acid mine water treatment: A review. Korean Journal of Chemical Engineering, 36(9), pp.1389-1400.

Aghapour, A.A., Nemati, S., Mohammadi, A., Nourmoradi, H. and Karimzadeh, S., 2016. Nitrate removal from water using alum and ferric chloride: a comparative study of alum and ferric chloride efficiency. Environmental Health Engineering and Management Journal, 3(2), pp.69-73.

Akcil, A. and Koldas, S., 2006. Acid Mine Drainage (AMD): causes, treatment and case studies. Journal of Cleaner Production, 14(12-13), pp.1139-1145.

Akpor, O.B., 2011. September. Wastewater effluent discharge: Effects and treatment processes. In International Conference on Chemical, Biological and Environmental Engineering, 20, pp. 85-91.

Alagha, O., Manzar, M.S., Zubair, M., Anil, I., Mu'azu, N.D. and Qureshi, A., 2020. Magnetic Mg-Fe/LDH intercalated activated carbon composites for nitrate and phosphate removal from wastewater: insight into behavior and mechanisms. Nanomaterials, 10(7), pp.1361.

Alekseenko, V.A., Bech, J., Alekseenko, A.V., Shvydkaya, N.V. and Roca, N., 2018. Environmental impact of disposal of coal mining wastes on soils and plants in Rostov Oblast, Russia. Journal of Geochemical Exploration, 184, pp.261-270.

Ali, H., Khan, E. and Ilahi, I., 2019. Environmental chemistry and ecotoxicology of hazardous heavy metals: environmental persistence, toxicity, and bioaccumulation. Journal of Chemistry, 2019.

Ali, H.E.B., Neculita, C.M., Molson, J.W., Maqsoud, A. and Zagury, G.J., 2019. Performance of passive systems for mine drainage treatment at low temperature and high salinity: A review. Minerals Engineering, 134, pp.325-344

Almomani, F., Al Ketife, A., Judd, S., Shurair, M., Bhosale, R.R., Znad, H. and Tawalbeh, M., 2019. Impact of CO2 concentration and ambient conditions on microalgal growth and nutrient removal from wastewater by a photobioreactor. Science of The Total Environment, 662, pp.662-671.

Alshameri, A., Yan, C. and Lei, X., 2014. Enhancement of phosphate removal from water by TiO2/Yemeni natural zeolite: preparation, characterization and thermodynamic. Microporous and Mesoporous Materials, 196, pp.145-157.

An, B., Lee, S., Kim, H.G., Zhao, D., Park, J.A. and Choi, J.W., 2019. Organic/inorganic hybrid adsorbent for efficient phosphate removal from a reservoir affected by algae bloom. Journal of Industrial and Engineering Chemistry, 69, pp.211-216.

Andjelkovic, M., Buha Djordjevic, A., Antonijevic, E., Antonijevic, B., Stanic, M., Kotur-Stevuljevic, J., Spasojevic-Kalimanovska, V., Jovanovic, M., Boricic, N., Wallace, D. and Bulat, Z., 2019. Toxic effect of acute cadmium and lead exposure in rat blood, liver, and kidney. International Journal of Environmental Research and Public Health, 16(2), pp.274.

Atobatele, E.O. and Olutona, G.O., 2013. Spatio-seasonal physico-chemistry of Aiba stream, Iwo, Nigeria. African Journal of Biotechnology, 12(14), pp. 1684-5315.

Ayyasamy, P.M., Shanthi, K., Lakshmanaperumalsamy, P., Lee, S.J., Choi, N.C. and Kim, D.J., 2007. Two-stage removal of nitrate from groundwater using biological and chemical treatments. Journal of bioscience and bioengineering, 104(2), pp.129-134.

Baker, B.J. and Banfield, J.F., 2003. Microbial communities in acid mine drainage. FEMS Microbiology Ecology, 44(2), pp.139-152.

Banu, H.A.T., Karthikeyan, P. and Meenakshi, S., 2019. Comparative studies on revival of nitrate and phosphate ions using quaternized corn husk and jackfruit peel. Bioresource Technology Reports, 8, pp.100331.

Barca, C., Gérente, C., Meyer, D., Chazarenc, F. and Andrès, Y., 2012. Phosphate removal from synthetic and real wastewater using steel slags produced in Europe. Water Research, 46(7), pp.2376-2384.

Bell, F.G., Bullock, S.E.T., Hälbich, T.F.J. and Lindsay, P., 2001. Environmental impacts associated with an abandoned mine in the Witbank Coalfield, South Africa. International Journal of Coal Geology, 45(2-3), pp.195-216.

Benefield, L.D., Judkins, J.F. and Weand, B.L., 1982. Process chemistry for water and wastewater treatment. Englewood Cliffs, New Jersey. Prentice hall Inc, pp.449.

Benner, S.G., Gould, W.D. and Blowes, D.W., 2000. Microbial populations associated with the generation and treatment of acid mine drainage. Chemical Geology, 169(3-4), pp.435-448.

Birbas D., 2011. Preparation of activated carbon: Forest residues activated with phosphoric acid and zinc sulfate. Master Thesis in Chemical Engineering. Kungliga Tekniska Högskolan.

Biswas, A.K., Tortajada, C. and Izquierdo, R., 2014. Water quality management: present situations, challenges and future perspectives. Routledge. New York, USA: Taylor & Francis.

Blowes, D.W., Ptacek, C.J., Jambor, J.L. and Weisener, C.G., 2003. The geochemistry of acid mine drainage. Treatise on Geochemistry, 44, pp. 149–204.

Booker, N.A., Priestley, A.J. and Fraser, I.H., 1999. Struvite formation in wastewater treatment plants: opportunities for nutrient recovery. Environmental Technology, 20(7), pp.777-782.

Breytus, A., Hasson, D., Semiat, R. and Shemer, H., 2020. Removal of nitrate from groundwater by Donnan dialysis. Journal of Water Process Engineering, 34, pp.101157.

Bricker, N.S., 1971. On the pathogenesis of the uremic state: An exposition of the “trade-off hypothesis”. New England Journal of Medicine, 286(20), pp.1093-1099.

Chadwick, M.J., Highton, N.H. and Lindman, N. eds., 2013. Environmental impacts of coal mining & utilization: a complete revision of environmental implications of expanded coal utilization. Elsevier.

Chan, T.Y., 1996. Food-borne nitrates and nitrites as a cause of methemoglobinemia. Southeast Asian Journal of Tropical Medicine & Public Health, 27(1), pp.189-192.

Chaoua, S., Boussaa, S., El Gharmali, A. and Boumezzough, A., 2019. Impact of irrigation with wastewater on accumulation of heavy metals in soil and crops in the region of Marrakech in Morocco. Journal of the Saudi Society of Agricultural Sciences, 18(4), pp.429-436.

Chimenos, J.M., Fernandez, A.I., Villalba, G., Segarra, M., Urruticoechea, A., Artaza, B. and Espiell, F., 2003. Removal of ammonium and phosphates from wastewater resulting from the process of cochineal extraction using MgO-containing by-product. Water Research, 37(7), pp.1601-1607.

Choi, J.H., Maruthamuthu, S., Lee, H.G., Ha, T.H. and Bae, J.H., 2009. Nitrate removal by electro-bioremediation technology in Korean soil. Journal of Hazardous Materials, 168(2-3), pp.1208-1216.

Cong, W.F., Suriyagoda, L.D. and Lambers, H., 2020. Tightening the Phosphorus Cycle through Phosphorus-Efficient Crop Genotypes. Trends in Plant Science.

Correia, L.G.C.S., Ehrlich, M. and Mendonca, M.B., 2017. The effect of submersion in the ochre formation in geotextile filters. Geotextiles and Geomembranes, 45(1), pp.1-7.

Costello, C., 2003. Acid mine drainage: innovative treatment technologies. Washington DC: US Environmental Protection Agency Office of Solid Waste and Emergency Response.

Dai, H., Lu, X., Peng, Y., Yang, Z. and Zhsssu, H., 2017. Effects of supersaturation control strategies on hydroxyapatite (HAP) crystallization for phosphorus recovery from wastewater. Environmental Science and Pollution Research, 24(6), pp.5791-5799.

Dai, H., Lu, X., Peng, Y., Zou, H. and Shi, J., 2016. An efficient approach for phosphorus recovery from wastewater using series-coupled air-agitated crystallization reactors. Chemosphere, 165, pp.211-220.

Daneshvar, E., Zarrinmehr, M.J., Koutra, E., Kornaros, M., Farhadian, O. and Bhatnagar, A., 2019. Sequential cultivation of microalgae in raw and recycled dairy wastewater: microalgal growth, wastewater treatment and biochemical composition. Bioresource Technology, 273, pp.556-564.

Diz, H.R., 1997. Chemical and biological treatment of acid mine drainage for the removal of heavy metals and acidity (Doctoral dissertation, Virginia Tech).

Donnert, D. and Salecker, M., 1999. Elimination of phosphorus from wastewater by crystallization. Environmental Technology, 20(7), pp.735-742.

Doyle, J.D., Philp, R., Churchley, J. and Parsons, S.A., 2000. Analysis of struvite precipitation in real and synthetic liquors. Process Safety and Environmental Protection, 78(6), pp.480-488.

Draman, S.F.S., Khalid, S.A., Sidek, N.M., Abdullah, S.R.S. and Anuar, N., 2020, March. Phytotoxicity Study of Native Plants in ex-mining lake water treatment. In IOP Conference Series: Materials Science and Engineering, 808(1), pp. 012040.

Du, H., Chen, Z., Mao, G., Chen, L., Crittenden, J., Li, R.Y.M. and Chai, L., 2019. Evaluation of eutrophication in freshwater lakes: a new non-equilibrium statistical approach. Ecological Indicators, 102, pp.686-692.

Duan, P., Qi, Y., Feng, S., Peng, X., Wang, W., Yue, Y., Shang, Y., Li, Y., Gao, B. and Xu, X., 2020. Enhanced degradation of clothianidin in peroxymonosulfate/catalyst system via core-shell FeMn@ NC and phosphate surrounding. Applied Catalysis B: Environmental, 267, pp.118717.

Dutta, M., Islam, N., Rabha, S., Narzary, B., Bordoloi, M., Saikia, D., Silva, L.F. and Saikia, B.K., 2020. Acid mine drainage in an Indian high-sulfur coal mining area: Cytotoxicity assay and remediation study. Journal of Hazardous Materials, 389, pp.121851

Ebbers, B., Ottosen, L.M. and Jensen, P.E., 2015. Electrodialytic treatment of municipal wastewater and sludge for the removal of heavy metals and recovery of phosphorus. Electrochimica Acta, 181, pp.90-99.

Edao, H.G., 2017. Heavy metals pollution of soil; toxicity and phytoremediation techniques. International Journal of Advanced Research, 1(1), pp.2456-9992.

El Diwani, G., El Rafie, S., El Ibiari, N.N. and El-Aila, H.I., 2007. Recovery of ammonia nitrogen from industrial wastewater treatment as struvite slow releasing fertilizer. Desalination, 214(1-3), pp.200-214.

El-Shazly, A.H., Al-Zahrani, A.A. and Al-Shahrani, S.S., 2011. Improvement of NO_3^- removal from wastewater by using batch electrocoagulation unit with vertical monopolar aluminum electrodes. International Journal of Electrochemical Science, 6, pp.4141-4149.

Engwa, G.A., Ferdinand, P.U., Nwalo, F.N. and Unachukwu, M.N., 2019. Mechanism and health effects of heavy metal toxicity in humans. Poisoning in The Modern World-new Tricks For an Old Dog, 10, pp. 12.

Ezeabara, C.A., Okanume, O.E., Emeka, A.N., Okeke, C.U. and Mbaekwe, E.I., 2014. Heavy metal contamination of herbal drugs: implication for human health-a review. Int J Trop Dis Health, 4(10), pp.1044-58.

Feng, D., Van Deventer, J.S.J. and Aldrich, C., 2004. Removal of pollutants from acid mine wastewater using metallurgical by-product slags. Separation and Purification Technology, 40(1), pp.61-67.

Fernando, W.A.M., Ilankoon, I.M.S.K., Syed, T.H. and Yellishetty, M., 2018. Challenges and opportunities in the removal of sulphate ions in contaminated mine water: A review. Minerals Engineering, 117, pp.74-90.

Fletcher, I.J., Woodward, A.J. and Henwood, N.G., 1991. Design and Construction of an Ion-Exchange Denitrification Plant in South Staffordshire. Water and Environment Journal, 5(5), pp.566-572.

Flyhammar, P., 1995, October. Leachate quality and environmental effects at active Swedish municipal landfill. In Regulations, environmental impact and aftercare. Proceedings Sardinia, 95, pp. 549-557.

Foladori, P., Petrini, S., Nessenzia, M. and Andreottola, G., 2018. Enhanced nitrogen removal and energy saving in a microalgal–bacterial consortium treating real municipal wastewater. Water Science and Technology, 78(1), pp.174-182.

Foudhaili, T., Rakotonimaro, T.V., Neculita, C.M., Coudert, L. and Lefebvre, O., 2019. Comparative efficiency of microbial fuel cells and electrocoagulation for the treatment of iron-rich acid mine drainage. Journal of Environmental Chemical Engineering, 7(3), p.103149.

Fungaro, D.A., Yamaura, M. and Craesmeyer, G.R., 2012. Uranium removal from aqueous solution by zeolite from fly ash-iron oxide magnetic nanocomposite. International Review of Chemical Engineering, 4(3), pp.353-358.

Ghaly, A.E., Ananthashankar, R., Alhattab, M.V.V.R. and Ramakrishnan, V.V., 2014. Production, characterization and treatment of textile effluents: a critical review. Journal of Chemical Engineering Process Technology, 5(1), pp.1-18.

Gitari, M.W., Petrik, L.F., Etchebers, O., Key, D.L., Iwuoha, E. and Okujeni, C., 2006. Treatment of acid mine drainage with fly ash: removal of major contaminants and trace elements. Journal of Environmental Science and Health Part A, 41(8), pp.1729-1747.

Gonah, T., 2017. Impact of Acid Mine Drainage on Water Resources in South Africa. Management and Mitigation of Acid Mine Drainage in South Africa: Input for Mineral Beneficiation in Africa, 53, pp.41.

Gouran-Orimi, R., Mirzayi, B., Nematollahzadeh, A. and Tardast, A., 2018. Competitive adsorption of nitrate in fixed-bed column packed with bio-inspired polydopamine coated zeolite. Journal of Environmental Chemical Engineering, 6(2), pp.2232-2240.

Guan, T., Kuang, Y., Li, X., Fang, J., Fang, W. and Wu, D., 2020. The recovery of phosphorus from source-separated urine by repeatedly usable magnetic Fe_3O_4@ ZrO_2 nanoparticles under acidic conditions. Environment International, 134, pp.105322.

Hallberg, K.B. and Johnson, D.B., 2003. Passive mine water treatment at the former Wheal Jane tin mine, Cornwall: important biogeochemical and microbiological lessons. Land Contamination and Reclamation, 11(2), pp.213-220.

Hallberg, K.B., 2010. New perspectives in acid mine drainage microbiology. Hydrometallurgy, 104(3-4), pp.448-453.

Hardwick, E., Hardwick, J. and Sole, K.C., 2016. An overview of the use of ion exchange to extract wealth from mine waters. In International Mine Waters Association Conference 2016.

Harris, W.G., Wilkie, A.C., Cao, X. and Sirengo, R., 2008. Bench-scale recovery of phosphorus from flushed dairy manure wastewater. Bioresource technology, 99(8), pp.3036-3043.

He, H., Huang, Y., Yan, M., Xie, Y. and Li, Y., 2020. Synergistic effect of electrostatic adsorption and ion exchange for efficient removal of nitrate. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 584, pp.123973.

He, Y., Lin, H., Dong, Y. and Wang, L., 2017. Preferable adsorption of phosphate using lanthanum-incorporated porous zeolite: characteristics and mechanism. Applied Surface Science, 426, pp.995-1004.

Hell, F., Lahnsteiner, J., Frischherz, H. and Baumgartner, G., 1998. Experience with full-scale electrodialysis for nitrate and hardness removal. Desalination, 117(1-3), pp.173-180.

Hodges, A., Fica, Z., Wanlass, J., VanDarlin, J. and Sims, R., 2017. Nutrient and suspended solids removal from petrochemical wastewater via microalgal biofilm cultivation. Chemosphere, 174, pp.46-48.

Holloway, R.W., Childress, A.E., Dennett, K.E. and Cath, T.Y., 2007. Forward osmosis for concentration of anaerobic digester centrate. Water Research, 41(17), pp.4005-4014.

Holloway, R.W., Regnery, J., Nghiem, L.D. and Cath, T.Y., 2014. Removal of trace organic chemicals and performance of a novel hybrid ultrafiltration-osmotic membrane bioreactor. Environmental Science and Technology, 48(18), pp.10859-10868.

Hosni, K., Moussa, S.B., Chachi, A. and Amor, M.B., 2008. The removal of PO_4^{3-} by calcium hydroxide from synthetic wastewater: optimisation of the operating conditions. Desalination, 223(1-3), pp.337-343.

Hsieh, N.H., Chung, S.H., Chen, S.C., Chen, W.Y., Cheng, Y.H., Lin, Y.J., You, S.H. and Liao, C.M., 2017. Anemia risk in relation to lead exposure in lead-related manufacturing. BMC Public Health, 17(1), pp.1-12.

Hughes, T.A. and Gray, N.F., 2013. Removal of metals and acidity from acid mine drainage using municipal wastewater and activated sludge. Mine Water and the Environment, 32(3), pp.170-184.

Humphries, M.S., McCarthy, T.S. and Pillay, L., 2017. Attenuation of pollution arising from acid mine drainage by a natural wetland on the Witwatersrand. South African Journal of Science, 113(1-2), pp.1-9.

Hutnik, N., Kozik, A., Mazienczuk, A., Piotrowski, K., Wierzbowska, B. and Matynia, A., 2013. Phosphates (V) recovery from phosphorus mineral fertilizers industry wastewater by continuous struvite reaction crystallization process. Water Research, 47(11), pp.3635-3643.

Iakovleva, E. and Sillanpää, M., 2013. The use of low-cost adsorbents for wastewater purification in mining industries. Environmental Science and Pollution Research, 20(11), pp.7878-7899.

Ibrahim, K.N., Yet, Z.R., Som, A.M., Razali, N., Rahaizah, N.A.M., Othman, E.N., Burok, N.A., Yunos, Y.M., Othman, R. and Yahya, T.F.T., 2015. Heavy metal concentration (Pb, Cu, Fe, Zn, Ni) in plant parts of Zea mays L. cultivated in agricultural area near Alor Gajah, Melaka, Malaysia. American Journal of Environmental Engineering, 5, pp.8-12.

Ibrahim, R., Zubair, A., Selintung, M. and Dwirachma, A.R., 2020, June. Phytoremediation of Fe and Mn Metal in Acid Mine Drainage Using Typha Angustifolia. In IOP Conference Series: Materials Science and Engineering, 875(1), pp. 012025.

Ichihashi, O. and Hirooka, K., 2012. Removal and recovery of phosphorus as struvite from swine wastewater using microbial fuel cell. Bioresource Technology, 114, pp.303-307.

Jabr, G., Saidan, M. and Al-Hmoud, N., 2019. Phosphorus recovery by struvite formation from Al Samra municipal wastewater treatment plant in Jordan. Desalination and Water Treatment, 146, pp.315-325.

Jagessar, R.C. and Sooknundun, L., 2011. Determination of nitrate anion in wastewater from nine selected areas of coastal Guyana via a spectrophotometric method. International Journal of Research and Reviews in Applied Sciences, 7(2), pp.203-212.

Jain, J. and Gauba, P., 2017. Heavy metal toxicity-implications on metabolism and health. Internation Journal of Pharmaceutical and Biologcal Science, 8(4), pp.452-460.

Jamal, A., Yadav, H.L. and Pandey, S.S., 2015. Heavy metals from acid mine drainage in coal mines-a case study. European Journal of Advances in Engineering and Technology, 2(8), pp.16-20.

Jiao, G.J., Ma, J., Li, Y., Jin, D., Guo, Y., Zhou, J. and Sun, R., 2021. Enhanced adsorption activity for phosphate removal by functional lignin-derived carbon-based adsorbent: Optimization, performance and evaluation. Science of The Total Environment, 761, pp.143217.

Johnson, D.B. and Hallberg, K.B., 2003. The microbiology of acidic mine waters. Research in microbiology, 154(7), pp.466-473.

Johnson, D.B. and Hallberg, K.B., 2005. Acid mine drainage remediation options: a review. Science of the Total Environment, 338(1-2), pp.3-14.

Jones, S.N. and Cetin, B., 2017. Evaluation of waste materials for acid mine drainage remediation. Fuel, 188, pp.294-309.

Jouini, M., Neculita, C.M., Genty, T. and Benzaazoua, M., 2020. Environmental behavior of metal-rich residues from the passive treatment of acid mine drainage. Science of The Total Environment, 712, pp.136541.

Kalombe, R.M., Ojumu, T.V., Katambwe, V.N., Nzadi, M., Bent, D., Nieuwouldt, G., Madzivire, G., Kevern, J. and Petrik, L.F., 2020. Treatment of acid mine drainage with coal fly ash in a jet loop reactor pilot plant. Minerals Engineering, 159, pp.106611.

Karabegovic, L., Uldal, M., Werker, A. and Morgan-Sagastume, F., 2013. Phosphorus recovery potential from a waste stream with high organic and nutrient contents via struvite precipitation. Environmental Technology, 34(7), pp.871-883.

Karthikeyan, P. and Meenakshi, S., 2019. Synthesis and characterization of Zn–Al LDHs/activated carbon composite and its adsorption properties for phosphate and nitrate ions in aqueous medium. Journal of Molecular Liquids, 296, pp.111766.

Karunanithi, R., Szogi, A.A., Bolan, N., Naidu, R., Loganathan, P., Hunt, P.G., Vanotti, M.B., Saint, C.P., Ok, Y.S. and Krishnamoorthy, S., 2015. Phosphorus recovery and reuse from waste streams. Advances in Agronomy, 131, pp.173-250.

Kaur, G., Couperthwaite, S.J., Hatton-Jones, B.W. and Millar, G.J., 2018. Alternative neutralisation materials for acid mine drainage treatment. Journal of Water Process Engineering, 22, pp.46-58.

Kefeni, K.K., Msagati, T.A. and Mamba, B.B., 2017. Acid mine drainage: Prevention, treatment options, and resource recovery: A review. Journal of Cleaner Production, 151, pp.475-493.

Kefeni, K.K., Msagati, T.A. and Mamba, B.B., 2017. Acid mine drainage: prevention, treatment options, and resource recovery: a review. Journal of Cleaner Production, 151, pp.475-493.

Keller, J., Owens, C.T., Lai, J.C. and Devaud, L.L., 2005. The effects of 17β-estradiol and ethanol on zinc-or manganese-induced toxicity in SK-N-SH cells. Neurochemistry International, 46(4), pp.293-303.

Khan, A., Khan, S.K.M.A., Khan, M.A., Aamir, M., Ullah, H., Nawab, J., Rehman, I.U. and Shah, J., 2019. Heavy metals effects on plant growth and dietary intake of trace metals in vegetables cultivated in contaminated soil. International journal of Environmental Science and Technology, 16(5), pp.2295-2304.

Kirk Nordstrom, D., 2020. Geochemical Modeling of Iron and Aluminum Precipitation during Mixing and Neutralization of Acid Mine Drainage. Minerals, 10(6), pp.547.

Kotowska, U., Karpinska, J., Kapelewska, J., Kowejsza, E.M., Piotrowska-Niczyporuk, A., Piekutin, J. and Kotowski, A., 2018. Removal of phthalates and other contaminants from municipal wastewater during cultivation of Wolffia arrhiza. Process Safety and Environmental Protection, 120, pp.268-277.

Kotsiopoulos, A. and Harrison, S.T.L., 2017. Application of fine desulfurised coal tailings as neutralising barriers in the prevention of acid rock drainage. Hydrometallurgy, 168, pp.159-166.

Li, L., Pang, H., He, J. and Zhang, J., 2019. Characterization of phosphorus species distribution in waste activated sludge after anaerobic digestion and chemical precipitation with Fe3+ and Mg2+. Chemical Engineering Journal, 373, pp.1279-1285.

Li, Y., Li, W., Xiao, Q., Song, S., Liu, Y. and Naidu, R., 2018. Acid mine drainage remediation strategies: A review on migration and source controls. Minerals & Metallurgical Processing, 35(3), pp.148-158.

Liu, Q., Chen, B., Haderlein, S., Gopalakrishnan, G. and Zhou, Y., 2018. Characteristics and environmental response of secondary minerals in AMD from Dabaoshan Mine, South China. Ecotoxicology and Environmental Safety, 155, pp.50-58.

Liu, X. and Wang, J., 2019. Impact of calcium on struvite crystallization in the wastewater and its competition with magnesium. Chemical Engineering Journal, 378, pp.122121.

Liu, Y., Kumar, S., Kwag, J.H. and Ra, C., 2013. Magnesium ammonium phosphate formation, recovery and its application as valuable resources: a review. Journal of Chemical Technology & Biotechnology, 88(2), pp.181-189.

Loganathan, P., Vigneswaran, S., Kandasamy, J. and Bolan, N.S., 2014. Removal and recovery of phosphate from water using sorption. Critical Reviews in Environmental Science and Technology, 44(8), pp.847-907.

Loganathan, P., Vigneswaran, S., Kandasamy, J. and Naidu, R., 2013. Defluoridation of drinking water using adsorption processes. Journal of Hazardous Materials, 248, pp.1-19.

Luptáková, A., Mačingová, E., Kotuličová, I. and Rudzanová, D., 2016. Sulphates removal from acid mine drainage. In IOP Conference Series: Earth and Environmental Science 44(5), pp. 052040.

Machado, C.S., Fregonesi, B.M., Alves, R.I., Tonani, K.A., Sierra, J., Martinis, B.S., Celere, B.S., Mari, M., Schuhmacher, M., Nadal, M. and Domingo, J.L., 2017. Health risks of environmental exposure to metals and herbicides in the Pardo River, Brazil. Environmental Science and Pollution Research, 24(25), pp.20160-20172.

Madzivire, G., Maleka, P.P., Vadapalli, V.R., Gitari, W.M., Lindsay, R. and Petrik, L.F., 2014. Fate of the naturally occurring radioactive materials during treatment of acid mine drainage with coal fly ash and aluminium hydroxide. Journal of Environmental Management, 133, pp.12-17.

Manikam, M.K., Halim, A.A., Hanafiah, M.M. and Krishnamoorthy, R.R., 2019. Removal of ammonia nitrogen, nitrate, phosphorus and COD from sewage wastewater using palm oil boiler ash composite adsorbent. Desalin. Water Treat, 149, pp.23-30.

Masindi, V. and Muedi, K.L., 2018. Environmental contamination by heavy metals. Heavy Metals, 10, pp.115-132.

Masindi, V., Osman, M.S., Mbhele, R.N. and Rikhotso, R., 2018. Fate of pollutants post treatment of acid mine drainage with basic oxygen furnace slag: Validation of experimental results with a geochemical model. Journal of Cleaner Production, 172, pp.2899-2909.

Mativenga, P.T. and Marnewick, A., 2018. Water quality in a mining and water-stressed region. Journal of Cleaner Production, 171, pp.446-456.

McCarthy, T.S. and Humphries, M.S., 2013. Contamination of the water supply to the town of Carolina, Mpumalanga, January 2012. South African Journal of Science, 109(9-10), pp.01-10.

McCarthy, T.S., 2011. The impact of acid mine drainage in South Africa. South African Journal of Science, 107(5-6), pp.01-07.

Medhi, K. and Thakur, I.S., 2018. Bioremoval of nutrients from wastewater by a denitrifier Paracoccus denitrificans ISTOD1. Bioresource Technology Reports, 1, pp.56-60.

Melidis P., 2012. Designing, operating problems, optimization and process control: Phosphate removal.

Mikhak, A., Sohrabi, A., Kassaee, M.Z., Feizian, M. and Disfani, M.N., 2017. Removal of nitrate and phosphate from water by clinoptilolite-supported iron hydroxide nanoparticle. Arabian Journal for Science and Engineering, 42(6), pp.2433-2439.

Minnaar, A., 2020. Water Pollution and Contamination from Gold Mines: Acid Mine Drainage in Gauteng Province, South Africa. In Water, Governance, pp. 193-219.

Mitrogiannis, D., Psychoyou, M., Baziotis, I., Inglezakis, V.J., Koukouzas, N., Tsoukalas, N., Palles, D., Kamitsos, E., Oikonomou, G. and Markou, G., 2017. Removal of phosphate from aqueous solutions by adsorption onto $Ca(OH)_2$ treated natural clinoptilolite. Chemical Engineering Journal, 320, pp.510-522.

Mohan, D. and Chander, S., 2006. Removal and recovery of metal ions from acid mine drainage using lignite—a low cost sorbent. Journal of Hazardous Materials, 137(3), pp.1545-1553.

Monge-Amaya, O., Certucha-Barragán, M.T., Almendariz-Tapia, F.J. and Figueroa-Torres, G.M., 2015. Removal of Heavy Metals from Aqueous Solutions by Aerobic and Anaerobic Biomass. Biomass Production and Uses, p.31.

Moodley, I., Sheridan, C.M., Kappelmeyer, U. and Akcil, A., 2018. Environmentally sustainable acid mine drainage remediation: Research developments with a focus on waste/by-products. Minerals Engineering, 126, pp.207-220.

Moriyama, Y., Yamaura, H., Fukui, R. and Becker, J.O., 2020. The role of phosphorus in growing tomatoes in near water-saturated soil. Journal of Plant Nutrition, 43(8), pp.1091-1103.

Muhmood, A., Lu, J., Dong, R. and Wu, S., 2019. Formation of struvite from agricultural wastewaters and its reuse on farmlands: Status and hindrances to closing the nutrient loop. Journal of Environmental Management, 230, pp.1-13.

Mujtaba, G. and Lee, K., 2017. Treatment of real wastewater using co-culture of immobilized Chlorella vulgaris and suspended activated sludge. Water Research, 120, pp.174-184.

Münch, E.V. and Barr, K., 2001. Controlled struvite crystallisation for removing phosphorus from anaerobic digester sidestreams. Water Research, 35(1), pp.151-159.

Musilova, J., Arvay, J., Vollmannova, A., Toth, T. and Tomas, J., 2016. Environmental contamination by heavy metals in region with previous mining activity. Bulletin of Environmental Contamination and Toxicology, 97(4), pp.569-575.

Nagy, A., Magyar, T., Juhász, C. and Tamás, J., 2020. Phytoremediation of acid mine drainage using by-product of lysine fermentation. Water Science and Technology, 81 (7), pp 1507–1517.

Naidu, G., Ryu, S., Thiruvenkatachari, R., Choi, Y., Jeong, S. and Vigneswaran, S., 2019. A critical review on remediation, reuse, and resource recovery from acid mine drainage. Environmental Pollution, 247, pp.1110-1124.

Nejad, M.H., Takdastan, A., Jaafarzadeh, N., Mogadam, M.A. and Mengelizadeh, N., 2013. Removal of orthophosphate from municipal wastewater using chemical precipitation process in Ahvaz wastewater treatment plant, Iran. Asian Journal of Chemistry, 25(5), pp.2565.

Nleya, Y., Simate, G.S. and Ndlovu, S., 2016. Sustainability assessment of the recovery and utilisation of acid from acid mine drainage. Journal of Cleaner Production, 113, pp.17-27.

Nodeh, H.R., Sereshti, H., Afsharian, E.Z. and Nouri, N., 2017. Enhanced removal of phosphate and nitrate ions from aqueous media using nanosized lanthanum hydrous doped on magnetic graphene nanocomposite. Journal of Environmental Management, 197, pp.265-274.

Noor, M.H., Rahman, M., Gazali, A., Kania, N., Rahma, A., Rampun, E.L.A., Pratiwi, A.E. and Elma, M., 2020. Comparison of Phytoremediation and Filtration for Diamond-mine-tailings Water Treatment. Makara Journal of Technology, 24(1), pp.43-52.

Ogunkunle, C.O. and Fatoba, P.O., 2013. Pollution Loads and the Ecological Risk Assessment of Soil Heavy Metals around a Mega Cement Factory in Southwest Nigeria. Polish Journal of Environmental Studies, 22(2), pp.1230-1485.

Olías, M., Cánovas, C.R., Macías, F. and Nieto, J.M., 2017, June. Water resources degradation by acid mine drainage: the Sancho Reservoir (Odiel River Basin, SW Spain). In Proceedings 13th International Mine Water Association Congress, pp. 1389.

Orden, S., Macías, F., Cánovas, C.R., Nieto, J.M., Pérez-López, R. and Ayora, C., 2021. Eco-sustainable passive treatment for mine waters: Full-scale and long-term demonstration. Journal of Environmental Management, 280, pp.111699.

Owa, F.W., 2014. Water pollution: sources, effects, control and management. International Letters of Natural Sciences, 3, 1-6.

Pak, G., Jung, M., Kim, H., Mallari, K.J.B., Chung, G., Kim, S., Kim, Y., Oa, S. and Yoon, J., 2016. Assessment of Metals Loading in an Acid Mine Drainage Watershed. Mine Water and the Environment, 35(1), pp.44-54.

Park, I., Tabelin, C.B., Jeon, S., Li, X., Seno, K., Ito, M. and Hiroyoshi, N., 2019. A review of recent strategies for acid mine drainage prevention and mine tailings recycling. Chemosphere, 219, pp.588-606.

Peleka, E.N. and Deliyanni, E.A., 2009. Adsorptive removal of phosphates from aqueous solutions. Desalination, 245(1-3), pp.357-371.

Pham, T.L. and Bui, M.H., 2020. Removal of nutrients from fertilizer plant wastewater using Scenedesmus sp.: formation of bioflocculation and enhancement of removal efficiency. Journal of Chemistry, 2020.

Pierzynski G.M, Vance G.F and Sims J.T. (2005). Soils and environmental quality: CRC press

Qian, D., Yan, C., Xiu, L. and Feng, K., 2018. The impact of mining changes on surrounding lands and ecosystem service value in the Southern Slope of Qilian Mountains. Ecological complexity, 36, pp.138-148.

Qiao, D., Wang, G., Li, X., Wang, S. and Zhao, Y., 2020. Pollution, sources and environmental risk assessment of heavy metals in the surface AMD water, sediments and surface soils around unexploited Rona Cu deposit, Tibet, China. Chemosphere, 248, p.125988.

Qiao, H., Mei, L., Chen, G., Liu, H., Peng, C., Ke, F., Hou, R., Wan, X. and Cai, H., 2019. Adsorption of nitrate and phosphate from aqueous solution using amine cross-linked tea wastes. Applied Surface Science, 483, pp.114-122.

Qin, J., Cui, X., Yan, H., Lu, W. and Lin, C., 2019. Active treatment of acidic mine water to minimize environmental impacts in a densely populated downstream area. Journal of Cleaner Production, 210, pp.309-316.

Rahaman, M.S., Mavinic, D.S., Meikleham, A. and Ellis, N., 2014. Modeling phosphorus removal and recovery from anaerobic digester supernatant through struvite crystallization in a fluidized bed reactor. Water Research, 51, pp.1-10.

Rai, P.K., Lee, S.S., Zhang, M., Tsang, Y.F. and Kim, K.H., 2019. Heavy metals in food crops: Health risks, fate, mechanisms, and management. Environment International, 125, pp.365-385.

Rakotondrabe, F., Ngoupayou, J.R.N., Mfonka, Z., Rasolomanana, E.H., Abolo, A.J.N. and Ako, A.A., 2018. Water quality assessment in the Bétaré-Oya gold mining area (East-

Cameroon): multivariate statistical analysis approach. Science of The Total Environment, 610, pp.831-844.

Rakotonimaro, T.V., Neculita, C.M., Bussière, B., Benzaazoua, M. and Zagury, G.J., 2017. Recovery and reuse of sludge from active and passive treatment of mine drainage-impacted waters: a review. Environmental Science and Pollution Research, 24(1), pp.73-91.

Rasalingam, S., Peng, R. and Koodali, R.T., 2014. Removal of hazardous pollutants from wastewaters: applications of TiO_2-SiO_2 mixed oxide materials. Journal of Nanomaterials, 214, pp.217- 405

Retka, J., Rzepa, G., Bajda, T. and Drewniak, L., 2020. The Use of Mining Waste Materials for the Treatment of Acid and Alkaline Mine Wastewater. Minerals, 10(12), pp.1061.

Rey, V., Ríos, C.A., Vargas, L.Y. and Valente, T.M., 2020. Use of natural zeolite-rich tuff and siliceous sand for mine water treatment from abandoned gold mine tailings. Journal of Geochemical Exploration, 220, pp.106660.

Rezaie, B. and Anderson, A., 2020. Sustainable resolutions for environmental threat of the acid mine drainage. Science of The Total Environment, 717, pp.137211.

Richard, Y.R., 1989. Operating Experiences of Full‐Scale Biological and Ion‐Exchange Denitrification Plants in France. Water and environment journal, 3(2), pp.154-167.

Rodríguez-Galán, M., Baena-Moreno, F.M., Vázquez, S., Arroyo-Torralvo, F., Vilches, L.F. and Zhang, Z., 2019. Remediation of acid mine drainage. Environmental Chemistry Letters, 17(4), pp.1529-1538.

Rogalla, F., De Larminat, G., Coutelle, J. and Godart, H., 1991. Experience with nitrate-removal methods from drinking water. In nitrate contamination springer, Berlin, Heidelberg, pp. 369-383.

Ronteltap, M., 2009. Phosphorus recovery from source-separated urine through the precipitation of struvite (Doctoral dissertation, ETH Zurich).

Rosli, S.S., Wong, C.Y., Yunus, N.M., Lam, M.K., Show, P.L., Cheng, C.K., Wang, D.K., Da Oh, W. and Lim, J.W., 2020. Optimum interaction of light intensity and CO2 concentration in bioremediating N-rich real wastewater via assimilation into attached microalgal biomass as the feedstock for biodiesel production. Process Safety and Environmental Protection, 141, pp.355-365.

Ruppenthal, S., 2007. Nitrate removal solutions for drinking water: how a flexible approach can deliver reliable results. Journal-American Water Works Association, 99(6), pp.28-30.

Saha, S. and Sinha, A., 2018. A review on treatment of acid mine drainage with waste materials: a novel approach. Global Nest Journal, 20(3), pp.512-528.

Sahu, S., Mallik, L., Pahi, S., Barik, B., Sahu, U.K., Sillanpää, M. and Patel, R.K., 2020. Facile synthesis of poly o-toluidine modified lanthanum phosphate nanocomposite as a superior adsorbent for selective fluoride removal: A mechanistic and kinetic study. Chemosphere, 252, pp.126551.

Sarode, S., Upadhyay, P., Khosa, M.A., Mak, T., Shakir, A., Song, S. and Ullah, A., 2019. Overview of wastewater treatment methods with special focus on biopolymer chitin-chitosan. International Journal of Biological Macromolecules, 121, pp.1086-1100.

Sayadi, M.H., Ahmadpour, N., FALLAHI, C.M. and Rezaei, M.R., 2016. Removal of nitrate and phosphate from aqueous solutions by microalgae: An experimental study. Global Journal of Environmental Science and Management Fall, 2(4), pp. 357- 364.

Sedibe, M., Achilonu, M.C., Tikilili, P., Shale, K. and Ebenebe, P.C., 2017. South African mine effluents: Heavy metal pollution and impact on the ecosystem. International Journal of Chemical Science, 15(4), pp. 198.

Sellner, B.M., Hua, G., Ahiablame, L.M., Trooien, T.P., Hay, C.H. and Kjaersgaard, J., 2019. Evaluation of industrial by-products and natural minerals for phosphate adsorption from subsurface drainage. Environmental Technology, 40(6), pp.756-767.

Sengar, A., Aziz, A., Farooqi, I.H. and Basheer, F., 2018. Development of denitrifying phosphate accumulating and anammox micro-organisms in anaerobic hybrid reactor for removal of nutrients from low strength domestic sewage. Bioresource Technology, 267, pp.149-157.

Shih, R.D., Marcus, S.M., and Gnense, C.A., 1997. Methemoglobinemia attributable to nitrate contamination of potable water through boiler fluid additives-New Jersey, Morb.Mortal Wkly Rep, 46, pp. 202-204.

Silambarasan, S., Logeswari, P., Sivaramakrishnan, R., Incharoensakdi, A., Cornejo, P., Kamaraj, B. and Chi, N.T.L., 2021. Removal of nutrients from domestic wastewater by microalgae coupled to lipid augmentation for biodiesel production and influence of deoiled algal biomass as biofertilizer for Solanum lycopersicum cultivation. Chemosphere, 268, pp.129323.

Simate, G.S. and Ndlovu, S., 2014. Acid mine drainage: Challenges and opportunities. Journal of Environmental Chemical Engineering, 2(3), pp.1785-1803.

Singh, K.P., Singh, V.K., Malik, A. and Basant, N., 2006. Distribution of nitrogen species in groundwater aquifers of an industrial area in alluvial Indo-Gangetic Plains: a case study. Environmental Geochemistry and Health, 28(5), pp.473-485.

Singh, U. and Kausual, R.K., 2013. Treatment of wastewater with low-cost adsorbent a review. VSRD International Journal of Technical & Non-Technical Research, 4, PP. 2319-2216.

Skousen, J., Zipper, C.E., Rose, A., Ziemkiewicz, P.F., Nairn, R., McDonald, L.M. and Kleinmann, R.L., 2017. Review of passive systems for acid mine drainage treatment. Mine Water and the Environment, 36(1), pp.133-153.

Skousen, J.G., Ziemkiewicz, P.F. and McDonald, L.M., 2019. Acid mine drainage formation, control and treatment: Approaches and strategies. The Extractive Industries and Society, 6(1), pp.241-249.

Sole, K.C., Mooiman, M.B. and Hardwick, E., 2018. Ion exchange in hydrometallurgical processing: an overview and selected applications. Separation & Purification Reviews, 47(2), pp.159-178.

Song, H., Zhou, Y., Li, A. and Mueller, S., 2012. Selective removal of nitrate from water by a macroporous strong basic anion exchange resin. Desalination, 296, pp.53-60.

Sribas, G., 2015. Impact of Coal Mining on Environment. European Researcher, 92(3), pp.185-196.

Suh, J., Kim, S.M., Yi, H. and Choi, Y., 2017. An overview of GIS-based modeling and assessment of mining-induced hazards: Soil, water, and forest. International Journal of Environmental Research and Public Health, 14(12), pp.1463.

Sulaiman, A., Othman, A. and Ibrahim, I., 2018. The use of magnesium oxide in acid mine drainage treatment. Materials Today: Proceedings, 5(10), pp.21566-21573.

Sun, Z., Xie, X., Wang, P., Hu, Y. and Cheng, H., 2018. Heavy metal pollution caused by small-scale metal ore mining activities: A case study from a polymetallic mine in South China. Science of the Total Environment, 639, pp.217-227.

Syers, K., Bekunda, M., Cordell, D., Corman, J., Johnston, J., Rosemarin, A. and Salcedo, I., 2011. Phosphorus and food production. UNEP year book, pp.34-45.

Tabelin, C.B., Veerawattananun, S., Ito, M., Hiroyoshi, N. and Igarashi, T., 2017. Pyrite oxidation in the presence of hematite and alumina: I. Batch leaching experiments and kinetics modeling cal-culations. Science of Total Environment, 580, pp. 687-698.

Tarayre, C., De, C.L., Charlier, R., Michels, E., Meers, E., Camargo-Valero, M. and Delvigne, F., 2016. New perspectives for the design of sustainable bioprocesses for phosphorus recovery from waste. Bioresources Technology, 206, pp. 264-274.

Taušová, M., Čulková, K., Domaracká, L., Drebenstedt, C., Muchová, M.S., Koščo, J., Behúnová, A., Drevková, M. and Benčöová, B., 2017. The importance of mining for socio-economic growth of the country. Acta Montanistica Slovaca, 22(4), pp. 359-367.

Tepanosyan, G., Sahakyan, L., Belyaeva, O., Asmaryan, S. and Saghatelyan, A., 2018. Continuous impact of mining activities on soil heavy metals levels and human health. Science of The Total Environment, 639, pp.900-909.

Tomiyama, S., Igarashi, T., Tabelin, C.B., Tangviroon, P. and Ii, H., 2019. Acid mine drainage sources and hydrogeochemistry at the Yatani mine, Yamagata, Japan: A geochemical and isotopic study. Journal of Contaminant Hydrology, 225, pp.103502.

Tutu, H., McCarthy, T.S. and Cukrowska, E., 2008. The chemical characteristics of acid mine drainage with particular reference to sources, distribution and remediation: The Witwatersrand basin, South Africa as a case study. Applied Geochemistry, 23(12), pp. 3666– 3684.

Tyagi, S., Rawtani, D., Khatri, N. and Tharmavaram, M., 2018. Strategies for nitrate removal from aqueous environment using nanotechnology: a review. Journal of Water Process Engineering, 21, pp.84-95.

Ugya, A.Y., Ajibade, F.O. and Ajibade, T.F., 2018. Water pollution resulting from mining activity: an overview, Proceedings of the 2018 Annual Conference of the School of Engineering & Engineering Technology, FUTA, pp. 17-19.

Uludag-Demirer, S. and Othman, M., 2009. Removal of ammonium and phosphate from the supernatant of anaerobically digested waste activated sludge by chemical precipitation, Bioresource Technology, 100(13), 3236-3244.

Usha, M.T., Chandra, T.S., Sarada, R. and Chauhan, V.S., 2016. Removal of nutrients and organic pollution load from pulp and paper mill effluent by microalgae in outdoor open pond. Bioresource Technology, 214, pp.856-860.

Valsami-Jones, E., 2001. Mineralogical controls on phosphorus recovery from wastewaters. Mineralogical magazine, 65(5), pp.611-620.

Van der Linde, M. and Feris, L., 2010. Compendium of South African Environmental Legislation. Pretoria, South Africa: Pretoria University Law Press.

Van Ginkel, C.E., 2011. Eutrophication: Present reality and future challenges for South Africa. Water SA, 37(5), pp.693-702.

Vanotti, M.B., Szogi, A.A., Hunt, P.G., Millner, P.D. and Humenik, F.J., 2007. Development of environmentally superior treatment system to replace anaerobic swine lagoons in the USA. Bioresource Technology, 98(17), pp.3184-3194.

Vikram, S., Yadav, H.L., Srivastav, S.K. and Jamal A., 2017. Overview of Active and Passive Systems for Treating Acid Mine Drainage. International Advanced Research Journal in Science, Engineering and Technology, 4, pp. 2394-1588

Vyawahre, A. and Rai, S., 2016. Acid mine drainage: a case study of an Indian coal mine. International Journal of Scientific Research in Science, Engineering and Technology, 2, pp.1297-1301.

Wan Zuhairi, W.Y., Nur SYuhadah, M.P. and Hazwani, A.M., 2009. Acid mine drainage and heavy metals contamination at abandoned and active mine sites in Pahang. Bulletin of the Geological Society of Malaysia, 55, pp.15 – 20.

Wang, L.P., Ponou, J., Matsuo, S., Okaya, K., Dodbiba, G., Nazuka, T. and Fujita, T., 2013. Integrating sulfidization with neutralization treatment for selective recovery of copper and zinc over iron from acid mine drainage. Minerals Engineering, 45, pp.100-107.

Wang, M., Liang, B., Zhang, W., Chen, K., Zhang, Y., Zhou, H., Cheng, Y., Liu, H., Zhong, X., Li, Y. and Liu, Y., 2019. Dietary lead exposure and associated health risks in Guangzhou, China. International Journal of Environmental Research and Public health, 16(8), pp.1417.

Weiner, E.R. 2008. Applications of environmental aquatic chemistry. CRC Press, Taylor and Francis Group, Florida.

Westholm, L.J., Repo, E. and Sillanpää, M., 2014. Filter materials for metal removal from mine drainage—a review. Environmental Science and Pollution Research, 21(15), pp.9109-9128.

Williams, A.T., Zitomer, D.H. and Mayer, B.K., 2015. Ion exchange-precipitation for nutrient recovery from dilute wastewater. Environmental Science: Water Research & Technology, 1(6), pp.832-838.

Williams, S., 1999. Struvite precipitation in the sludge stream at Slough wastewater treatment plant and opportunities for phosphorus recovery. Environmental Technology, 20(7), pp.743-747.

Win, T.S., Dwiki, S., Hamanaka, A., Sasaoka, T., Shimada, H., Mastumoto, S. and Kusuma, G.J., 2020. Application of Fly Ash and Organic Material as Dry Cover System in Prevention of Acid Mine Drainage Generation. Journal of Geoscience and Environment Protection, 8(5), pp.56-64.

Wright, I.A., Paciuszkiewicz, K. and Belmer, N., 2018. Increased water pollution after closure of Australia’s longest operating underground coal mine: a 13-month study of mine drainage, water chemistry and river ecology. Water, Air, & Soil Pollution, 229(3), pp.1-20.

Wu, H.L., Du, Y.J., Yu, J., Yang, Y.L. and Li, V.C., 2020. Hydraulic conductivity and self-healing performance of Engineered Cementitious Composites exposed to Acid Mine Drainage. Science of The Total Environment, 716, pp.137095.

Wu, K., Li, Y., Liu, T., Huang, Q., Yang, S., Wang, W. and Jin, P., 2019. The simultaneous adsorption of nitrate and phosphate by an organic-modified aluminum-manganese bimetal oxide: Adsorption properties and mechanisms. Applied Surface Science, 478, pp.539-551.

Wuana, R.A., Okieimen, F.E. and Imborvungu, J.A., 2010. Removal of heavy metals from a contaminated soil using organic chelating acids. International Journal of Environmental Science & Technology, 7(3), pp.485-496.

Xue, Y., Hou, H. and Zhu, S., 2009. Characteristics and mechanisms of phosphate adsorption onto basic oxygen furnace slag. Journal of Hazardous Materials, 162(2-3), pp.973-980.

Yadav, H.L. and Jamal, A., 2016. Treatment of acid mine drainage: a general review. International Advanced Research Journal in Science, Engineering and Technology, 3(11), pp.116-122.

Yadav, M., Gupta, R. and Sharma, R.K., 2019. Green and sustainable pathways for wastewater purification. In Advances in Water Purification Techniques, pp. 355-383.

Yan, J., Yuan, W., Liu, J., Ye, W., Lin, J., Xie, J., Huang, X., Gao, S., Xie, J., Liu, S. and Chen, W., 2019. An integrated process of chemical precipitation and sulfate reduction for treatment of flue gas desulphurization wastewater from coal-fired power plant. Journal of Cleaner Production, 228, pp.63-72.

Yang, F., Zhang, S., Sun, Y., Tsang, D.C., Cheng, K. and Ok, Y.S., 2019. Assembling biochar with various layered double hydroxides for enhancement of phosphorus recovery. Journal of Hazardous Materials, 365, pp.665-673.

Yin, Q., Zhang, B., Wang, R. and Zhao, Z., 2017. Biochar as an adsorbent for inorganic nitrogen and phosphorus removal from water: a review. Environmental Science and Pollution Research, 24(34), pp.26297-26309.

Yu, J., Xiang, C., Zhang, G., Wang, H., Ji, Q. and Qu, J., 2019. Activation of lattice oxygen in LaFe (oxy) hydroxides for efficient phosphorus removal. Environmental Science and Technology, 53(15), pp.9073-9080.

Zamani, N., Noshadi, M., Amin, S., Niazi, A. and Ghasemi, Y., 2012. Effect of alginate structure and microalgae immobilization method on orthophosphate removal from wastewater. Journal of Applied Phycology, 24(4), pp.649-656.

Zamparas, M. and Zacharias, I., 2014. Restoration of eutrophic freshwater by managing internal nutrient loads. A review. Science of the Total Environment, 496, pp.551-562.

Zhang, J., Xia, Q., Hong, X., Chen, J. and Liu, D., 2021. Synthesis of layered double hydroxides with nitrate and its adsorption properties of phosphate. Water Science and Technology, 83(1), pp.100-110.

Zhang, X., Tang, S., Wang, M., Sun, W., Xie, Y., Peng, H., Zhong, A., Liu, H., Zhang, X., Yu, H. and Giesy, J.P., 2019. Acid mine drainage affects the diversity and metal resistance gene profile of sediment bacterial community along a river. Chemosphere, 217, pp.790-799.

Zueva, S.B., 2018. Current legislation and methods of treatment of wastewater coming from waste electrical and electronic equipment processing. In Waste Electrical and Electronic Equipment Recycling, pp. 213-240.

CHAPTER THREE

METHODOLOGY

This section seeks to give discussion on the materials and methods which were used to achieve the outlined objectives of this study. A conceptual framework of the methodology, optimization experiments, and characterisation of aqueous and solid samples, geochemical models, and quality control procedures were duly elucidated.

3.1 General methodology

- Calcium hydroxide was utilized for the treatment of MWW with an attempt to remove nitrate and recover phosphate as calcium phosphate.
- Optimization of the proposed methods was carried out to obtain the optimum condition for the treatment of MWW with calcium hydroxide.
- Full characterization of the raw calcium hydroxide and product sludge obtained after the interaction of calcium hydroxide with municipal wastewater was carried out to gain the physio-chemical behaviour.
- Where applicable, modelling of the data (e.g., PHREEQC geochemical modelling) were carried out to point out the mineral phases which are likely to precipitate at a selected pH.
- The obtained product mineral sludge were them utilized for the treatment of acidic effluents and similar procedure as for the treatment of MWW was done for AMD using the sludge.
- Calcium hydroxide and the product sludge were then used (optimized condition) to real wastewater samples to test their applicability from parameters such as recovery.

Figure 3.1 and **Figure 3.2** displays the general flow chart of the experimental order for the removal the synthesis of calcium phosphate from MWW (**paper I**) and treatment of AMD with the synthesised calcium phosphate (**paper II**), respectively.

3.2 Conceptual framework and design

This section highlighted the configuration of the conceptual framework which was utilised to fulfil the objectives of this study using flow chart.

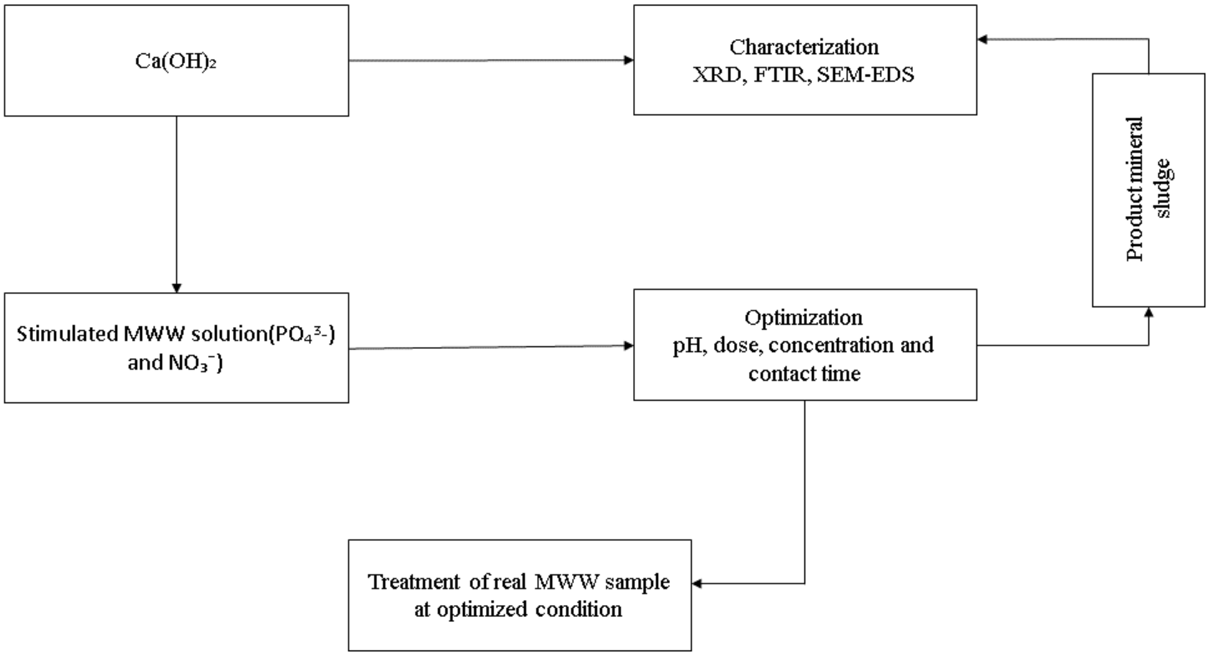

Figure 3. 1. A general scheme for the research methodology for the removal nitrate and synthesis of calcium phosphate from MWW with calcium hydroxide.

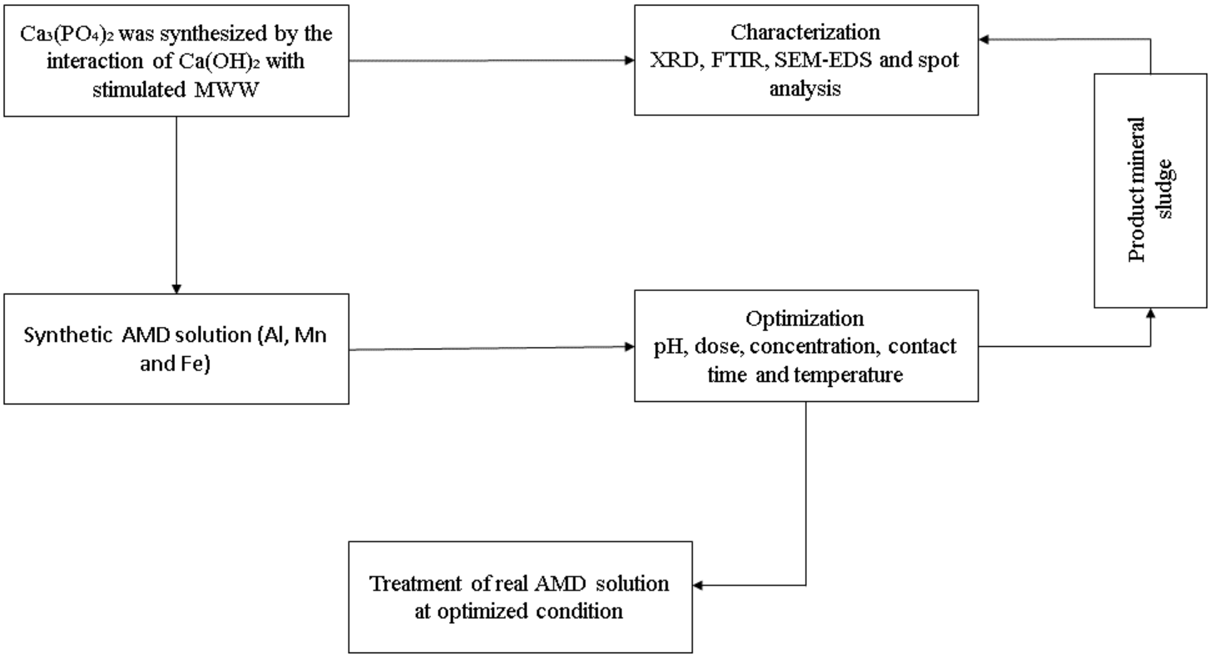

Figure 3. 2. A general scheme for the research methodology for the treatment of AMD with calcium phosphate synthesized from stimulated municipal wastewater.

CHAPTER FOUR

This chapter comprises of **paper I** manuscript prepared for examination. This manuscript is structured into the style requirement of the journal as per the requirements of the journal. This manuscript will be submitted soon. Furthermore, this chapter is dedicated to answer the undermentioned objectives such as (1) evaluation of the treatment of MWW using calcium hydroxide by means of batch approach and exploration of the interaction chemistry thereof, and the processed water quality, (2) Investigation of the mineralogical transformation and chemical characterization of resultant solid residues, and (4) the use of geochemical model to substantiate experimental findings.

Synthesis of calcium phosphate from stimulated municipal wastewater using calcium hydroxide: Experimental and geochemical modelling approach

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Abstract

Excessive discharge of effluents rich in nitrate (NO_3^-) and phosphate (PO_4^{3-}) into water ways is the major factor that causes eutrophication. The development of an effective and low-cost method for the removal of nitrate and phosphate from wastewater is significant nowadays. In this study, calcium hydroxide was utilised for the removal of nitrate and phosphate from municipal wastewater. The primarily quest was to synthesize calcium phosphate that could be utilised for secondary applications. Batch experimental method was utilized to fulfil the goals of this study. The influential parameters effecting the capturing of phosphate were pH, feed dosage, contact time, and initial concentration were evaluated. Characterisation of feed and precipitated solid product were done using the HR-SEM-EDS whilst the mineralogical properties and metals-functional groups were determined using XRD and FTIR techniques, respectively. The obtained results suggested 45 min of equilibration and 0.06 of dosage in 100 mL at 120 rpm of mixing speed are adequate for the synthesis of calcium phosphate. Interaction of calcium hydroxide with municipal wastewater led to the removal efficacy $\geq$ 99% for phosphate and $\leq$ 30% removal efficacy for nitrate. The X-ray diffraction confirmed the formation of new peaks for calcium phosphate. Similarly, the HR-SEM-EDS confirmed the presence of P in the product sludge thus confirming the formation of calcium phosphate. This was further corroborated by the FTIR results and PHREEQC geochemical model. This study confirmed that authentic calcium hydroxide can be successfully utilized for the removal of phosphate ions than nitrate ions from municipal wastewater.

Keywords: Phosphate, nitrate, calcium hydroxide, calcium phosphate, geochemical model, precipitation, wastewater treatment.

4.1 Introduction

Water pollution is currently considered a major problem worldwide and the increase in utilization of limited clean water supplies creates a need for efficient purification (Fazi et al., 2016). Recently, the wastewater treatment industries have discovered the discharge of inorganic anions such as nitrate and phosphate into water bodies which poses a serious threat to the natural environment and to human health (Huong, et al., 2019). Nitrogen and phosphorus are essential macronutrients for plants and animal growth (Sellner et al., 2019). Generally, nitrogen and phosphorus exist in the form of $NH_4^{+,}$ NO_3^{-}, and PO_4^{3-} in the water ways (Ahlström and Cornell, 2018). Due to agricultural drainage, urban storm water runoff, municipal, industrial, and domestic wastewater discharge, a large amount of nitrate and phosphate enter aquatic environments resulting in eutrophication and deterioration of water quality, which has become water pollution problem worldwide (Yin et al., 2018; Boeykens et al., 2017; Yang et al., 2018). In addition, excessive discharge of nitrate ions in drinking water poses serious health problems to humans, such as diarrhea, vomiting, hypertension, spontaneous abortions, respiratory tract infections and methemoglobinemia (blue baby syndrome) (Kumar and Viswanathan, 2020; Qiao et al., 2019). Thus, drinking water contaminated with high concentrations of nitrates and phosphates causes a significant risk to human health (Wu et al., 2019). Currently, the removal of nitrate and phosphate ions from water bodies has received a great interest by many researchers (Gao et al., 2019). Therefore, it is highly important to develop desirable methods which can effectively remove nitrate and phosphate from wastewater prior to their discharge into the aquatic environment.

Various treatment methods for the removal of nitrate and phosphate from wastewaters have been explored including biological process (Chiu et al. 2015), chemical precipitation (Yang et al., 2016), membrane process, electrodialysis (Guedes et al. 2016), phytoremediation (Wu et al. 2015) and adsorption (Fink et al. 2016; Aswin Kumar and Viswanathan, 2017). Consequently, the precipitation method has gained great interest since it is an effective, quick, easy, environmentally friendly, low cost, and suitable at industrial application (Huong et al., 2019).

Thenceforth, there is a seriously need for the use of low-cost precipitants prior to the removal of nitrate and phosphate from water ways. A carbon-based material known as biochar have become effectively used for the removal these nutrients, due to its potential advantages and benefits (Huong et al., 2019). However, most of the current biochar studies are based on biochars which are converted from agricultural residues and biochar coated with calcium for the removal of phosphate (Choi et al., 2018; Wang et al., 2018; Dhillon and Kumar, 2017).

Calcium based materials such as calcium hydroxide, calcium carbonate and magnesite would be more effective for phosphate removal as compared to nitrate since calcium binds phosphate (Sujitha and Ravindhranath, 2017; Han et al., 2017; Li et al., 2019; Darshana Senarathna et al., 2020). Moreover, the addition of calcium hydroxide to the wastewater lead to an increase in pH. It is therefore expected that calcium hydroxide would be highly effective for wastewater treatment for nutrients recovery. The use of calcium hydroxide for the synthesis of calcium phosphate is widely known but the use of PHREEQC geochemical model to substantiate the reported finding has never been explored. Therefore, this is the first study in design and execution to explore the use of calcium hydroxide for the removal of phosphate from aqueous solution.

4.2 Materials and methods

4.2.1 Collection of the samples

The real municipal wastewater sample, rich in phosphate and nitrate, was collected from Rietvlei municipal wastewater treatment plant in Limpopo, South Africa. The treatment sector receives wastewater from several activities from the surrounding area.

4.2.2 Chemicals and reagents

All reagents were of analytical reagent grade and were used as supplied. Reagents and solutions were prepared with 18.2 MΩ-cm deionized water. The adsorbent $Ca(OH)_2$ was purchased from the Merck Group (Merck, Darmstadt, Germany). In addition, KH_2PO_4, KNO_3, NaOH, and HCl were purchased from Sigma-Aldrich (St. Louis, MO, USA).

4.2.3 Preparation of nitrate and phosphate stock solutions

Nitrate and phosphate stock solutions of (1000 mg L^{-1}) was prepared by dissolving appropriate masses of KNO_3 and KH_2PO_4 in distilled water. The stock solution was further diluted to get the desired concentrations of experimental working standard solutions. Mixing and stirring was done to completely dissolve KNO_3 and KH_2PO_4 prior to the chemical treatment of the synthetic solution.

4.2.4 Quality control and quality assurance

Experiments were performed in triplicate, providing similar results, and are reported as mean average values. To ensure reliable, accurate, and high precision results inter laboratory analysis was also undertaken, i.e., for validation and verification purposes.

4.2.5 Batch approach

Batch experiments were conducted by dissolving 0.06 g of calcium hydroxide with 100 mL of the solutions containing known concentration of nitrate and phosphate at room temperature. The pH of the working solutions was adjusted in the range of 2.0 – 11 to optimize the removal process. The experiments were conducted to particularly determine the effects of contact time (5 – 180 min). In addition, the effect of the initial concentration of nitrate and phosphate in the solution was also investigated over the concentration range of 20 – 100 mg L^{-1}. After interacting calcium hydroxide with municipal wastewater, the mixtures were immediately filtered through a 0.20 μm syringe filter. The effects of parameters governing the removal process such as sample pH, feedstock dosage, initial ions concentration and contact time were investigated. The pH of the working solution was adjusted to the desired value by the addition of 0.1M HCl and NaOH. The percentage removal of NO_3^- and PO_4^{3-} from the aqueous solution were calculated according to Equations (4.1).

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} \times 100 \qquad (4.1)$$

Where Co is the initial NO_3^- and PO_4^{3-} concentration in mg L^{-1} while C_e denotes equilibrium concentration in mg L^{-1}.

4.2.6 Characterization

4.2.6.1 Characterisation of aqueous samples

The pH, electrical conductivity (EC) and total dissolved solids (TDS) were monitored using CRISON MM40 portable pH/EC/TDS/Temperature multimeter probe (Shenzhen, China). Aqueous samples were analysed using 850 professional IC Metrohm (Herisau, Switzerland).

4.2.6.2 Characterisation of solid samples

The mineralogical properties were done using X-ray diffraction (XRD), PANalytical X'Pert PRO-diffractometer equipped with Philips PW 1710 Diffractometer with graphite secondary monochromatic source (Almelo, Netherlands). Functional groups analysis were done with Fourier Transform Infrared Spectrometer (FTIR) equipped with Perkin-Elmer Precisely Universal Attenuated Total Reflectance (ATR) sampling accessory with a diamond crystal (Bruker, USA). Morphology, mapping and elemental analysis, was done using a High Resolution (HR)-field emission scanning electron microscope (FESEM) equipped with energy-dispersive X-ray spectroscopy (EDS), Auriga Cobra FIB-FESEM, Carl Zeiss FE-SEM (Oberkochen, Germany).

4.2.5 PHREEQC geochemical modelling

To complement the experimental results and determine the mineral phases that are more likely to be synthesized from the interaction of AMD with the MWW dewatering effluent (MWW thereafter), geochemical modelling was applied. The primary aim was to calculate the saturation indices (SIs) of the mineral phases, based on solution compositions and their respective concentrations. To this end, the geochemical model PHREEQC along with the WATEQ4F chemical speciation model were used. Thenceforth, the chemical species which were more likely to precipitate were determined using the modelled SI numbers. In this case, SI values lower than unity (< -1) denote an under saturated solution, SI values equal to unity (= 1) denote a saturated solution and, lastly, SI values higher than unity (> 1) denote a supersaturated solution.

4.3 Results and discussion

4.3.1 Characterization

4.3.1.1 Mineralogical analysis

The mineralogical properties of calcium hydroxide and product mineral formed after interacting calcium hydroxide with municipal wastewater were determine using X-ray Diffraction (XRD) and are shown in **Figure 4.1a,b**.

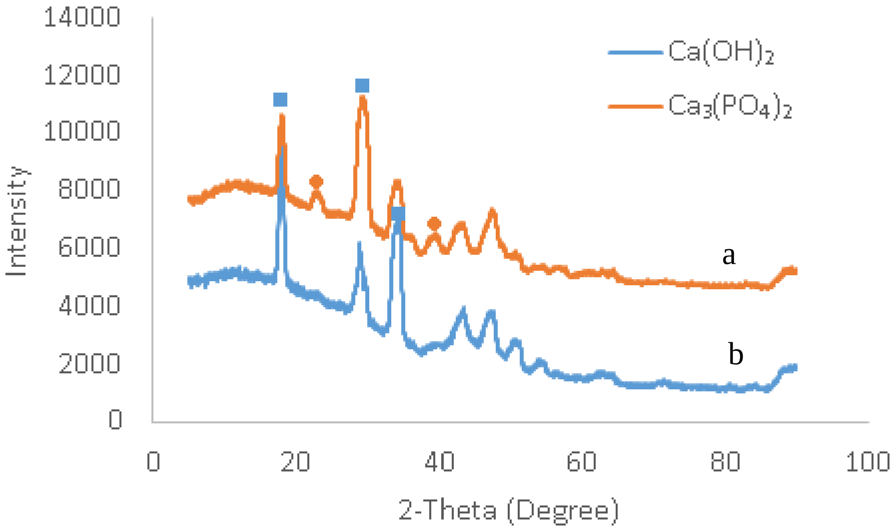


Figure 4. 1: The mineralogical properties of (a) calcined hydroxide and (b) calcium phosphate.

As shown in **Figure 4.1a, b**, it was observed that there was no significant difference on the diffraction patterns peak of the raw calcium hydroxide and the product sludge obtained after the interaction of calcium hydroxide and municipal wastewater. However, the intensity of the peaks at 2θ = 18° and 34° which were assigned to $Ca(OH)_2$ were reduced (**Figure 4.1a**) indicating that the reaction had took place. After 60 min of reaction time, new characteristic peaks appeared at 2θ = 24° and 40° were associated with whitlockite ($Ca_3(PO_4)_2$) (**Figure 4.1b**). This was an indication that phosphate was adsorbed by the feed leading to the formation of calcium phosphate as denoted in equation (4.2).

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \qquad (4.2)$$

These results were similar to those reported by Jingjing et al. (2020). Furthermore, the obtained peaks at 2θ = 24°, and 40° are in good agreement with those reported by Le et al. (2018) and Sani et al. (2020). This further confirmed that the reaction between calcium hydroxide and the wastewater led to the formation of calcium phosphate as denoted by equation (4.2). Since the reaction between calcium hydroxide and the wastewater produced calcium phosphate, it should be noted that the reaction cannot be reversed during the process and the product obtained can be beneficial for soil amendments for agriculture purposes. After all, the occurrence of Ca from calcium hydroxide participated towards the increasing in pH of the wastewater and generating Ca^{2+} and hydroxyl group ions as illustrated by equation (4.3).

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \qquad (4.3)$$

4.3.1.2 Metal-Functional group analysis

Figure 4.2 shows the FTIR spectra of calcium hydroxide before and after reacted with municipal wastewater while **Table 4.1** lists the identified functional groups, their wavenumber (cm^{-1}) and citations for relevant studies dealing with the identified anion and cation functional groups.

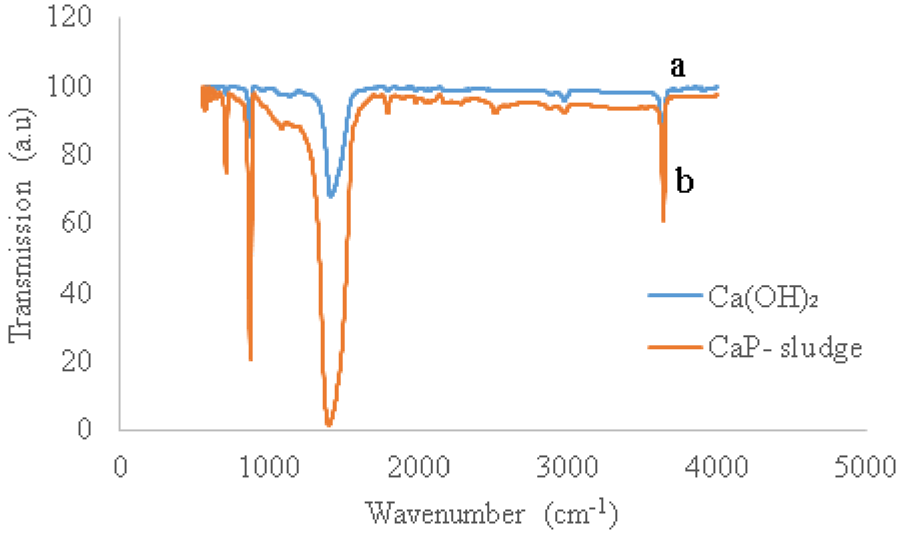


Figure 4. 2: The functional groups of (a) calcium hydroxide and (b) product mineral sludge.

As shown in **Figure 4.2a**, the FTIR spectrum of calcium hydroxide shows the bands at 3642 and 914 cm^{-1} attributed to the free stretching O-H vibration in the Ca(OH)2 crystals. In addition, the bands at 1416 and 874 cm^{-1} are attributed to the vibration of the C-O bond of carbonates. The presence of peak at 876 cm^{-1} band confirms that this spectrum mainly belongs to carbonates. Moreover, this compound has been hydrated and mixed with a low amount of calcite. Furthermore, FTIR spectrum also showed the weak band at 614 cm^{-1}, which was attributed to metal oxide vibration peak for Ca–O stretching. **Figure 4.2b** shows the FTIR spectrum of CaP- sludge obtained after the interaction of stimulated municipal wastewater with calcium hydroxide. As shown in **Figure 4.2b**, the characteristic of OH^{-} bands at 3642 and 712 cm^{-1} and PO_4^{3-} bands at 1798 cm^{-1}. The band at 874 cm^{-1} assigned to HPO_4 group of CaP-sludge product. Additional bands are observed at 712 cm^{-1}, 1406 cm^{-1} 1798 cm^{-1} and 2520 cm^{-1} which do not appear in **Figure 4.2a**. The band at 2520 cm^{-1} and 1406 cm^{-1} was attributed to the carbonate (CO_2^{3-}) derived bands. An increase in intensity of OH^{-} (3642 cm^{-1} and 914 cm^{-1}) related to absorption bands was also observed after interacting calcium hydroxide with stimulated municipal wastewater. **Table 4.1** summarises the anion and cation functional groups of calcium hydroxide and Ca-P mineral sludge. The FTIR results also corroborate the ones obtained by the XRD studies and technique.

Table 4. 1. The identified functional groups of calcium hydroxide and product mineral sludge

Mineral	Wavenumber (cm^{-1})	Functional group	Reference
Calcium hydroxide	914	-OH (Water)	(Blesa et al., 2003; Jamil et al., 2020; Darroudi et al., 2016; Liu et al., 2010)
	3642	-OH (Water)	
	1416	CO_3	
	874	CO_3	
	614	Ca-O	
Ca-P- sludge	874	HPO_4	(Pakravanan et al., 2019; Howard et al., 2020; Jamil et al., 2018; Song et al., 2012)
	1798	PO_3^{3-}	
	2520	CO_3	
	1406	CO_3	
	712	-OH (Water)	
	3642	-OH (Water)	

4.3.1.3 Morphological characteristics

The surface morphology of the raw $Ca(OH)_2$ before and after phosphate and nitrate treatment as field emission-scanning electron microscopy (FE-SEM) micrographs are shown in **Figure 4.3 (a and b)**, respectively. **Figure 4.3a** shows the irregular rough surface with abundant pore structure for the $Ca(OH)_2$ material. This surface may provide more active sites and high adsorption for both phosphate and nitrate and thus, enhancing the ability to release Ca^{2+} and OH^{-}, promoting the formation of phosphate precipitate. Furthermore, the morphological properties of the calcium hydroxide surface were observed to remain the same regardless of the different magnification used, i.e. from 1µm to 100 nm. Interestingly, after phosphate and nitrate treatment, it was clearly observed that the porous structure of the $Ca(OH)_2$ disappeared completely after 60 min of reaction. The structure became round to octagonal nano-sheets with a flower like structure and smashed with moulded smooth surface morphology, which might be the precipitate product of phosphate, nitrate, and calcium (**Figure 4.3b**). The noticeable changes could be observed that the phosphate and nitrate ions were adsorbed onto $Ca(OH)_2$ surface.

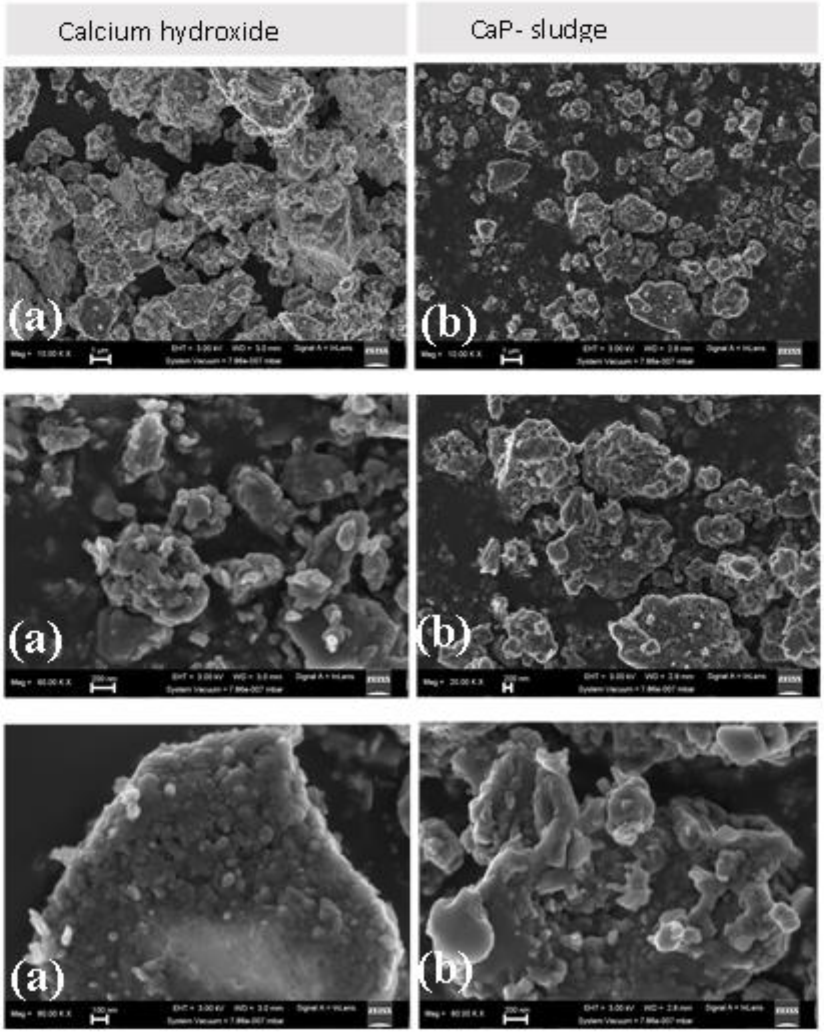
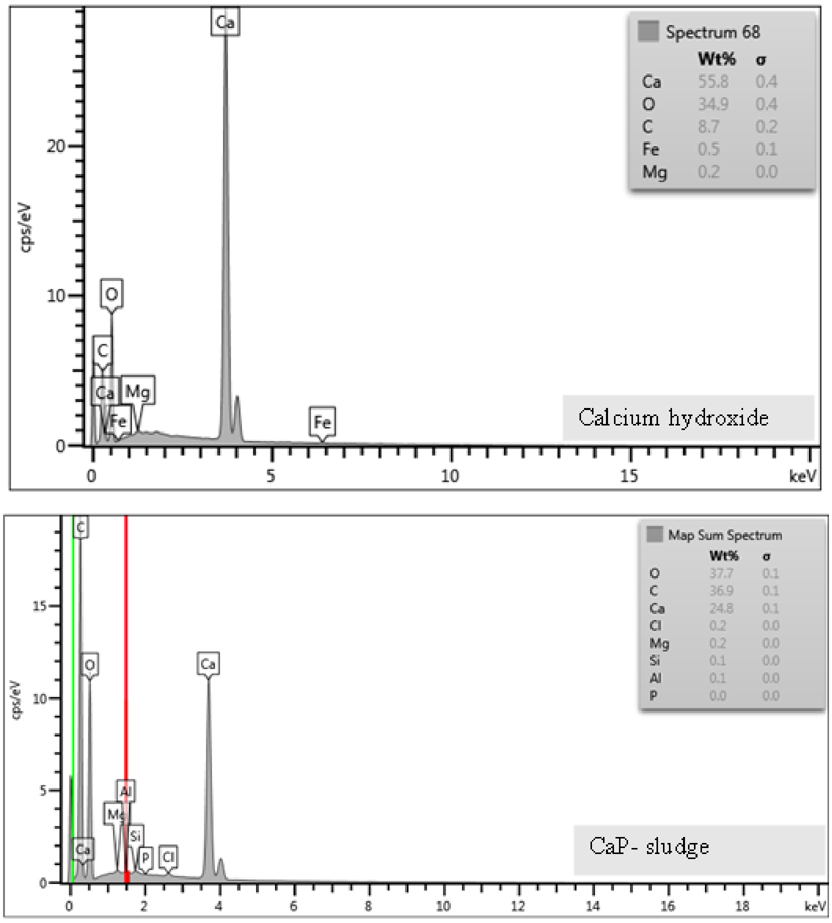


Figure 4. 3: The HR-FESEM images showing the changes in morphological properties of calcium hydroxide and Ca-P-sludge after interaction of calcium hydroxide with stimulated municipal wastewater from lower to higher magnification, i.e. (a) 1 µm, 200 nm and 100nm (b) 1 µm, 200 nm and 100 nm.

4.3.1.4 Elemental composition using EDS

Figure 4.4 shows the elemental composition of calcium hydroxide and CaP-sludge. As shown in **Figure 4.4**, calcium hydroxide comprised of Ca and O as major elements. The presence of Ca further confirms that this will aid in the removal of phosphate from municipal wastewater hence forming Ca-P as the by-product. After interacting calcium hydroxide with municipal wastewater, the product sludge with phosphate was observed in the EDS results. This could be attributed to the formation of calcium phosphate during the interaction of Ca and P in municipal wastewater. Predominant elements were observed to be O and Ca whereas P was present in a small amount. The presence of phosphate in small amount could be attributed to its low concentration utilized during the optimization studies with calcium hydroxide. Traces of other impurities were observed but these could be attributed to other chemicals that were embodied in stimulated municipal wastewater.



Spectrum 68

	Wt%	σ
Ca	55.8	0.4
O	34.9	0.4
C	8.7	0.2
Fe	0.5	0.1
Mg	0.2	0.0

Map Sum Spectrum

	Wt%	σ
O	37.7	0.1
C	36.9	0.1
Ca	24.8	0.1
Cl	0.2	0.0
Mg	0.2	0.0
Si	0.1	0.0
Al	0.1	0.0
P	0.0	0.0

Figure 4. 4: Elemental composition of calcium hydroxide and Ca-P-sludge after reaction of calcium hydroxide with stimulated municipal wastewater.

4.3.1.5 Elemental mapping

To further confirm the elemental composition of calcium hydroxide and the synthesized calcium phosphate, spot-mapping analysis by means of Auriga Cobra FIB- FESEM instrument, which includes an EDS detector, was used. The morphological spot-analysis of calcium hydroxide and synthesized calcium phosphate are shown in **Figure 4.5 – 4.6**.

As shown in **Figure 4.5**, sandy-like structures were observed on the surface of calcium hydroxide. Elemental analysis further indicate that the predominant elements were Ca and O, as well as traces of Mg, Si. Furthermore, the distribution of Mg were also observed to be scattered on the surfaces of calcium hydroxide. This results are also in agreement with the XRD and FTIR results for calcium hydroxide. Therefore, it was concluded that Ca was an instrumental too in increasing the pH of the raw wastewater effluent.

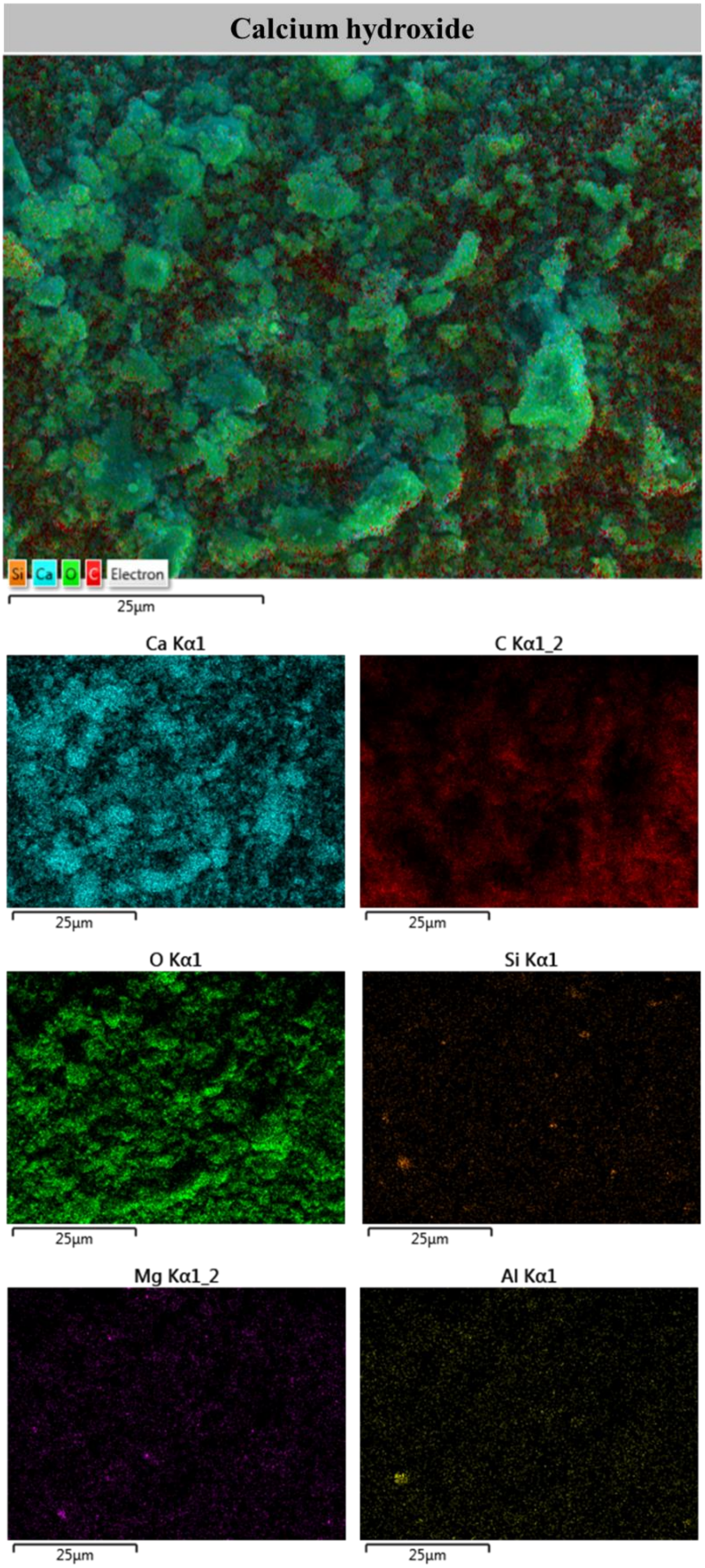


Figure 4. 5: Elemental mapping of calcium hydroxide

As shown in **Figure 4.6**, the crystal clear stoney- like and homogenous crystals were observed after the interaction of calcium hydroxide with municipal wastewater. Furthermore, it was observed that product mineral sludge obtained after the interaction of calcium hydroxide and municipal wastewater was predominated by Ca and O with some traces of Cl, Al, Mg, P and Si. The presence of P on spot analysis confirmed the formation of calcium phosphate. It should be noted that only the soluble component of calcium hydroxide will contribute to the formation of calcium phosphate and the rest will remain in solution. Finally, the availability of Si and Mg suggested the co-precipitation of calcium phosphate with those impurities. The obtained results are aligned with the ones of the XRD and FTIR analysis

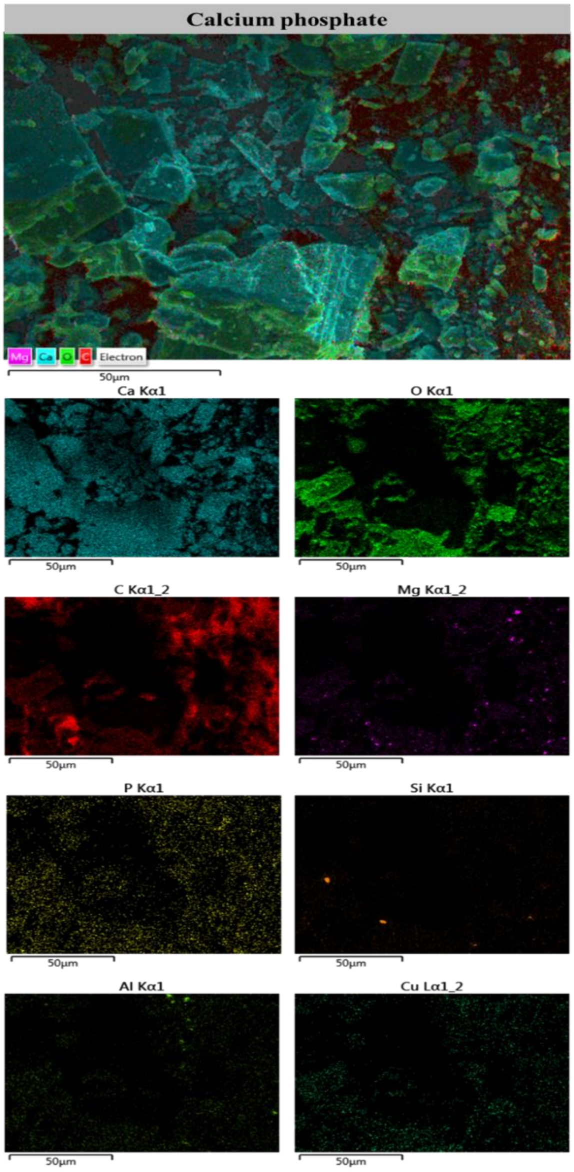


Figure 4. 6: Elemental mapping of synthesized calcium phosphate

4.3.2 PHREEQC geochemical modelling

The modelling results revealed that phosphate existed as oxyanion in aqueous solution with calcium existing as Ca^{2+}, $CaH_2PO_4^{+}$, $CaHCO^{3+}$, $CaPO_4^{-}$, $CaCO_3$ and $CaOH^{+}$ while phosphate existed as $H_2PO_4^{-}$, $CaH_2PO_4^{+}$, $CaHPO_4$, HPO_4^{2-}, $CaPO_4^{-}$, $NaHPO_4^{-}$ and PO_4^{3-} at the maximum pH (12.45) obtained after interaction real municipal wastewater with calcium hydroxide. However, the mineral phases which were predicted to precipitate are shown in **Table 4.2**. Findings from this study corroborated results reported in FTIR, HR-SEM-EDS, and XRD by confirming that calcium phosphate will precipitate from the chemical interaction.

Table 4. 2: Geochemical modelling mineral phase predicted to precipitate

Mineral phase	**SI**	**Log IAP**	**Log KT**
Al(OH)3 (a)	2.14	12.94	10.80
Calcite (b)	-0.14	-8.48	-8.34
CH4	-118.01	-120.87	-2.86
CO2	-0.58	-2.05	-1.47
Hydroxyapatite	9.91	6.48	-3.42
whitlockite	-1.953	-1.932	0.020

4.3.2 Optimization studies

This section will discuss the optimization results for batch experimental studies that were undertaken to determine conditions that are suitable for the scavenging of phosphate for the synthesis of calcium phosphate.

4.3.2.1 Effect of solution pH

Variation in percentage removal of nitrate and phosphate with an increase in solution pH during the treatment of municipal wastewater with calcium hydroxide is shown in **Figure 4.7**.

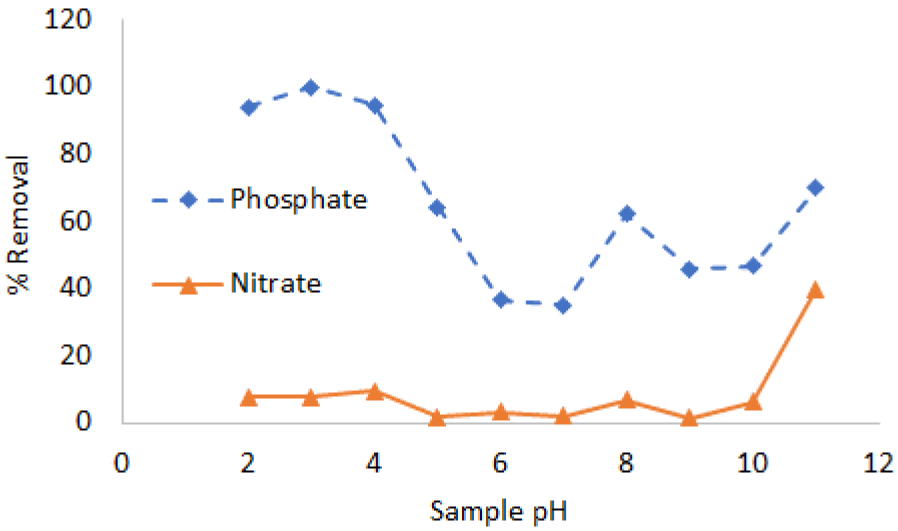


Figure 4. 7: Effect of solution pH on the removal of nitrate and phosphate using calcium hydroxide. (Conditions: Stirring speed = 120 rpm, concentration = 50 mg L^{-1}, feedstock dosage = 0.05 g, contact time = 60 min and room temperature).

As shown in **Figure 4.7**, pH of a solution is an influential parameter during the removal process of chemical species from wastewater as it can significantly affect the physicochemical properties of the precipitant (Calcium hydroxide), nature of phosphate and nitrate species such as H_3PO_4, $H_2PO_4^{-}$, HPO_4^{2-}, PO_4^{3-} and NO_2^{-} which are likely to be present in the solution and even the precipitated product (Fu et al., 2018; Xie et al., 2014). This was also confirmed by PHREEQC geochemical model. Normally, the solubility of calcium hydroxide can be significantly influenced by the pH of solution. This is due to the fact that, at low pH value, the dissolution of Ca^{2+} ions become relatively higher, which slowly decreases with increasing pH (Xiong et al., 2011). For this reason, the dissolved Ca^{2+} ions then initiate to precipitate at pH > 9.0 due to the overload of water with calcium hydroxide. Furthermore, the pH value significantly changes the existing form of phosphate in solutions due to its polyprotic nature. The equilibrium dissociation of phosphate in an aqueous solution with respective pK values is described by equation (4.4) - (4.6).

$$H_3PO_4 \leftrightarrow H_2PO_4^{-} + H^{+} \quad [pK_1 \approx 2.4] \tag{4.4}$$

$$H_2PO_4^{-} + H^{+} \leftrightarrow HPO_4^{2-} + 2H^{+} \quad [pK_1 \approx 7.3] \tag{4.5}$$

$$HPO_4^{2-} + 2H^{+} \leftrightarrow PO_4^{3-} + 3H^{+} \quad [pK_1 \approx 12.3] \tag{4.6}$$

Now, at pH < 2.4, phosphate was present in the form of H_3PO_4 because of solution acidity, and in that way, the precipitation of phosphate in the form of hydroxyapatite or tricalcium phosphate was not possible. In contrast, when pH value is 7.3, the dominant form was mostly $H_2PO_4^-$ and could form a precipitated product. When pH > 7.3, the dominant form of phosphate was HPO_4^{2-} and PO_4^{3-} which can be the form of phosphate most suited for the nucleation with Ca^{2+} ions to form the precipitated product (Xing et al., 2020). Furthermore, it was observed in **Figure 4.7** that phosphate removal was decreasing with an increase in pH from the lowest at pH 2.0 and the highest at pH 4.0 and slowly increased from pH 7.0 to 11.0. This could be attributed to the fact that phosphate removal is linked to the Ca^{2+} ions dissolution from calcium hydroxide, which then reacts with the phosphate species present in the solution (Yuan et al., 2015). As the pH value was >7.3, HPO_4^{2-} and PO_4^{3-} was the dominant specie in the solution. According to Yan et al. (2007), precipitation of calcium phosphate is the leading mechanism at higher pH value. This control takes place by the dissolution of Ca^{2+} from the calcium hydroxide, and Ca^{2+} will then reacts with HPO_4^{2-} to form calcium phosphate. According to dos Reis et al. (2020), the concentration of dissolved Ca^{2+} decreases as the initial pH increases, which enhances calcium phosphate precipitation. The solubility of hydroxyapatite and tricalcium phosphate usually follow the behaviour like that of calcium hydroxide. Its solubility is very high at low pH, which slowly decreases and almost becomes insoluble at pH > 7.3 with $Ksp \sim 10^{-44.33}$ and $Ksp \sim 10^{-28.92}$ at room temperature (Teoh et al., 2016). This is the reason that even with high solubility of calcium hydroxide at low pH, hydroxyapatite and tricalcium phosphate cannot be precipitated. In the case of nitrate, the removal efficiency increased as the initial pH were increased from 2.0 to 11. This was ascribed by the fact that the calcium hydroxide surface would have been highly protonated in a highly acidic media and the active sites on the surface would be surrounded by more H^+ (Qiao et al., 2019). Also, under highly acidic condition, some nitrate might have been converted into HNO_3 which reduced the removal of nitrate. Based on the results, pH 10 was taken as the optimal for preceding experiments.

4.3.2.2 Effect of the feedstock dosage

Variation in percentage removal of nitrate and phosphate with an increase dosage during the treatment of municipal wastewater with calcium hydroxide is shown in **Figure 4.8**.

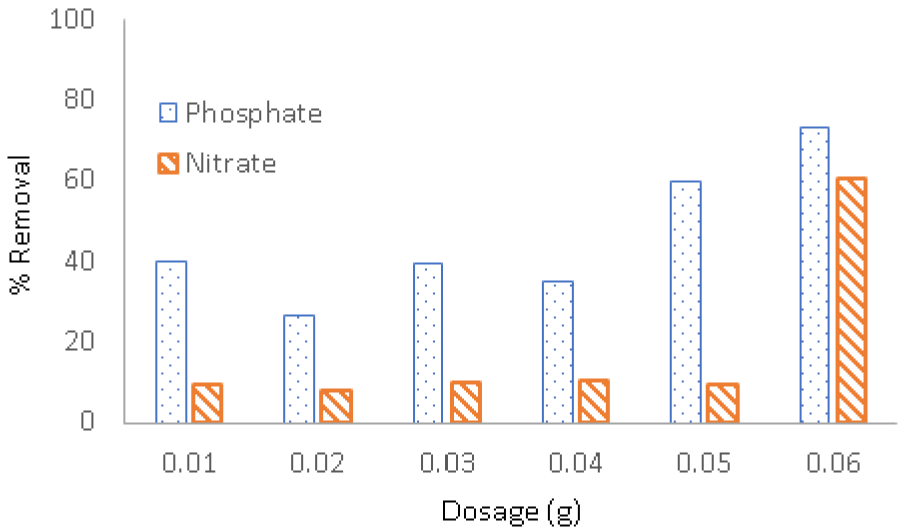


Figure 4. 8: Effects of the feedstock dose on removal of nitrate and phosphate. (Conditions: Stirring speed = 120 rpm, concentration = 50 mg L^{-1}, pH = 10, contact time = 60 min and room temperature).

The variation of calcium hydroxide dose on the removal of nitrate and phosphate from wastewater are demonstrated in **Figure 4.8**. It was observed that increasing the quantity of calcium hydroxide from 0.01 - 0.06 g led to an increase on the percentage removal of nitrate and phosphate from 9.5% to 29.4% and 39.8% to 74.3%, respectively. The dosage dependency can be explained by the fact that an increase in calcium hydroxide dosage resulted in the increased solution pH, hence enhancing the precipitation process (Guan et al., 2020; Nodeh et al., 2017). Therefore, calcium hydroxide could be considered as a material with high removal performance towards phosphate than nitrate. This could be associated with the existence of important available active sites for electrostatic interaction and the presence of high calcium ions contents that could enhance the precipitation of calcium phosphate (Haddad et al., 2018) in the form $Ca_3(PO4)_2$ with the ions Ca^{2+} and OH^- as indicated from equation (4.2) and (4.3). In addition, it was also observed that the phosphate removal reached 39.8% at the dose of 0.01 g, which indicated that the calcium hydroxide had a strong affinity for phosphate. Similar results were presented by Liao et al. (2020) using calcined Mg-Al layered double hydroxides. The optimal dose was selected to be 0.06 g for the subsequent experiments.

4.3.2.3 Effect of chemical species concentration

Variation in percentage removal of nitrate and phosphate with an increase in initial concentration during the treatment of municipal wastewater with calcium hydroxide is shown in **Figure 4.9**

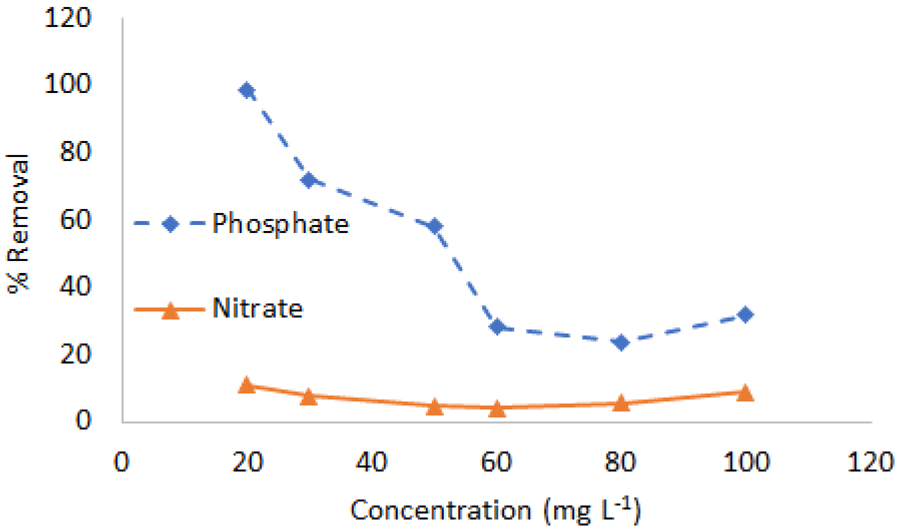


Figure 4. 9: Effect of initial concentration of nitrate and phosphate using calcium hydroxide. (Conditions: Stirring speed = 120 rpm, pH = 10, Feedstock dose = 0.06 g, contact time = 60 min and room temperature).

As shown in **Figure 4.9**, it was observed that the percentage removal of phosphate and nitrate were decreasing as the concentration was increasing. This could be explained by the insufficient dosage which was used to provide high removal at high concentration. The removal of phosphate decreased from 98.7% to 31.9%, while that of nitrate decreased from 10.8 to 8.8% when the inlet concentration of phosphate was increased from 20 to 100 mg L^{-1} in the solution. The high removal efficiency of phosphate at low concentration indicated that the precipitation of calcium phosphate was effectively crystallized, however, the low dosage of Ca led to low efficacy in higher concentration. This could be attributed to the depletion of Ca suitable for phosphate adsorption or binding. A low initial phosphate concentration enhanced the supersaturation index and increased the removal efficiency (Xiong et al., 2011). Similar results were obtained by Karthikeyan and Meenakshi (2020) using surfactant-assisted biopolymeric hybrid membrane. As such, 20 mg L^{-1} was chosen to be the optimal and used for the preceding experiments.

4.3.2.4 Effect of contact time

Variation in percentage removal of nitrate and phosphate with an increase in contact time during the treatment of municipal wastewater with calcium hydroxide is shown in **Figure 4.10**.

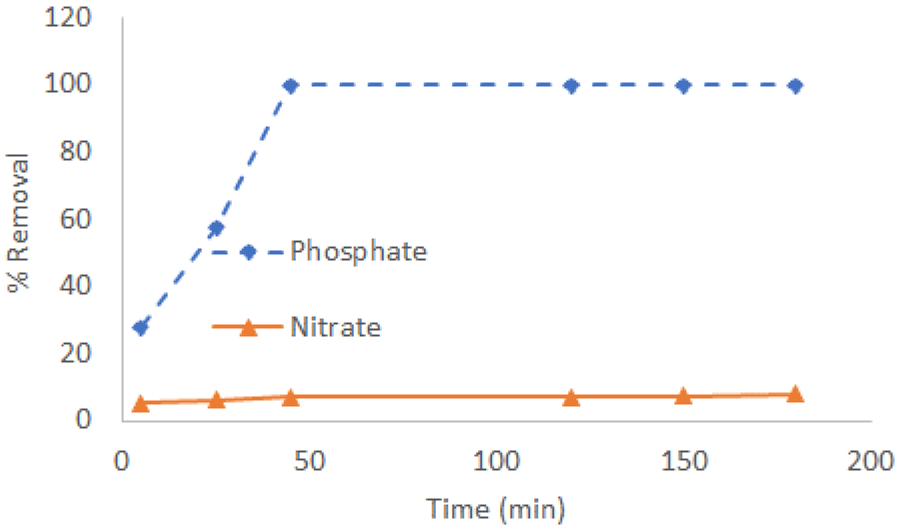


Figure 4. 10: Effect of contact time on the removal of nitrate and phosphate using calcium hydroxide. (Conditions; Stirring speed = 120 rpm, concentration = 20 mg L^{-1}, pH = 10, adsorbent dosage = 0.06 g and room temperature).

The performance of the calcium hydroxide on the removal of phosphate and nitrate as a function of time were investigated from 5 to 180 min as presented in **Figure 4.10**. It was observed that phosphate removal rates were rapid during the initial 30 min and then gradually reached equilibrium conditions in approximately 45 min. The rapid uptake could be due to the wide accessibility of calcium hydroxide surface area for phosphate ions contact to promote chemical reaction. At this time, the percentage removal was 7.8% and 99.9% for nitrate and phosphate, respectively. Further increase in contact time has no significance increase on the percentage removal of both nitrate and phosphate. The removal of nitrate by the calcium hydroxide was not effective as the removal efficiency was very little even after 180 min of shaking as compared to that of phosphate which were quickly removed and attained equilibrium at 45 min. Calcium hydroxide possesses high percentage removal towards phosphate than nitrate. The experimental results indicated that the percentage removal attained equilibrium stage, and this might be explained by the vacant site of the calcium hydroxide being completely occupied (Huanhuan et al., 2019; Mohammadi et al., 2019). Similar results were presented by Karthikeyan et al. (2019) on the removal of phosphate and nitrate ions from aqueous solution using La^{3+} incorporated chitosan biopolymeric matrix membrane. Therefore, 45 min was chosen as optimum and used for subsequent experiments.

4.3.2.5 Treatment of MWWTPs at optimized conditions

The feed and product water constituents for municipal wastewater are reported in **Table 4.3**.

Table 4. 3: The feed and product water constituents for treated municipal wastewater.

Parameter	SANS 241	Influents	Effluents	Treated water
pH	≥ 5 to ≤ 9.7	6.67	7.13	12.45
TDS (mg L^{-1})	≤ 1200	884	701	337
EC (µS m^{-1})	≤ 170	1473	1169	690
Fluoride (mg L^{-1})	≤ 1.5	14.87	0.870	bdl
Chloride (mg L^{-1})	≤ 200	81.91	45.73	bdl
Nitrate (mg L^{-1})	≤ 11	1736	1509	292.3
Phosphate (mg L^{-1})	≤ 0.25	41.33	32.30	bdl
Sulphate (mg L^{-1})	≤ 250	55.68	36.60	28.39

bdl- below detection limit

As shown in **Table 4.3**, there was an effective removal of pollutants from municipal wastewater effluents using calcium hydroxide at optimised conditions. It was observed that the pH increased from 7.13 to 12.45 after the addition of calcium hydroxide, suggesting that there was a chemical reaction which was taking place that led to an increase in pH. Total dissolved solids (TDS) and electric conductivity (EC) were observed to decrease after contacting municipal wastewater effluents with calcium hydroxide which indicated that there was attenuation of chemical species from the aqueous solution to the sludge during treatment process. Phosphate was removed from 32.30 mg L^{-1} to below detection limit which confirmed a > 99% removal efficiency, and a possible formation of calcium phosphate. The performance of calcium hydroxide toward nitrate was not effective enough compared to phosphate where the removal decreased from 1509 to 292.3 mg L^{-1} (80.63% removal efficiency) which were still above the acceptable level in water. Furthermore, sulphate was also reduced from 36.60 to 28.39 mg L^{-1}, thus suggesting the possible formation of gypsum. Based on the results, it can be concluded that calcium hydroxide will be a good applicant for the removal of phosphate than nitrate from aqueous solution. However, some contaminants were observed to surpass SANS 241 requirements after treatment with calcium hydroxide signifying that there is a necessity for a secondary treatment process unless the ultimate target is to discharge the treated water to the neighbouring river.

4.4 Conclusions

The findings from study confirmed the feasibility of removing phosphate and nitrate from municipal wastewater. However, nitrate was not effectively removed from municipal wastewater by calcium hydroxide. The removal of phosphate and nitrate was done at solid ratio 0.05: 100 mL of calcium hydroxide and municipal wastewater. The optimum conditions were observed to be 45 minutes of equilibration and 0.06 g of dosage in 100 mL at 120 rpm of mixing speed. Addition of calcium hydroxide in municipal wastewater led to close to 99% removal efficacy for phosphate and close to 30% removal efficacy of nitrate. XRD confirmed the removal of phosphate and nitrate. The pH was observed to be ≥ 9.0 and this was suitable for attenuation of calcium phosphate. The removal of phosphate from municipal wastewater was observed to be technically viable than that of nitrate. Similarly, PHREEQC geochemical model confirmed the removal of phosphate as calcium phosphate and this has corroborated the XRD, HR-SEM-EDS, and FTIR results. Thus, this technology could be employed for the precipitation of phosphate from municipal wastewater effluents for the effective and sustainable management of wastewater effluents. This will minimize the footprints of eutrophication in receiving water bodies and other different spheres of the environment. In light of the above, future research should focus on the development of a low-cost method that could effectively remove nitrate from water matrices.

REFERENCES

REFFERENCES

Ahlström, H. and Cornell, S.E., 2018. Governance, polycentricity and the global nitrogen and phosphorus cycles. Environmental Science & Policy, 79, pp.54-65.

Berkessa, Y.W., Mereta, S.T. and Feyisa, F.F., 2019. Simultaneous removal of nitrate and phosphate from wastewater using solid waste from factory. Applied Water Science, 9(2), pp.28.

Blesa, M.J., Miranda, J.L. and Moliner, R., 2003. Micro-FTIR study of the blend of humates with calcium hydroxide used to prepare smokeless fuel briquettes. Vibrational Spectroscopy, 33(1-2), pp.31-35.

Boeykens, S.P., Piol, M.N., Legal, L.S., Saralegui, A.B. and Vázquez, C., 2017. Eutrophication decrease: phosphate adsorption processes in presence of nitrates. Journal of Environmental Management, 203, pp.888-895.

Choi, Y.K., Jang, H.M., Kan, E., Wallace, A.R., Sun, W., Choi, Y.K., Jang, H.M., Kan, E., Wallace, A.R. and Sun, W., 2018. Adsorption of phosphate in water on a novel calcium hydroxide-coated dairy manure-derived biochar. Environmental Engineering Research, 24(3), pp.434-442.

Darroudi, M., Bagherpour, M., Hosseini, H.A. and Ebrahimi, M., 2016. Biopolymer-assisted green synthesis and characterization of calcium hydroxide nanoparticles. Ceramics International, 42(3), pp.3816-3819.

Darshana Senarathna, D.D.T.T., Namal Abeysooriya, K.H.D., Dunuweera, S.P., Ekanayake, B.P.K., Wijenayake, W.M.H.K. and Rajapakse, R.M.G., 2020. Removal of Phosphate from Aqueous Solutions Using Chemically Synthesized Vaterite Polymorph of Porous Calcium Carbonate Nanoparticles under Optimized Conditions. Journal of Nanomaterials, 2020.

Dhillon, A. and Kumar, D., 2017. Dual adsorption behaviour of fluoride from drinking water on Ca-Zn (OH) 2CO3 adsorbent. Surfaces and Interfaces, 6, pp.154-161.

dos Reis, G.S., Cazacliu, B.G., Correa, C.R., Ovsyannikova, E., Kruse, A., Sampaio, C.H., Lima, E.C. and Dotto, G.L., 2020. Adsorption and recovery of phosphate from aqueous solution by the construction and demolition wastes sludge and its potential use as phosphate-based fertiliser. Journal of Environmental Chemical Engineering, 8(1), pp.103605.

Dunets, C.S. and Zheng, Y., 2014. Removal of phosphate from greenhouse wastewater using hydrated lime. Environmental Technology, 35(22), pp.2852-2862.

Fan, C. and Zhang, Y., 2018. Adsorption isotherms, kinetics and thermodynamics of nitrate and phosphate in binary systems on a novel adsorbent derived from corn stalks. Journal of Geochemical Exploration, 188, pp.95-100.

Fazi, S., Amalfitano, S., Casentini, B., Davolos, D., Pietrangeli, B., Crognale, S., Lotti, F. and Rossetti, S., 2016. Arsenic removal from naturally contaminated waters: a review of methods combining chemical and biological treatments. Rendiconti Lincei, 27(1), pp.51-58.

Fink, J.R., Inda, A.V., Bavaresco, J., Barrón, V., Torrent, J. and Bayer, C., 2016. Adsorption and desorption of phosphorus in subtropical soils as affected by management system and mineralogy. Soil and Tillage Research, 155, pp.62-68.

Fu, H., Yang, Y., Zhu, R., Liu, J., Usman, M., Chen, Q. and He, H., 2018. Superior adsorption of phosphate by ferrihydrite-coated and lanthanum-decorated magnetite. Journal of Colloid and Interface Science, 530, pp.704-713.

Gao, Q., Wang, C.Z., Liu, S., Hanigan, D., Liu, S.T. and Zhao, H.Z., 2019. Ultrafiltration membrane microreactor (MMR) for simultaneous removal of nitrate and phosphate from water. Chemical Engineering Journal, 355, pp.238-246.

Guan, T., Kuang, Y., Li, X., Fang, J., Fang, W. and Wu, D., 2020. The recovery of phosphorus from source-separated urine by repeatedly usable magnetic Fe_3O_4@ ZrO_2 nanoparticles under acidic conditions. Environment International, 134, pp.105–322.

Haddad, K., Jellali, S., Jeguirim, M., Trabelsi, A.B.H., Limousy, L., 2018. Investigations on phosphorus recovery from aqueous solutions by biochars derived from magnesium-pretreated cypress sawdust. Journal of Environmental Management. 216, 305–314.

Han, C., Lalley, J., Iyanna, N. and Nadagouda, M.N., 2017. Removal of phosphate using calcium and magnesium-modified iron-based adsorbents. Materials Chemistry and Physics, 198, pp.115-124.

He, Y., Lin, H., Dong, Y., Li, B., Wang, L., Chu, S., Luo, M. and Liu, J., 2018. Zeolite supported Fe/Ni bimetallic nanoparticles for simultaneous removal of nitrate and phosphate: synergistic effect and mechanism. Chemical Engineering Journal, 347, pp.669-681.

Howard, J., Gardner, L., Saifee, Z., Geleil, A., Nelson, I., Colombo, J.S., Naleway, S.E. and Carlson, K., 2020. Synthesis and characterization of novel calcium phosphate glass-derived cements for vital pulp therapy. Journal of Materials Science: Materials in Medicine, 31(1), pp.1-12.

Huang, H., Liu, J., Zhang, P., Zhang, D. and Gao, F., 2017. Investigation on the simultaneous removal of fluoride, ammonia nitrogen and phosphate from semiconductor wastewater using chemical precipitation. Chemical Engineering Journal, 307, pp.696-706.

Huong, P.T., Jitae, K., Giang, B.L., Nguyen, T.D. and Thang, P.Q., 2019. Novel lanthanum-modified activated carbon derived from pine cone biomass as ecofriendly bio-sorbent for removal of phosphate and nitrate in wastewater. Rendiconti Lincei. Scienze Fisiche e Naturali, 30(3), pp.637-647.

Jamil, M., Elouahli, A., Abida, F., Khallok, H., Gourri, E., Kheribech, A. and Hatim, Z., 2020. Development of Triphasic Hydroxyapatite/(α and β)-Tricalcium Phosphate Based Composites by Sintering Powder of Calcium-Apatite in the Presence of Montmorillonite. Journal of Inorganic and Organometallic Polymers and Materials, 30, pp.1-10.

Jamil, M., Elouatli, B., Khallok, H., Elouahli, A., Gourri, E., Ezzahmouly, M., Abida, F. and Hatim, Z., 2018. Silicon substituted hydroxyapatite: preparation with solid-state reaction, characterization and dissolution properties. Journal of Material and Environmental Science, 9(8), pp.2322.

Kalaruban, M., Loganathan, P., Kandasamy, J., Naidu, R. and Vigneswaran, S., 2017. Enhanced removal of nitrate in an integrated electrochemical-adsorption system. Separation and Purification Technology, 189, pp.260-266.

Karthikeyan, P. and Meenakshi, S., 2020. Removal of toxic ions from aqueous solutions by: Synthesis, characterization and toxic ions removal performance. Journal of Environmental Chemical Engineering, 8(3), pp.103717

Kumar, I.A. and Viswanathan, N., 2020. Fabrication of zirconium (IV) cross-linked alginate/kaolin hybrid beads for nitrate and phosphate retention. Arabian Journal of Chemistry, 13(2), pp.4111-4125.

Li, C., Yu, Y., Li, Q., Zhong, H. and Wang, S., 2019. Kinetics and equilibrium studies of phosphate removal from aqueous solution by calcium silicate hydrate synthesized from electrolytic manganese residue. Adsorption Science & Technology, 37(7-8), pp.547-565.

Li, J., Fang, X., Yang, M., Tan, W., Zhang, H., Zhang, Y., Li, G. and Wang, H., 2020. The adsorption properties of functionalization vetiver grass-based activated carbon: the simultaneous adsorption of phosphate and nitrate. Environmental Science and Pollution Research, pp.1-11.

Liao, W., Liu, X.P., Li, H.Q. and Yang, P., 2020. Simultaneous Removal of Phosphate and Nitrate on Calcined Mg-Al Layered Double Hydroxides. Polish Journal of Environmental Studies, 29(1), pp 187–195.

Lin, J., Jiang, B. and Zhan, Y., 2018. Effect of pre-treatment of bentonite with sodium and calcium ions on phosphate adsorption onto zirconium-modified bentonite. Journal of Environmental Management, 217, pp.183-195.

Liu, T., Zhu, Y., Zhang, X., Zhang, T., Zhang, T. and Li, X., 2010. Synthesis and characterization of calcium hydroxide nanoparticles by hydrogen plasma-metal reaction method. Materials Letters, 64(23), pp.2575-2577.

Luo, W., Huang, Q., Zhang, X., Antwi, P., Mu, Y., Zhang, M., Xing, J., Chen, H. and Ren, S., 2020. Lanthanum/Gemini surfactant-modified montmorillonite for simultaneous removal of phosphate and nitrate from aqueous solution. Journal of Water Process Engineering, 33, pp.101036.

Luo, W., Phan, H.V., Xie, M., Hai, F.I., Price, W.E., Elimelech, M. and Nghiem, L.D., 2017. Osmotic versus conventional membrane bioreactors integrated with reverse osmosis for water reuse: biological stability, membrane fouling, and contaminant removal. Water Research, 109, pp.122-134.

Manjunath, S.V. and Kumar, M., 2018. Evaluation of single-component and multi-component adsorption of metronidazole, phosphate and nitrate on activated carbon from Prosopıs julıflora. Chemical Engineering Journal, 346, pp.525-534.

Mitrogiannis, D., Psychoyou, M., Baziotis, I., Inglezakis, V.J., Koukouzas, N., Tsoukalas, N., Palles, D., Kamitsos, E., Oikonomou, G. and Markou, G., 2017. Removal of phosphate from aqueous solutions by adsorption onto $Ca(OH)_2$ treated natural clinoptilolite. Chemical Engineering Journal, 320, pp.510-522.

Mohammadi, E., Daraei, H., Ghanbari, R., Athar, S.D., Zandsalimi, Y., Ziaee, A., Maleki, A. and Yetilmezsoy, K., 2019. Synthesis of carboxylated chitosan modified with ferromagnetic nanoparticles for adsorptive removal of fluoride, nitrate, and phosphate anions from aqueous solutions. Journal of Molecular Liquids, 273, pp.116-124.

Nodeh, H.R., Sereshti, H., Afsharian, E.Z. and Nouri, N., 2017. Enhanced removal of phosphate and nitrate ions from aqueous media using nanosized lanthanum hydrous doped on magnetic graphene nanocomposite. Journal of Environmental Management, 197, pp.265-274

Pakravanan, K., Rezaee Roknabadi, M., Farzanegan, F., Hashemzadeh, A. and Darroudi, M., 2019. Amorphous calcium phosphate nanoparticles-based mouthwash: preparation, characterization, and anti-bacterial effects. Green Chemistry Letters and Reviews, 12(3), pp.278-285.

Qiao, H., Mei, L., Chen, G., Liu, H., Peng, C., Ke, F., Hou, R., Wan, X. and Cai, H., 2019. Adsorption of nitrate and phosphate from aqueous solution using amine cross-linked tea wastes. Applied Surface Science, 483, pp.114-122.

Sellner, B.M., Hua, G. and Ahiablame, L.M., 2019. Fixed bed column evaluation of phosphate adsorption and recovery from aqueous solutions using recycled steel byproducts. Journal of Environmental Management, 233, pp.595-602.

Shamshiri, A., Alimohammadi, V., Sedighi, M., Jabbari, E. and Mohammadi, M., 2020. Enhanced removal of phosphate and nitrate from aqueous solution using novel modified natural clinoptilolite nanoparticles: process optimization and assessment. International Journal of Environmental Analytical Chemistry, 203, pp.1-20.

Song, C.W., Kim, T.W., Kim, D.H., Jin, H.H., Hwang, K.H., Lee, J.K., Park, H.C. and Yoon, S.Y., 2012. In situ synthesis of silicon-substituted biphasic calcium phosphate and their performance in vitro. Journal of Physics and Chemistry of Solids, 73(1), pp.39-45.

Sowmya, A. and Meenakshi, S., 2014. Zr (IV) loaded cross-linked chitosan beads with enhanced surface area for the removal of nitrate and phosphate. International Journal of Biological Macromolecules, 69, pp.336-343.

Sujitha, R. and Ravindhranath, K., 2017. Extraction of phosphate from polluted waters using calcium alginate beads doped with active carbon derived from A. aspera plant as adsorbent. Journal of Analytical Methods in Chemistry, 2017.

Teoh, Y.Y., Athanassiadis, B. and Walsh, L.J., 2016. The influence of aqueous and PEG 400 solvent vehicles on hydroxyl ion release from calcium hydroxide medicaments. International Dentistry, 11, pp.42-50.

Wang, S., Kong, L., Long, J., Su, M., Diao, Z., Chang, X., Chen, D., Song, G. and Shih, K., 2018. Adsorption of phosphorus by calcium-flour biochar: Isotherm, kinetic and transformation studies. Chemosphere, 195, pp.666-672.

Wu, H., Zhang, J., Ngo, H.H., Guo, W., Hu, Z., Liang, S., Fan, J. and Liu, H., 2015. A review on the sustainability of constructed wetlands for wastewater treatment: design and operation. Bioresource Technology, 175, pp.594-601.

Wu, K., Li, Y., Liu, T., Huang, Q., Yang, S., Wang, W. and Jin, P., 2019. The simultaneous adsorption of nitrate and phosphate by an organic-modified aluminum-manganese bimetal oxide: Adsorption properties and mechanisms. Applied Surface Science, 478, pp.539-551.

Xie, J., Wang, Z., Lu, S., Wu, D., Zhang, Z. and Kong, H., 2014. Removal and recovery of phosphate from water by lanthanum hydroxide materials. Chemical Engineering Journal, 254, pp.163-170.

Xing, B., Ouyang, M., Graham, N. and Yu, W., 2020. Enhancement of phosphate adsorption during mineral transformation of natural siderite induced by humic acid: Mechanism and application. Chemical Engineering Journal, 393, p.124730.

Xiong, J., Qin, Y., Islam, E., Yue, M., Wang, W., 2011. Phosphate removal from solution using powdered freshwater mussel shells. Desalination, 276, pp. 317−321.

Yamashita, T., Aketo, T., Minowa, N., Sugimoto, K., Yokoyama, H., Ogino, A. and Tanaka, Y., 2013. Simultaneous removal of colour, phosphorus and disinfection from treated wastewater using an agent synthesized from amorphous silica and hydrated lime. Environmental Technology, 34(8), pp.1017-1025.

Yan, J., Kirk, D.W., Jia, C.Q. and Liu, X., 2007. Sorption of aqueous phosphorus onto bituminous and lignitous coal ashes. Journal of Hazardous Materials, 148(1-2), pp.395-401.

Yang, Q., Wang, X., Luo, W., Sun, J., Xu, Q., Chen, F., Zhao, J., Wang, S., Yao, F., Wang, D. and Li, X., 2018. Effectiveness and mechanisms of phosphate adsorption on iron-modified biochars derived from waste activated sludge. Bioresource Technology, 247, pp.537-544.

Yang, S., Jin, P., Wang, X., Zhang, Q. and Chen, X., 2016. Phosphate recovery through adsorption assisted precipitation using novel precipitation material developed from building waste: behavior and mechanism. Chemical Engineering Journal, 292, pp.246-254.

Yin, Q., Wang, R. and Zhao, Z., 2018. Application of Mg–Al-modified biochar for simultaneous removal of ammonium, nitrate, and phosphate from eutrophic water. Journal of Cleaner Production, 176, pp.230-240.

CHAPTER FIVE

This chapter is devoted to **paper II** manuscript prepared for examination. This manuscript is structured into the style requirement of the journal as per the requirements of the journal. This manuscript will be submitted soon. Furthermore, this chapter is dedicated to achieve the undermentioned objective and they comprise (1) optimization of conditions that are suitable for the removal of metals using calcium phosphate, (2) characterization of the feed and product minerals and chemical during the interaction of water and the feedstock, and lastly (3), the simulation of the interactions between the synthesized calcium phosphate and metal-rich effluent using PHREEQC geochemical model.

Utilization of the synthesized calcium phosphate for the removal of metals from acidic effluents

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Abstract

The discharge of acidic effluents that are rich in toxic and hazardous metals has been an issue of paramount concern in national, regional, and international research communities. The quest for alternative and eco-friendly technologies that could be used for the removal of metals from acidic effluents is ongoing albeit with minimal success. This study aims to explore the utilization of calcium phosphate for the removal of metals from acidic effluents. Batch experimental was used to achieve the objectives of this study, specifically the one-factor-at-a-time (OFAAT). The optimized parameters include the effects of pH, feedstock dosage, contact time, concentration, and temperature. Characterisation of the feed and product solid samples were ascertained using XRD, HR-SEM-EDS and FTIR. The aqueous samples were characterised using GFAAS, ICP-OES and multi-parameter probes. The obtained results revealed that 10 min of mixing time and 1.0 g of dosage in 100 mL of metal-rich effluent. The mixture was equilibrated at 90 rpm. Interaction of calcium phosphate with AMD led to ≥ 99% removal efficacy for Fe, Mn, Zn and Cu except for Al, which demonstrated ≥ 80% removal efficacy. The removal of heavy metals ions from AMD was observed to be dependent on pH and temperature. The maximum pH was observed to be ≥ 10, which was adequate for the removal of metals via precipitation. PHREEQC geochemical model also confirmed that the metals existed as divalent and trivalent ions, and they precipitated out of solution as metals hydroxides. The XRD confirmed the formation of new mineral phases. This was further ascertained by FTIR and FIB-HR-SEM-EDS technique. In light of the above, findings from this study confirmed that calcium phosphate could be recovered from real municipal wastewater and subsequently employed for the removal of metals from acidic effluents. This play are central role in minimizing the footprints of acidic effluents, acid mine drainage, and municipal wastewater afield.

Keywords: Calcium phosphate, acidic effluents; acid mine drainage, municipal wastewater, treatment, minerals recovery, minerals synthesis; heavy metals removal.

5.1 Introduction

Water is an omnipresent resource that require close management to eliminate potential threats due to contamination, however, anthropogenic activities has been noted to pose devastating to effects to water bodies in different ecological systems and compartments. Specifically, activities such as urban run-off (Roveri et al., 2020; Shajib, 2020), agricultural activities (Venmyn, 2013; Muratoglu, 2020), metallurgical processes (Nowińska and Adamczyk, 2021; de Andrade et al., 2020), industrial manufacturing (Wuand Ye , 2020), food and clothing processing (Kapp and Miller, 2020), construction (Andrić et al., 2015), wastewater treatment (Barceló et al. 2020), and mining activities (Haldar, 2013, Masindi et al., 2018; Tutu et al., 2008) have been noted to pose devastating effects to the aquasphere. Amongst these, acid mine drainage (AMD) from coal and gold mining activities and municipal wastewater (MWW) from wastewater treatment facilities have been noted to be problematic pollutants of ecological concern. This is primarily based on the extent and magnitude of their ecological impacts as gauged according to toxicity and epidemiology (Jouini et al., 2019).

Acid Mine Drainage (AMD) emanate from the weathering of sulphide minerals such as arsenopyrite, pyrite, and marcasite amongst others. These minerals get exposed to water and oxygen leading the formation of a very acidic drainage which is rich in acidity and elevated levels of metals. Low pH further accelerate the dissolution of metals from the surrounding geology leading to elevated levels of chemical species. According to literature, AMD is rich in Al, Fe, Mn, and sulphate including traces of As, Cr, Zn, Pb, Ni, and radionuclides (Yuan et al., 2019; Sahoo et al., 2013; Iakovleva et al., 2015; Wang et al., 2019; Sun et al., 2020). This can pose devastating effects to living organisms on exposure. On the other hand, poorly treated MWW effluents comprise elevated levels of nutrients (phosphate and ammonia), organic matter, and suspended solids amongst others (Mavhungu et al., 2021). When these effluents are discharged into the environment they enrich the water with nutrients leading to rapid growth of aquatic plants. When these plants dies, they deplete the water dissolved oxygen through aerobic decomposition. This will then affect the aesthetic value of the area due to scam of green algae and dead organic matter, odour from decaying plants and even the death or migration of fish and other aquatic organisms when the ecosystem is devoid of oxygen to support life (Mavhungu et al., 2019; Tanaka et al., 2014, Mavhungu et al., 2020; Marshall et al., 2017; Lei et al., 2018; Lei et al., 2019; Caddarao et al., 2018). According to stringent environmental regulations, these two wastewater streams need to be treated prior to discharge into different receiving environments.

Over the years, several active (Ileri and Yucel, 2020; Jafaripour, 2014, Nordstrom and Blowes, 2015), passive (Kaur et al., 2018; García-Valero et al., 2020), integrated (Sahoo et al., 2020; Shen et al., 2020), and hybrid (Vadapalli et al., 2020; Dlamini et al., 2019) treatment systems have been developed for the treatment of acid mine drainage (AMD). Albeit, each approach comprise their advantage and disadvantage (Teekere, 2020). Active treatment process require frequent additions of chemicals and energy whereas passive rely on natural energy and it is perceived eco-friendly. However, active treatment technology has been regarded the best due to their performance in relation to the required limit and ultimate intentions hence it was chosen for this study. In this technique, different alkaline generating agents are used and they include lime (Qureshi et al., 2016; Ileri and Yucel, 2020), limestone (Liu et al., 2017; Masindi et al., 2017), hydrated lime (Jin et al., 2020), dolomite (Chai et al., 2020; Hu et al., 2020; Calugaru et al., 20202), magnesite (Magagane et al., 2019; Masindi et al., 2018), periclase (Masindi et al., 2017), brucite (Hövelmann et al., 2018; Kaur et al., 2018), caustic soda (Skousen et al., 2019), soda ash (Farage et al., 2020; Sebogodi et al., 2020), and tailings rich in Mg , Ca , and Na (Akinwekomi et al., 2016; Heviánková, et al., 2014).

On the other hand, ammonia in municipal wastewater is removed using biological nutrients removal technique (Samimi and Moghadam, 2018; Liu et al., 2017) whereas phosphate is removed using lime (Mitrogiannis et al., 2017; Woo et al., 2019), ferric (Yousefi et al., 2019; Zhou et al., 2018), aluminium (Ano et al., 2019; Franco et al., 2017), and magnesium (Han et al., 2017; El Bouraie and Masoud, 2017). Interestingly, the use of lime to scavenge phosphate lead to the production of calcium phosphate that end-up being dumped onto the environment (Monballiu et al., 2020) with prospects to utilise for fertiliser (Lei et al., 2020) and phosphoric acid (Li et al., 2020) production. This could be the best initiative towards beneficiation and valorisation of product waste and this will reduce ecological footprints associated with AMD and MWW via devising a circular approach towards the generated products. The use of calcium phosphate for the treatment of acid mine drainage (AMD) or metal rich mine effluent has never been explored. To the best of our knowledge, this will then be the first study in design and execution to explore the use of calcium phosphate synthesized from municipal wastewater for the treatment of AMD or metal-rich and acidic effluents. This will foster the concept of materials re-use and recycle particularly viewed under the concept of circular economy and waste valorisation.

5.2 Materials and methods

This section will explicitly discuss the materials and methods which were employed to fulfil the objectives of this study**.**

5.2.1 Chemical materials

All chemicals used in this study are of analytical grade. Specifically, the $FeSO_4$, $MnSO_4{\cdot}H_2O$, $Al_2(SO_4)_2{\cdot}18H_2O$, NaOH, HCl and KH_2PO_4 were purchased from Merck (Darmstadt, Germany) and $Ca(OH)_2$ from Sigma-Aldrich (Miamisburg, USA). All chemicals were used without further purification. Solutions were prepared with deionized distilled water.

5.2.2 Preparation of stock solutions

A stock solution of Fe^{3+}, Mn^{2+} and Al^{3+} with an initial concentration of 1000 mg L^{-1} was prepared by dissolving 1.891 g, 4.331 g and 3.125 g in 1000 mL deionized water respectively, and further diluted to prepare the required initial concentration. Then, the pH of the solution was adjusted by HCl (0.1M) and NaOH (0.1M).

5.2.3 Collection of municipal wastewater and metal rich effluent

Real untreated wastewater, rich in phosphate, was collected in Makhado municipal wastewater treatment plant in Limpopo, South Africa. The treatment plant receives wastewater from a number of activities from the surrounding area. Similarly, AMD was collected from a coal mine in Mpumalanga, South Africa. High-density polyethylene wide-mouth plastic bottles were utilized for sample collection. Solids and debris were removed by filtration, using filter syringe filter (0.20 µm), and the samples were used immediately thereafter. In the context of this work, the wastewater was used as authentic with no dilution or pre-treatment.

5.2.4 Preparation of calcium phosphate

The collected municipal wastewater was used for the preparation of high-grade calcium phosphate for AMD treatment. Calcium phosphate was prepared through precipitation process. To achieve that, 60 min of equilibration, 5 g: 150 mL of solid: liquid ratio, ambient temperature and pH, and 90 rpm mixing speed were utilized for the preparation of calcium phosphate. The product was left to settle for 30 min. Thereafter, the supernatant was decanted from the beaker and the sludge was taken to the oven for overnight drying at 105°C. After drying, the samples were then grinded into fine powder and kept into an air-tight container for utilization in AMD treatment.

5.2.5 Treatment of acid mine drainage

The neutralization and metal ion removal (Fe^{3+}, Mn^{2+} and Al^{3+}) from AMD using calcium phosphate was investigated using batch approach. A known weight of calcium phosphate (e.g. 0.1–1.0 g) was equilibrated with 100 mL of AMD solution in a closed plastic bottles at different temperature in a mechanical shaker for different periods (10 min – 180 min) at a mixing rate of 90 rpm. The tests were performed in triplicate and the average results were presented. After equilibration, the suspension of the sludge was easily separated from the solution using Whatman no. 1 filter paper and syringe filter (0.20 µm). The concentration of metal ions remaining in solution was measured by GFAAS and ICP-OES. The influence of various parameters such as pH, feedstock dose, contact time, concentrations and temperature on the removal performance was examined. Then, the pH of the solution was adjusted by HCl (0.1M) and NaOH (0.1M). The results of these studies were used to obtain the optimum conditions for maximum metals ions removal from AMD solution. In all samples, the removal efficiency of all ions (%R) were obtained by equation (5.2).

$$\%\ \text{Removal} = \frac{\text{Co} - \text{Ce}}{\text{Ce}} \text{ X } 100 \qquad (5.2)$$

Where, C_o denotes initial metal concentration, and C_e equilibrium metal concentration in mg L^{-1}.

5.2.6 Characterization of feed and product samples

Different analytical techniques were used for the characterisation of liquid and solid samples generated from our laboratory experiments.

5.2.6.1 Characterisation of solid samples

The mineralogical properties were done using X-ray Diffraction (XRD), PANalytical X’Pert PRO-diffractometer equipped with Philips PW 1710 Diffractometer with graphite secondary monochromatic source (Almelo, Netherlands)). Functional groups analysis were done with Fourier Transform Infrared Spectrometer (FTIR) equipped with Perkin-Elmer Precisely Universal Attenuated Total Reflectance (ATR) sampling accessory with a diamond crystal

(Bruker, USA). Morphology, mapping and elemental analysis using field emission scanning electron microscope (FESEM) equipped with energy-dispersive X-ray spectroscopy (EDS), Auriga Cobra FIB-FESEM, Carl Zeiss FE-SEM (Oberkochen, Germany).

5.2.6.2 Characterisation of aqueous samples

The pH, electrical conductivity (EC) and total dissolved solids (TDS) were monitored using CRISON MM40 portable pH/EC/TDS/Temperature multimeter probe (Shenzhen, China). Chemical species concentrations were determined by means of inductively coupled plasma - optical emission spectrometry (5110 ICP-OES vertical dual view) (Georgia, USA). Ion chromatography (850 professional IC from Metrohm (Herisau, Switzerland). Graphite furnace atomic absorption spectroscopy PerkinElmer pinAAcle 900T (Massachusetts, USA)

5.2.7 Geochemical modelling

To verify the mineral phases that are more likely to be formed during the treatment of authentic AMD with calcium phosphate, PHREEQC geochemical modelling was utilized to calculate saturation indices of mineral phases based on the pH and solution concentrations of major ions in supernatants that were analysed at optimized conditions. PHREEQC geochemical modelling code using the WATEQ4F database was used (Parkhurst and Appelo, 1999). Species which were more likely to precipitate were determined using saturation index (SI). In this case, $\mathrm{SI} < 1 =$ under saturated solution, $\mathrm{SI} = 1 =$ saturated solution and $\mathrm{SI} > 1 =$ Supersaturated solution.

5.3 Results and discussions

The results for chemical composition post the reaction of calcium hydroxide with municipal wastewater to synthesize calcium phosphate are shown in **Table 5.1**.

5.3.1 Characterization of product materials

This section will meticulously discuss the fate of chemical species post the interaction of calcium phosphate with metals rich effluents.

5.3.1.1 Mineralogical analysis

The mineralogical properties of calcium hydroxide, calcium phosphate and AMD-reacted with calcium phosphate were ascertained using X-ray Diffraction (XRD) and are shown in **Figure 5.1**.

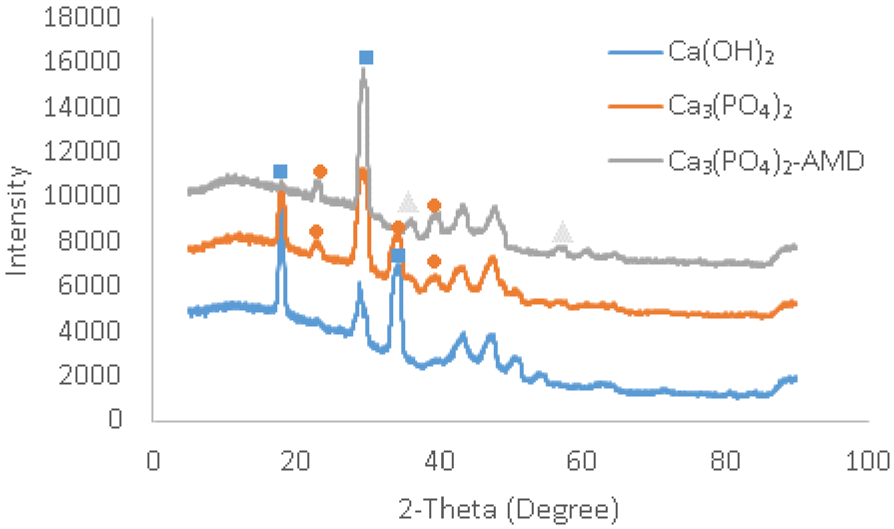


Figure 5. 1: The mineralogical properties of calcium hydroxide, calcium phosphate and AMD-reacted with calcium phosphate.

As shown in **Figure 5.1**, calcium hydroxide comprise of trace amount of calcite and other substantial amounts of amorphous fractions. This indicated that the material comprised of CaO as intermediates minerals and traces of other impurities. Thenceforth, after the interaction of calcium hydroxide with stimulated municipal wastewater, the product mineral was found to contain calcium phosphate (Ca-P). This was an indication that phosphate were adsorbed by the feed leading to the formation of calcium phosphate, as denoted in equation (5.3):

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \qquad (5.3)$$

It was clear from the XRD pattern that the intensities and narrow peaks observed for the $Ca_3(PO_4)_2$ sample increased as compared to that of calcium hydroxide which indicate that it exhibits good crystallization. Furthermore, the obtained peaks at 2 theta degrees of 23.26°, 34.64° and 39.96° for calcium phosphate agrees with what have been reported by Salama and Hesemann. (2020) and Jiang et al. (2017). Furthermore, the results confirms that the interaction between calcium hydroxide with municipal effluents led to the formation of calcium phosphate as a by-product. Basically, the presence of Ca in the feed contributes towards increasing the pH value of the wastewater and generating Ca^{2+} is shown in equation (5.4):

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \qquad (5.4)$$

Then, Ca^{2+} will react with PO_4^{3-} to form a complex, as denoted in equation (2). The very same principle will be employed for the treatment of AMD or metals rich effluents since the key component which is responsible for pH increase is crystals Ca, and it is embedded into the matrices of calcium phosphate. This could be used for mine water neutralization and chemical species attenuation. Thenceforth, the presence of Ca denotes the possibility of gypsum formation. The synthesized calcium phosphate was then utilized for the treatment of AMD. However, the product sludge was observed to be amorphous in nature with few crystal peaks at 2 theta degrees of 36.58° and 58.06° that could be assigned to basanite and Fe-hydroxide, respectively. The peaks obtained corroborate that which have been reported by Seo et al. (2017). This confirms that calcium phosphate can be a sink of metals from AMD. However, there are secondary processes such as the co-precipitation of metals and co-adsorption including surface complexation of constituents in AMD. For instance, phosphate has high affinity to Fe^{3+}, Al^{3+}, Mg^{2+}, and Ca^{2+} thus, it could be presumed that they bind to each other and eventually precipitate.

5.3.1.2 Functional group analysis

Figure 5.2 shows the FTIR spectrum of calcium phosphate and AMD-reacted with calcium phosphate while **Table 5.1** lists the identified metal functional groups, their wavenumber (cm^{-1}) and citations for relevant studies dealing with the identified metal functional groups.

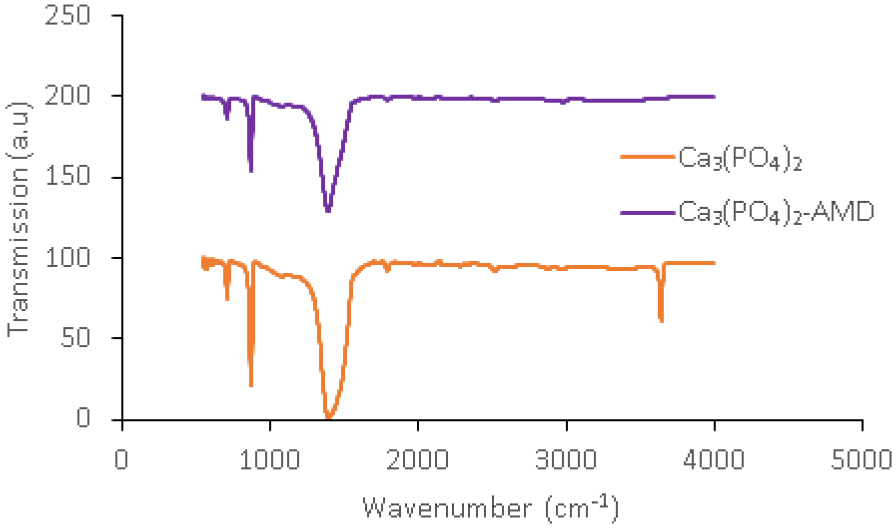


Figure 5. 2: The metal functional groups of synthesized calcium phosphate and AMD-reacted with calcium phosphate.

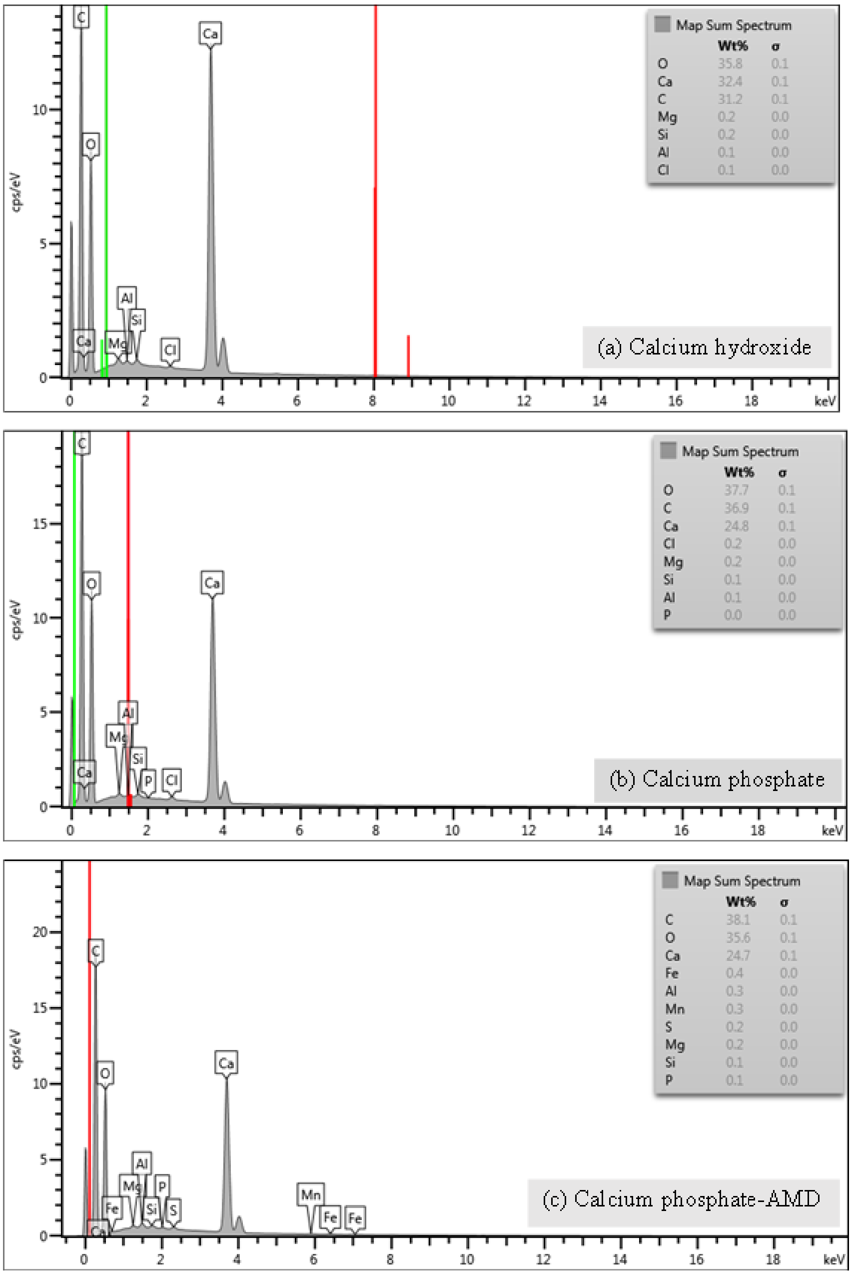
As shown in **Figure 5.2** and **Table 5.1**, the metal functional groups regarding the recovered calcium phosphate were observed to contain PO_4^{3-} and HPO_4 (**Table 5.1**), which confirmed that indeed, through the proposed technology, calcium phosphate was formed. Hydroxide along with carbonates were also observed to be present in the recovered product sludge mineral. The presence of hydroxide on the recovered Ca-P-sludge suggested the presence of calcium hydroxide, while the carbonates may have originated from calcite, as revealed by the XRD results. Finally, apart from suggesting that calcium hydroxide might be present, hydroxide also suggested that the synthesized calcium phosphate was hydrated. Furthermore, the interaction of calcium phosphate and AMD led to the formation of new minerals phases and metals functional groups. This could be explained by the precipitation of different metals and metalloids from the aqueous interface of AMD to the resultant sludge. Precisely, the Fe-OH group was observed and this denotes the precipitation of Fe^{3+} from AMD. This has been confirmed by other technique such XRD. The water quality results further attested to that finding. The presence of carbonates and hydroxyl group denotes the formation of hydroxides, oxyhydrosulphates and carbonates post the interaction of AMD with chemical components in calcium phosphate. This further confirmed that calcium phosphate can act as a sink of chemical species from AMD. This has been confirmed by different analytical techniques such as XRD, GFAAS and ICP-OES. The identified metal functional groups of synthesized calcium phosphate and AMD-reacted with calcium phosphate are shown in **Table 5.1**.

Table 5. 1. The identified metal functional groups of synthesized calcium phosphate and AMD-reacted with calcium phosphate.

Mineral	Wavenumber (cm^{-1})	Metal functional group	Reference
Calcium phosphate	874	HPO_4	(Pakravanan et al., 2019; Howard et al., 2020; Jamil et al., 2018; Song et al., 2012)
	1798	PO_4^{3-}	
	2520	CO_3	
	1406	CO_3	
	712	-OH (Water)	
	3642	-OH (Water)	
Ca-P- AMD	1398	CO_3^-	(Yahya et al., 2017; Mavhungu et al., 2021; Slavov et al., 2010)
	712	-OH (Water)	
	1070	Fe-OH group	

5.3.1.3 Elemental composition

As shown in **Figure 5.3 (a)**, calcium hydroxide was characterised of CaO as major elements. The presence of Ca further confirmed that this will aid in the removal of phosphate from municipal wastewater hence forming calcium phosphate as the by-product. After interacting calcium hydroxide with municipal wastewater (**Figure 5.3(b)**) led to the enrichment of product sludge with phosphate as shown in the EDS results. This could be attributed to the formation of calcium phosphate during the interaction of Ca and P in municipal wastewater. Predominant elements were observed to be O and Ca while P was present in a small amount. The present of phosphate in small amount could be attributed to its low concentration utilized during the synthesis process with calcium hydroxide. The results could be attested by the reduction in the levels of phosphate in municipal wastewater. Traces of other impurities were observed but these could be attributed to other chemicals that were embodied in municipal wastewater. Furthermore, the resultant sludge, i.e. calcium phosphate, was applied for the treatment of acid mine drainage (AMD). As shown in **Figure 5.3(c),** there levels of Al, Mn and Fe which are present in elevated concentration were observed. The main elements were Fe and Ca whereas intermediates elements were Al, Si, S, P and Mn. This was evident enough that the product sludge was acting as a sink of chemical species in AMD. The obtained results corroborates the water quality results. These results are also consistent to what has been reported in XRD and FTIR.



Map Sum Spectrum

	Wt%	σ
O	35.8	0.1
Ca	32.4	0.1
C	31.2	0.1
Mg	0.2	0.0
Si	0.2	0.0
Al	0.1	0.0
Cl	0.1	0.0

Map Sum Spectrum

	Wt%	σ
O	37.7	0.1
C	36.9	0.1
Ca	24.8	0.1
Cl	0.2	0.0
Mg	0.2	0.0
Si	0.1	0.0
Al	0.1	0.0
P	0.0	0.0

Map Sum Spectrum

	Wt%	σ
C	38.1	0.1
O	35.6	0.1
Ca	24.7	0.1
Fe	0.4	0.0
Al	0.3	0.0
Mn	0.3	0.0
S	0.2	0.0
Mg	0.2	0.0
Si	0.1	0.0
P	0.1	0.0

Figure 5. 3: Elemental composition of (a) calcium hydroxide, (b) calcium phosphate and (c) calcium phosphate reacted with AMD.

5.3.1.4 Morphological characteristics

The morphological structures of calcium hydroxide, calcium phosphate and AMD-reacted with calcium phosphate are shown in **Figure 5.4**. It can be observed that calcium hydroxide comprise of irregular particles, which are homogenously distributed across its surface. Furthermore, the morphological properties of the calcium hydroxide surface were observed to remain the same regardless of the different magnification used, i.e. from 1µm to 100 nm. The FESEM results also suggested that calcium hydroxide is a nanostructure with circular-like structures. However, post calcium phosphate synthesis, the morphology of calcium phosphate was observed to have changed to stony like structures. In addition, the FESEM result also revealed that calcium phosphate had also a flower like structure. This could be attributed to the fact that calcium phosphate synthesis led to the formation of new mineral phases, which suggested that a reaction had took place to form calcium phosphate. Moreover, other Ca based minerals, apart from CaO, could have influenced the morphology of the synthesized calcium phosphate, along with impurities associated within the hydrated lime matrices and micelles that would have been co-deposited with calcium phosphate during the synthesis process. Lastly, it demonstrated triangular sheets with homogenous arrangement onto the surface of AMD-reacted with calcium phosphate. The sheets also comprised of leafy-like structures. This result further confirmed the formation of new mineral phases on the matrices of each mineral, which was generated in different phase of the reaction.

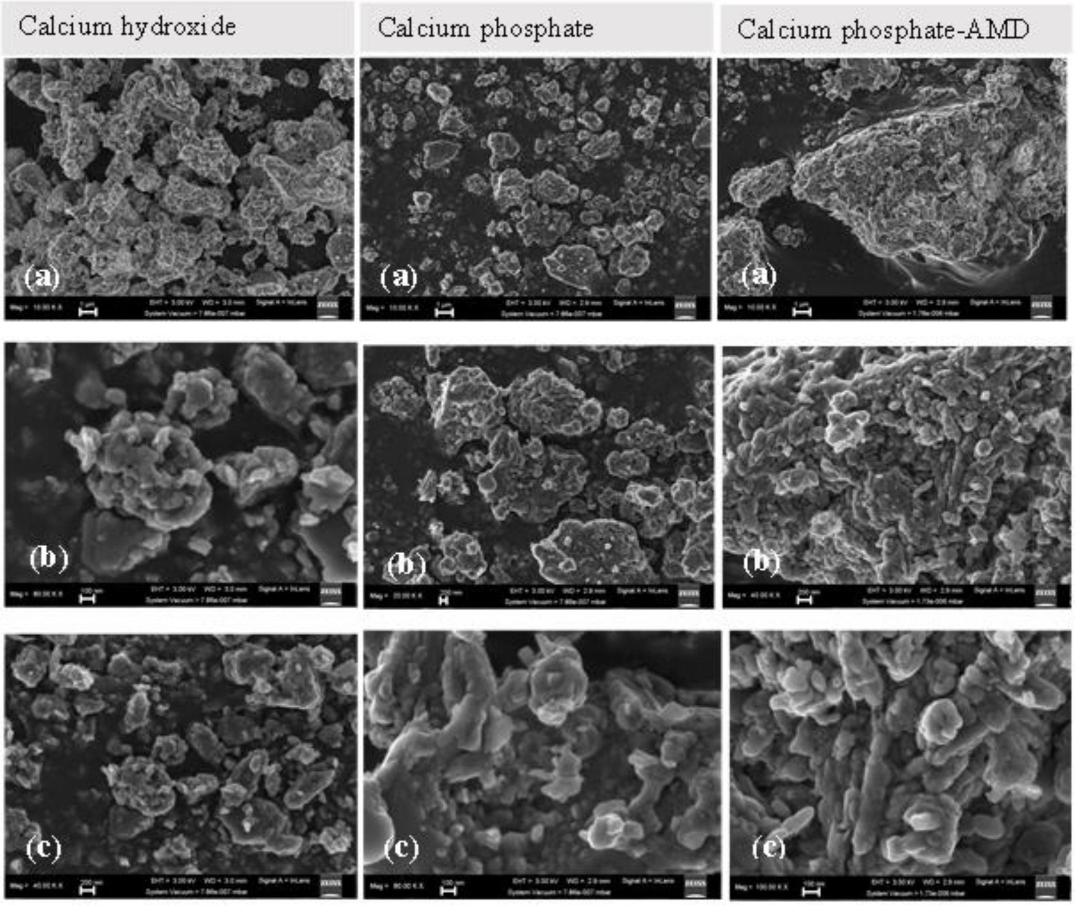


Figure 5. 4: The HR-FESEM images showing the changes in morphological properties of calcium hydroxide, synthesized calcium phosphate and AMD-reacted with calcium phosphate from lower to higher magnification, i.e. a) 1 µm, b) 200 nm, and c) 100 nm.

5.3.1.5 Elemental mapping using HR-SEM

To further corroborate the elemental composition of calcium hydroxide, synthesized calcium phosphate and AMD-reacted with calcium phosphate, spot-analysis, by means of Auriga Cobra FIB- FESEM instrument, which includes an EDS detector, was utilized. The morphological spot-analysis of calcium hydroxide, synthesized calcium phosphate and AMD-reacted with calcium phosphate are shown in **Figure 5.5**

As shown in **Figure 5.5**, calcium hydroxide is predominated by octagonal structures on its surface. Elemental analysis further revealed that the predominant elements are Ca and O, as well as traces of Mg, Si. The EDS spot analysis results are also in agreement with the XRD and FTIR results for calcium hydroxide. Furthermore, Ca was an instrumental in increasing the pH of the raw wastewater effluent. Scattered distribution of Mg were also observed on the surfaces of calcium hydroxide. The crystal clear flower like and homogenous crystals were observed in the synthesized calcium phosphate. Furthermore, it was identified that the synthesized calcium phosphate was predominated by Ca and O while traces of Cl, Al, Mg, P and Si were similarly observed. The presence of P on spot analysis confirmed the formation of calcium phosphate. It should be noted that only the soluble component of calcium hydroxide will contribute to the formation of calcium phosphate and the rest will remain in solution. Finally, the availability of Si and Mg suggested the co-precipitation of calcium phosphate with those impurities. The obtained results are aligned with the ones of the XRD and FTIR analysis. Lastly, spherical and sand-like structures were observed on the matrices of the AMD-reacted with calcium phosphate. As shown in **Figure 5.5**, it was apparent that the sand-like structure denotes a combination of Ca and S, thus implying the possibilities of synthesizing gypsum in the product mineral. This could further allude the attenuation of sulphate from AMD to the product sludge. The XRD, FTIR and EDS techniques further confirmed the results. The presence of Ca and O confirmed the presence of calcium hydroxide on the matrices of product minerals. Al, Fe and Mn were also observed to be present post the treatment of AMD with calcium phosphate. The presence of these chemical species certifies the removal of contaminants from AMD to the product sludge. This will further confirm that calcium phosphate can act as a sink of chemical species from AMD and any metalliferous drainage.

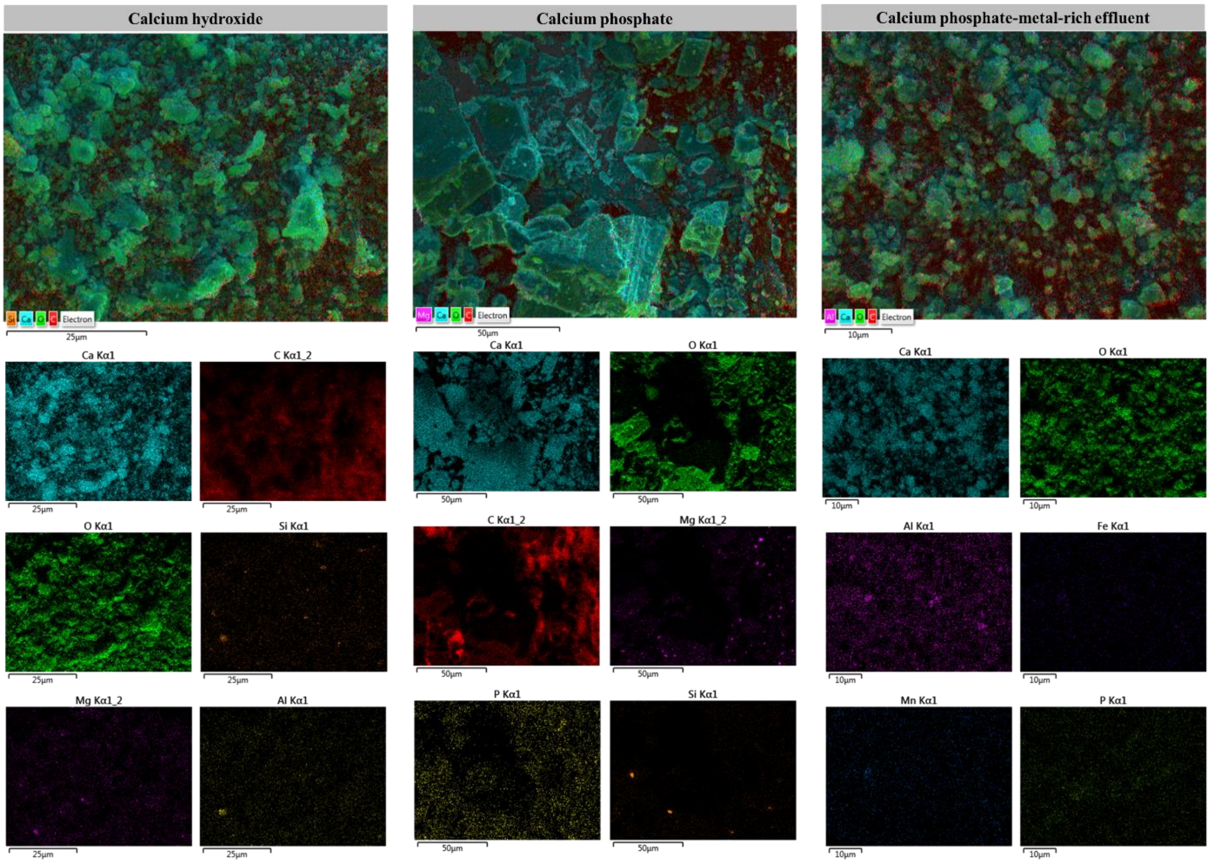


Figure 5. 5: Elemental mapping of calcium hydroxide, synthesized calcium phosphate and AMD-reacted with calcium phosphate.

5.3.1.6 PHREEQC geochemical modelling

The PHREEQC geochemical model were used to complement experimental results and to point out species that are more likely to precipitate during the interaction of calcium phosphate with acid mine drainage. The modelling results revealed that the speciation of heavy metals from acidic effluents existed as cation and hydroxide form in aqueous solution with calcium existing as $Ca^{2+,}$ $CaH_2PO_4^+$, $CaHCO_3^+$, $CaPO_4^-$, $CaCO_3$ and $CaOH^+$, magnesium existing as Mg^{2+}, $MgH_2PO_4^+$, $MgHPO_4$, $MgOH^+$ and $MgPO_4$ while the speciation of aluminium existed as Al^{3+}, $AlOH^{2+}$, $Al(OH)^{2+}$, $Al(OH)_3$ and $Al(OH)_4^-$, Iron existed as Fe^{2+}, $FeH_2PO_4^+$, $FeHPO_4$, $Fe(OH)^+$, Fe^{3+}, $FeH_2PO_4^{2+}$, $Fe(OH)^{2+}$, $FeOH^{2+}$, $FeHPO_4^+$, $Fe(OH)_3$, $Fe(OH)_4^-$, $Fe_2(OH)_2^{4+}$ and $Fe_3(OH)_4^{5+}$, manganese existing as Mn^{2+}, $MnOH^+$ and Mn^{3+}, while phosphate existed as $FeH_2PO_4^+$, $H_2PO_4^-$, $MgH_2PO_4^+$, $CaH_2PO_4^+$, $FeHPO_4$, $MgHPO_4$, HPO_4^{2-}, $CaHPO_4$, $FeH_2PO_4^{2+}$, $FeHPO_4^+$, $MgPO_4^-$, $CaPO_4^-$ and PO_4^{3-}. The predicted sludge materials are shown in **Table 5.4**. The obtained results suggest that Al, Fe and Mn were recovered at the optimum pH 11.04. This has proven that metal species in acid mine drainage can be fractionally recovered using calcium phosphate at any pH gradients in a sequential manner. The PHREEQC geochemical model results were consistent to the experimental results hence commending and attesting that the obtained results were valid and reputable. This was also confirmed by XRD and FTIR.

Table 5. 2: Geochemical modelling results for mineral phase predicted to precipitate

Mineral Phase	SI	logIAP	Log KT
$Al(OH)_3$ (a)	3.39	14.19	10.80
Fe(OH)3 (b)	-1.50	3.39	4.89
Hematite	10.85	6.84	-4.01
Goethite	4.41	3.41	-1.00
Siderite	2.82	-8.07	10.89
Fe3(PO4)2:8H2O	10.72	-25.28 -	36.00
Mn3O4 (c)	-21.71	39.32	61.03
Manganite	-10.20	15.14	25.34
Pyrochroite	-6.20	-6.20	15.20
Pyrolusite	-20.12	21.26	41.38
Rhodochrosite	1.77	-9.36	11.13
Calcite (d)	0.00	-8.48	8.48
Dolomite	0.25	-16.84	17.09

whitlokite	-0.24	-1.70	-1.47
Hydroxyapatite	5.88	2.46	-3.42

5.2 Optimization of parameters for AMD treatment

This section will discuss in detail the optimization process of AMD effluents using the synthesized calcium phosphate feedstock.

5.2.1 Treatment of AMD as a function of pH

Variation in pH with an increase in contact time prior to neutralization of AMD with calcium phosphate is shown in **Figure 5.6**.

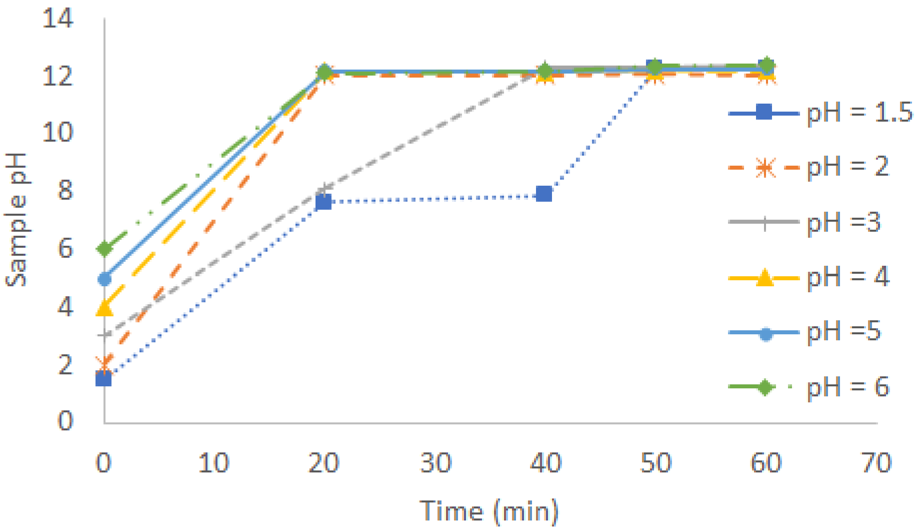


Figure 5. 6: Variation in pH with an increase in contact time prior to neutralization of AMD with calcium phosphate. (Conditions: contact time: 60 min; feedstock dose: 0.5 g; shaking speed 90 rpm and temperature: 25 ± 1°C)

Neutralization of AMD solution should probably be the first step in remediation of mine water. The effect of contact time on acidity neutralization was examined by considering a wide range of mixing durations, i.e. 0, 5, 10, 30, 45 and 60 min. As shown in **Figure 5.6**, the pH of the solution was observed to increase from 1.5 to 12.38 with an increase in contact time. However, it was observed to stabilize after 50 min of mixing duration. It was found that the dried sludge reduced the acidity of AMD fast. The increase of the initial pH of the AMD occurred at the contact of 20 - 40 min with 10 mg L^{-1} of metal ion concentration. After 60 min of shaking, the pH reached 12.28 - 12.38. The reaction rates decreased as equilibrium was reached. The pH increase was attributed to the progressive dissolution of the sorbent during the shaking process. The pH attained equilibrium after 60 min of contact time between the sorbent and adsorbate solution. The final pH was 12.38, indicating that effective neutralization of AMD took place.

Variation in percentage removal of Al, Mn, and Fe with an increase in pH during the treatment of AMD with calcium phosphate is shown in **Figure 5.7**.

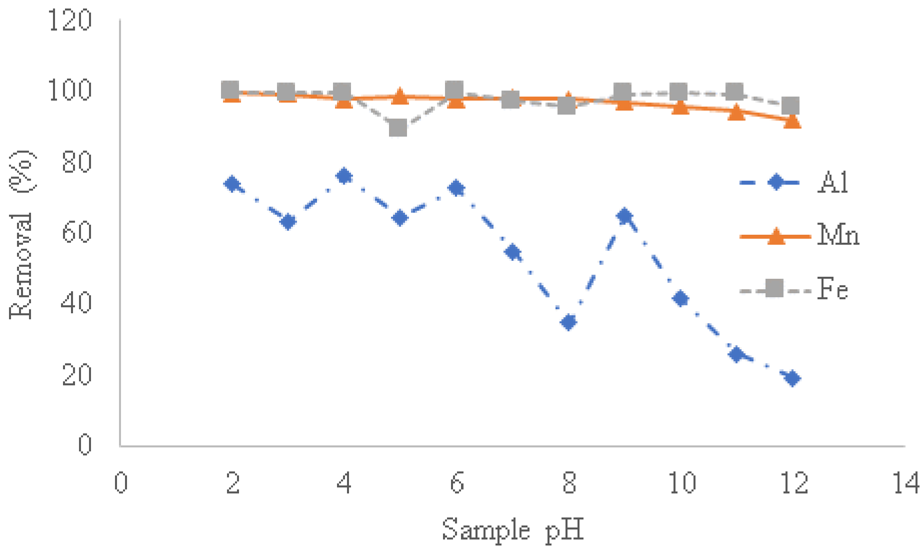


Figure 5. 7: Variation in the percentage removal of Al, Mn, and Fe with an increase in pH during the treatment of AMD with calcium phosphate. (Conditions: contact time: 60 min; feedstock dose: 0.5 g; initial metal ion concentration 10 mg L^{-1}, shaking speed 90 rpm and temperature: 25 ± 1°C)

The pH of a solution is the most significant and imperative parameter influencing the removal process of chemical species from aqueous solution, since it does not only affects the surface charge of feedstock, but also the extent of ionization of the metal ions in solution (Iakovleva et al., 2015; Mohammadi et al., 2019). As shown in **Figure 5.7**, it was clearly observed that the percentage removal of Al were slightly decreased with an increase in pH. This could be attributed to the fact that Al precipitate at pH ≤ 5.5 as $Al(OH)_3$. The recovery of Al reached 73.5–75.9% at pH 4. However, Fe and Mn showed no significance change as a result of increasing pH and almost complete removal occurred at all the pH values tested, suggesting that precipitation of Fe and Mn occurred from the initial pH. The reason for Fe to precipitate across the study range may be attributed to the progressively oxidation of Fe^{2+} to Fe^{3+} by oxygen in air and its precipitation in the form of $Fe(OH)_3$, which started at pH 2 and its recovery reached 99.4 – 99.9% at pH 10. This finding could be supported by the results obtained by Balintova and Petrilakova, (2011) and Seo et al. (2017). The fact that in the presence of excess Fe, the complete precipitation of Mn occured at pH 8 was confirmed. At this particular pH, 99.5% of Mn precipitated in AMD. Fe and Mn showed the behavior of being precipitated at pH 2 – 10 at the same time, resulted in lowering their own purity. Similar trend was observed by Elsheikh et al. (2020). Therefore, pH 6.0 was chosen as the optimum mass for the preceding experiment.

5.2.2 Treatment of AMD as a function of dosage

Variation in pH with an increase in calcium phosphate dosage during the treatment of AMD with calcium phosphate is shown in **Figure 5.8**.

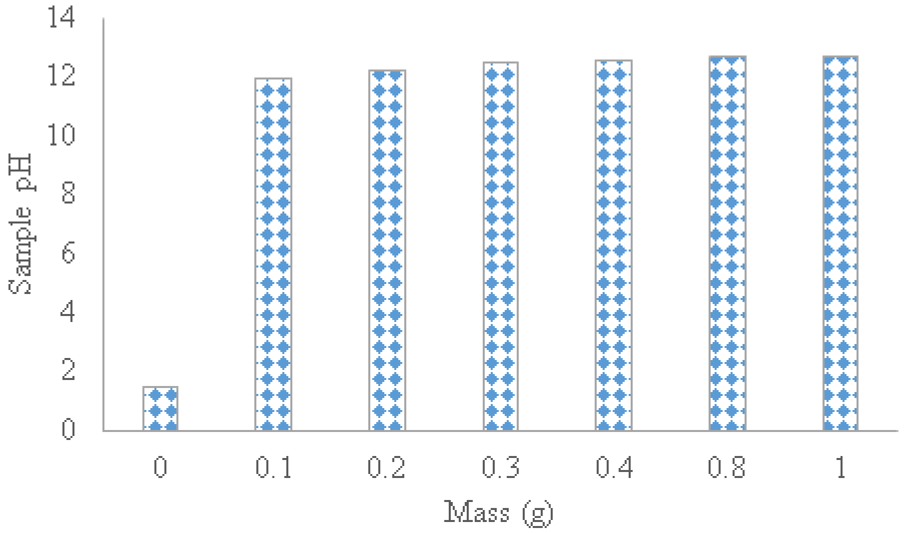


Figure 5. 8: Variation in pH with an increase in calcium phosphate dose prior to neutralization of AMD with calcium phosphate. (Conditions: contact time = 60 min, mixing speed = 90 rpm, AMD solution in 100 mL, pH = 1.5 and temperature: 25 ± 1°C).

The effect of feed dosage on acidity neutralization was examined by varying the dosages of calcium phosphate from 0.1 to 1 g. As shown in **Figure 5.8**, the pH was observed to increase with an increase in feed dosage. This could be attributed to an increase in mineral phases that are dissolving in water when calcium phosphate was introduced. According to **Figure 5.8**, calcium phosphate increased the pH from 1.5 to: 11.91 at 0.1 g, 12.22 at 0.2 g, 12.46 at 0.3 g, 12.55 at 0.4 g, 12.65 at 0.8 g and 12.68 at 1.0 g. After 60 min of reaction, the pH was 12.46 with a 0.3 g and 12.55 with 0.4 g dose of calcium phosphate, respectively. Further increase in pH was not observed with increasing calcium phosphate dose, and the pH stabilized at pH 12.68 at the 1.0 g dose. These results were consistent to the ones obtained by Masindi et al. (2017). The pH increase may have been ascribed to the presence of CaO, which dissolve and release hydroxyl ions, increasing the pH as expressed by equation (5.5).

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \quad (5.5)$$

Variation in percentage removal of Al, Fe and Mn with an increase in calcium phosphate dosage during the treatment of AMD with calcium phosphate is shown in **Figure 5.9**.

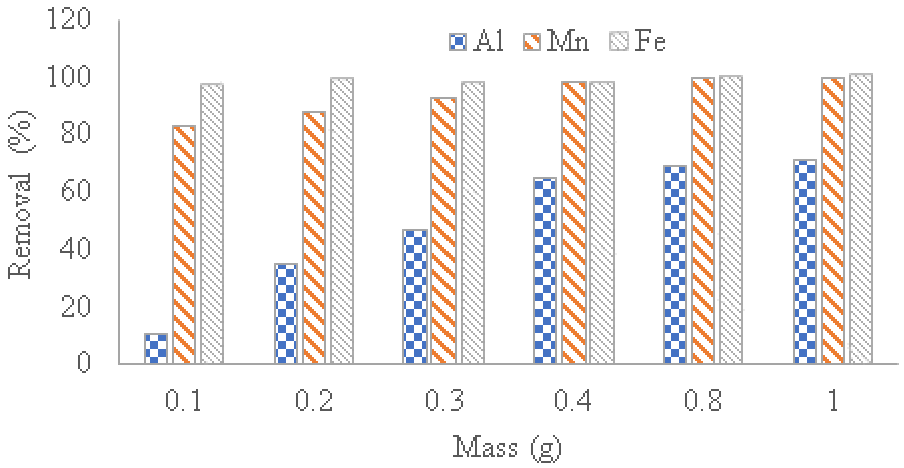


Figure 5. 9: Variation in the percentage removal of Al, Fe and Mn with an increase in calcium phosphate dosage during the treatment of AMD with calcium phosphate. (Conditions: pH: 6.0; contact time: 60 min; initial metal concentration: 10 mg L^{-1}, shaking speed 90 rpm and temperature: 25 ± 1°C)

As shown in **Figure 5.9**, there was a general increase in the percentage removal of Al and Mn during the interaction of AMD with increasing calcium phosphate dose. The recovery of Al increased from 10.8 - 71.3 % while Mn increased from 83.2 - 99.9% at the feed dose of 0.1 to 1 g. However, Fe displayed a rapid increase with the initial calcium phosphate dosage and no significant change was further observed with increasing feed doses and its recovery was 99%

throughout the dose tested. This could be attributed to the fact that Fe has a strong affinity towards PO_4^{3-} which could have formed a complex and precipitated out of the solution. This trend was similar to the one observed by Atasoy et al. (2019). The obtained results were expected because an increase in feed dose led to an increase in pH resulting in chemical species attenuation. Furthermore, an increase in the percentage removal as feed dose increased was aligned to the fact that different chemical species have their precipitation pH. Therefore 0.1 g was adequate for the removal of Fe whereas 0.3 g was adequate for the removal of Mn and lastly, 1 g was adequate for the removal of Al from aqueous solution. As such, 1 g was taken as the optimum dosage for the removal of different contaminants from AMD and it was used in subsequent experiments.

5.2.3 Treatment of AMD as a function of contact time

Variation in percentage removal of Al, Mn and Fe with an increase in contact time during the treatment of AMD with calcium phosphate is shown in **Figure 5.10**.

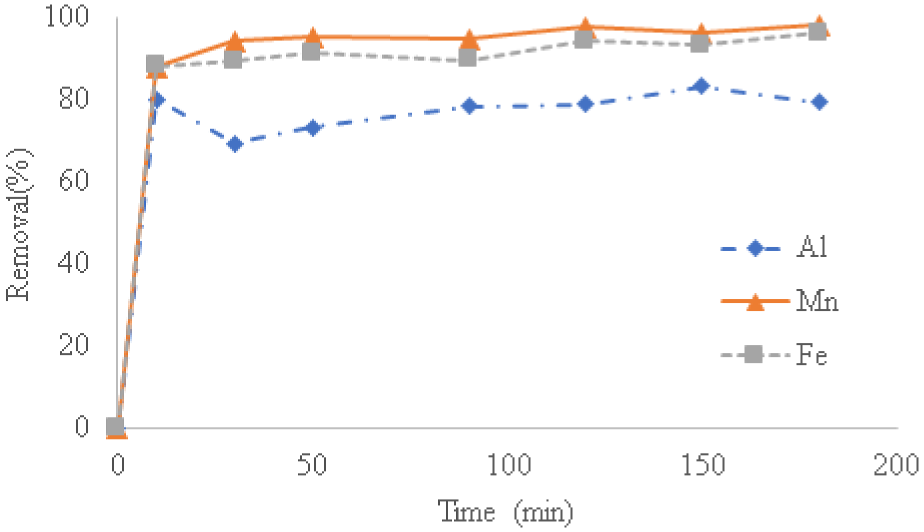


Figure 5. 10: Variation in the percentage removal of Al, Mn, and Fe with an increase in contact time during the treatment of AMD with calcium phosphate. (Conditions: pH: 6.0; initial metal concentration: 10 mg L^{-1}; feedstock dose: 1.0 g, shaking speed 90 rpm and temperature: 25 ± 1°C).

As shown in **Figure 5.10**, there was rapid increase in the percentage removal of Al, Mn and Fe during the interaction of AMD with calcium phosphate within 10 min, which were then followed by a slow increase until approximately 180 min. At that point, equilibrium was reached for all metals ion and attain the removal of 76%, 96% and 98% respectively. The rapid increase in the percentage removal at the beginning was attributed to the occurrence of the external mass transfer which involved rapid attachment of the metal ions to the surface of the feedstock (Núñez-Gómez et al., 2020). Further increase in contact time resulted with no significant change in percentage removal of chemical species. It can therefore be concluded that calcium phosphate can effectively remove chemical species from AMD in short period of time. However, 60 min was chosen as the optimum contact time for the preceding experiment.

5.2.4 Treatment of AMD as a function of concentration

Variation in percentage removal of Al, Mn and Fe with an increase in concentration during the treatment of AMD with calcium phosphate is shown in **Figure 5.11**.

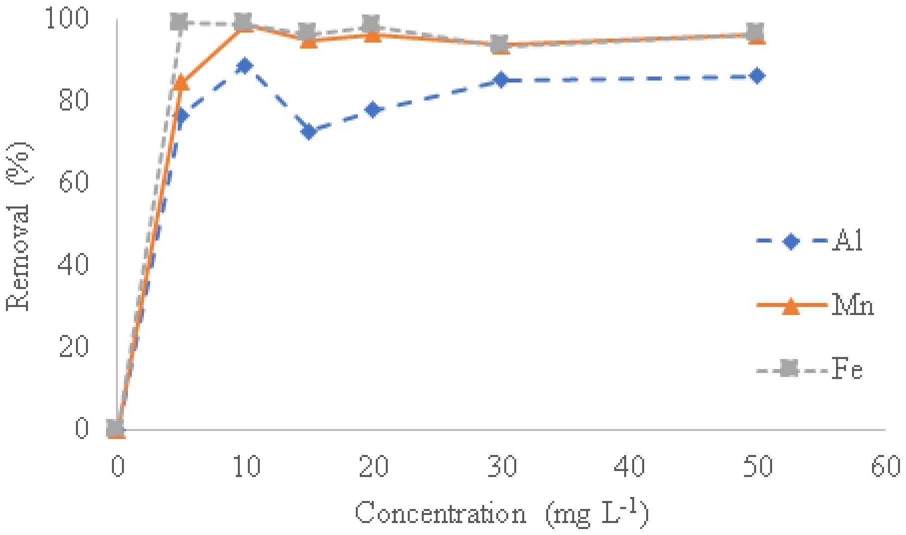


Figure 5. 11: Variation in the percentage removal of Al, Mn, and Fe with an increase in concentration during the treatment of AMD with calcium phosphate. (Conditions: pH: 6.0; contact time: 60; feedstock dose: 1.0 g, shaking speed 90 rpm and temperature: 25 ± 1°C).

As shown in **Figure 5.11**, the percentage removal was slightly decreasing with an increase in initial concentration of Al, Mn and Fe during the treatment of AMD with calcium phosphate. According to **Figure 5.11**, high removal of 89.9%, 98.87% and 99.1% for Al, Mn and Fe were attained at initial concentration of 10 mg L^{-1}, respectively. Further increase in concentration resulted in the decrease in percentage removal. This could have been attributed to the amount of feedstock used which may have been too little to effectively remove chemical species from AMD at high concentration. Similar results were observed by Zhao et al. (2020). As such, 20 mg L^{-1} of initial metal ions concentration was chosen as the optimum for the preceding experiment.

5.2.5 Treatment of AMD as a function of temperature

Variation in percentage removal of Al, Mn and Fe with an increase in temperature during the treatment of AMD with calcium phosphate is shown in **Figure 5.12**.

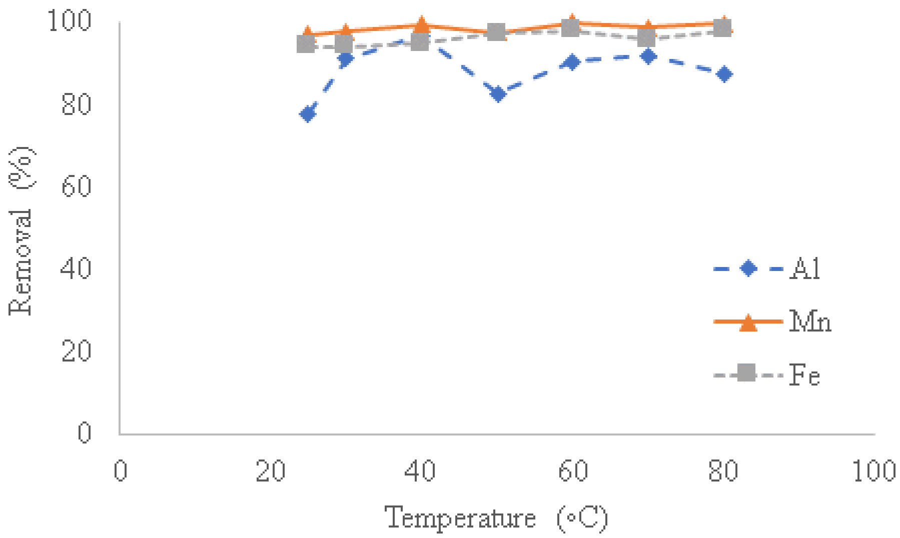


Figure 5. 12: Variation in the percentage removal of Al, Mn, and Fe with an increase in temperature during the treatment of AMD with calcium phosphate. (Conditions: pH: 6.0; contact time: 60; feedstock dose: 1.0 g, initial concentration: 20 mg L^{-1} and shaking speed 90 rpm).

To understand the influence that temperature has on the removal of Al, Mn and Fe during the treatment of AMD with calcium phosphate, variation of temperature from 25 to 80°C were investigated. As shown in **Figure 5.12**, there was rapid increase in percentage removal of Mn and Fe between the temperatures of 25 to 40°C. At this temperature, maximum percentage removal of Mn and Fe of 99.49% and 94.89% was attained, respectively. Afterwards, no significant change was observed in the percentage removal of Mn and Fe at elevated temperature. However, Al shows a different trend from that of Mn and Fe. It was observed that the percentage removal of Al increased with increasing temperature up to 40°C, thereafter further increase in temperature resulted in decrease on percentage removal. The percentage removal of Al increased from 77.88% to 94.49% and suddenly drops to 79.92%. The decrease in removal of Al could be due to the fact that high temperature results in high kinetic energy of the Al^{3+} ions, therefore failing the forces of attraction between the Al^{3+} ions and the feedstock. It was concluded that percentage removal of Mn and Fe shows little dependency on temperature since percentage removal was (> 90%) throughout all tested temperature conditions whereas that for Al shows dependency on temperature.

5.3 Treatment of AMD at optimized conditions

The feed and product water constituents for acid mine drainage are reported in **Table 4.3**.

Table 5. 3: The feed and product water qualities for treated AMD at optimized conditions.

Elements	Standards Limits	AMD	Treated AMD	% Removal
Fe (mg L^{-1})	≤ 2	96.239	13.127	86.36
Mn (mg L^{-1})	≤ 0.4	74.892	14.900	80.10
Co (mg L^{-1})	≤ 0.05	33.821	9.309	72.48
Cu (mg L^{-1})	≤ 2	25.959	8.776	66.19
Ni (mg L^{-1})	≤ 0.07	39.744	12.672	67.99
pH	≥ 5.00 to ≤ 9.70	2.37	11.04	-
Al (mg L^{-1})	≤ 0.03	59.601	11.383	80.90
EC (mS m^{-1})	≤ 170	1605	3260	-1655
TDS (mg L^{-1})	≤ 250	14900	13166	11.6
Zn (mg L^{-1})	≤ 5.0	115.158	36.127	68.23

- not determined.

As shown in **Table 5.3**, there was an effective removal of contaminants from AMD using calcium phosphate at optimised conditions. Specifically, chemical species of interest were removed from feed water. The pH was observed to increase from 2.3 to 11. 04 hence indicating that there was chemical reaction which was taking place that led to an increase in pH. Alkalinity of the resultant water was observed to have increase after contacting calcium phosphate hence indicating an enrichment of water bodies by base metals. Specifically, an increase in pH is mainly attributed to the chemical reactions in equation (5.3). The EC was observed to increase after the interaction of AMD with calcium phosphate at optimized conditions. This could be attributed to dissolution of chemical species such Ca during the attenuation of metals and sulphate from the aqueous solution. The presence of high level of Fe denotes that the genesis of this AMD was a result of weathering of pyrite (FeS) which was also associated with traces of other sulphide bearing minerals such as ZnS, CuS and NiS amongst others. This could be confirmed by the presence of those chemical species. Although, the major chemical species were observed to be Al, Fe, Mn and Zn. Notable levels of Cu, Ni and Co were also observed to be present in AMD interface. The assessed chemical species and parameters were out of the limits as stipulated in SANS 241 specifications. However, after the interaction of AMD with calcium phosphate, major chemicals such as Al, Fe and Mn were effectively removed from the AMD interface to the product sludge even though their concentration still remained out of the limit regulated by SANS 241. The incomplete removal of chemical species of interest could be attributed to insufficient level of Ca and its removal efficacy at high concentration since metal hydroxide was the main route for attenuation during the treatment of AMD. The levels of pH and EC were observed to have increased after the treatment of AMD with calcium phosphate. Additionally, other trace metals were also reduced in the product water after contacting AMD with calcium phosphate. The percentage removal of Al, Mn and Fe from AMD were close to ≥ 80% while ≥ 65% for other chemical species was attained. The attenuation of chemical species during the treatment of AMD with calcium phosphate could be represented by the following chemical reaction:

$$\mathrm{M^{n+} + nOH^- \rightarrow M(OH)_n \downarrow} \qquad (5.6)$$

In light of the obtained results, it can be concluded that calcium phosphate was a good candidate for the attenuation of chemical species in AMD. However utilizing high feed dose > 1 g would be required in order to completely remove chemical species from AMD solution to the required standards as stipulated in different water quality guidelines, requirements, specifications and standards.

5.4 Conclusions

The findings from this study confirmed the feasibility of synthesizing calcium phosphate and applied it for the treatment of acid mine drainage (AMD) or metal rich effluent. Specifically, the synthesis of calcium phosphate was successfully done at 5 g: 150 mL of calcium hydroxide and municipal wastewater. Thenceforth, the product calcium phosphate was used for the treatment of acid mine drainage or metals rich effluent. Optimum conditions were observed to be 60 min of equilibration and 1 g of dosage in 100 mL of AMD solution at 90 rpm of mixing speed. Interaction of calcium phosphate with AMD led to close to 99% removal efficacy for Fe, Mn and other metals except for Al, which demonstrated close to 80% removal efficacy. XRD confirmed the synthesis of calcium phosphate. This was further confirmed by presence of phosphate in EDS results. PHREEQC confirmed the existence of chemicals divalent ions, trivalent ions, and oxyanions including their potential to precipitate as metals hydroxide. This has corroborated the FTIR, XRD and HR-SEM-EDS results. Furthermore, it can be confirmed that the product mineral was effective enough for the removal of metals from AMD. The pH was observed to be $\geq$ 10 and this was suitable for attenuation of all the chemicals species in AMD. The removal of chemical species from municipal wastewater and acid mine drainage subsequently was observed to be technically viable. Thus, this technology could valorise calcium phosphate synthesized from municipal wastewater effluents and open new horizons for the effective and sustainable management of wastewater effluents and AMD. This will minimize the footprints of acid mine drainage and municipal wastewater on different spheres of the environment. In light of the above, future research should focus on the use of life cycle assessment tools to measure ecological footprints of this initiative. Employing geochemical modelling to substantiate this technique will further enhance the techno-viability of this technology.

REFERENCES

REFERENCES

Akinwekomi, V., Kefeni, K.K., Maree, J.P. and Msagati, T.A., 2016. Integrated acid mine drainage treatment using Mg (OH) 2 or Mg (HCO3) 2 and Ca (OH) 2: Implications for separate removal of metals and sulphate. International Journal of Mineral Processing, 155, pp.83-90.

Alegbe, M.J., Ayanda, O.S., Ndungu, P., Nechaev, A., Fatoba, O.O. and Petrik, L.F., 2019. Physicochemical characteristics of acid mine drainage, simultaneous remediation and use as feedstock for value added products. Journal of Environmental Chemical Engineering, 7(3), pp.103097.

Andrić, I., Jamali-Zghal, N., Santarelli, M., Lacarrière, B. and Le Corre, O., 2015. Environmental performance assessment of retrofitting existing coal fired power plants to co-firing with biomass: carbon footprint and emergy approach. Journal of Cleaner Production, 103, pp.13-27.

Ano, J., Assemian, A.S., Yobouet, Y.A., Adouby, K. and Drogui, P., 2019. Electrochemical removal of phosphate from synthetic effluent: a comparative study between iron and aluminum by using experimental design methodology. Process Safety and Environmental Protection, 129, pp.184-195.

Atasoy, A.D., Sagir, M. and Erdem, A.F., 2019. Adsorption of Fe, Mn and Cd in carbonate-rich clayey soils and assessment of environmental effcts. Environmental Engineering & Management Journal (EEMJ), 18(12), pp. 2605-2611.

Balintova, M. and Petrilakova, A., 2011. Study of pH influence on selective precipitation of heavy metals from acid mine drainage. Chemical Engineering Transactions, 25, pp.1-6.

Barceló, D., Žonja, B. and Ginebreda, A., 2020. Toxicity tests in wastewater and drinking water treatment processes: A complementary assessment tool to be on your radar. Journal of Environmental Chemical Engineering, 8(5), pp.104-262.

Caddarao, P.S., Garcia-Segura, S., Ballesteros Jr, F.C., Huang, Y.H. and Lu, M.C., 2018. Phosphorous recovery by means of fluidized bed homogeneous crystallization of calcium phosphate. Influence of operational variables and electrolytes on brushite homogeneous crystallization. Journal of the Taiwan Institute of Chemical Engineers, 83, pp.124-132.

Calugaru, I.L., Neculita, C.M., Genty, T. and Zagury, G.J., 2020. Removal and recovery of Ni and Zn from contaminated neutral drainage by thermally activated dolomite and hydrothermally activated wood ash. Water, Air, & Soil Pollution, 231(5), pp.1-12.

Chai, Y., Qin, P., Zhang, J., Wu, Z., Li, T., Xu, W. and Sun, H., 2020. Experimental study and application of dolomite aeration oxidation filter bed for the treatment of acid mine drainage. Minerals Engineering, 157, pp.106560.

Chai, Y., Qin, P., Zhang, J., Wu, Z., Li, T., Xu, W. and Sun, H., 2020. Experimental study and application of dolomite aeration oxidation filter bed for the treatment of acid mine drainage. Minerals Engineering, 157, pp.106560.

de Andrade, P.M., Dufrayer, C.R., Ionashiro, E.Y. and de Brito, N.N., 2020. The use of metallurgical waste for heterogeneous photo Fenton-Like treatment of cosmetic effluent. Journal of Environmental Chemical Engineering, 8(5), p.104148.

Dlamini, C.L., De Kock, L.A., Kefeni, K.K., Mamba, B.B. and Msagati, T.A.M., 2019. Acid mine drainage pollution remediation using hybrid chelating ion-exchange/HZrO 2 nanocomposite adsorbents. SN Applied Sciences, 1(12), pp.1-14.

Dutta, M., Islam, N., Rabha, S., Narzary, B., Bordoloi, M., Saikia, D., Silva, L.F. and Saikia, B.K., 2020. Acid mine drainage in an Indian high-sulfur coal mining area: Cytotoxicity assay and remediation study. Journal of hazardous materials, 389, pp.121851.

El Bouraie, M. and Masoud, A.A., 2017. Adsorption of phosphate ions from aqueous solution by modified bentonite with magnesium hydroxide Mg (OH) 2. Applied Clay Science, 140, pp.157-164.

Esmaeili, A., Mobini, M. and Eslami, H., 2019. Removal of heavy metals from acid mine drainage by native natural clay minerals, batch and continuous studies. Applied Water Science, 9(4), pp.97.

Etale, A., Nhlane, D. and Richards, H., 2021. Graphene oxide nanosheets for treatment of mine-drainage contaminated water: The effect of phosphate functionalisation on U (VI) removal. Materials Today: Proceedings, 38, pp.647-651.

Farage, R.M., Quina, M.J., Gando-Ferreira, L., Silva, C.M., de Souza, J.J.L. and Torres, C.M., 2020. Kraft pulp mill dregs and grits as permeable reactive barrier for removal of copper and sulfate in acid mine drainage. Scientific Reports, 10(1), pp.1-10.

Feng, G., Ma, J., Zhang, X., Zhang, Q., Xiao, Y., Ma, Q. and Wang, S., 2019. Magnetic natural composite Fe3O4-chitosan@ bentonite for removal of heavy metals from acid mine drainage. Journal of Colloid and Interface Science, 538, pp.132-141.

Franco, D., Lee, J., Arbelaez, S., Cohen, N. and Kim, J.Y., 2017. Removal of phosphate from surface and wastewater via electrocoagulation. Ecological Engineering, 108, pp.589-596.

Funke, N.S., Nienaber, S. and Gioia, C., 2012. An interest group at work: Environmental activism and the case of acid mine drainage on Johannesburg's West Rand. Africa Institute of South Africa.

García-Valero, A., Martínez-Martínez, S., Faz, A., Rivera, J. and Acosta, J.A., 2020. Environmentally sustainable acid mine drainage remediation: Use of natural alkaline material. Journal of Water Process Engineering, 33, pp.101064.

Groudev, S., Georgiev, P., Spasova, I. and Nicolova, M., 2008. Bioremediation of acid mine drainage in a uranium deposit. Hydrometallurgy, 94(1-4), pp.93-99.

Haldar, S.K., 2013. Environmental system management of mineral resources and sustainable development. Mineral Exploration Principles and Applications, pp.267-285.

Han, C., Lalley, J., Iyanna, N. and Nadagouda, M.N., 2017. Removal of phosphate using calcium and magnesium-modified iron-based adsorbents. Materials Chemistry and Physics, 198, pp.115-124.

Heviánková, S., Bestová, I. and Kyncl, M., 2014. The application of wood ash as a reagent in acid mine drainage treatment. Minerals Engineering, 56, pp.109-111.

Hövelmann, J., Putnis, C.V. and Benning, L.G., 2018. Metal sequestration through coupled dissolution–precipitation at the brucite–water interface. Minerals, 8(8), pp.346.

Hu, H., Zhang, Q., Li, X., Wu, L. and Liu, Y., 2020. Efficient heterogeneous precipitation and separation of iron in copper-containing solution using dolomite. Separation and Purification Technology, 248, pp.117021.

Iakovleva, E., Mäkilä, E., Salonen, J., Sitarz, M., Wang, S. and Sillanpää, M., 2015. Acid mine drainage (AMD) treatment: Neutralization and toxic elements removal with unmodified and modified limestone. Ecological Engineering, 81, pp.30-40.

Ileri, B. and Yucel, D.S., 2020. Metal removal from acid mine lake using ultrasound-assisted modified fly ash at different frequencies. Environmental Monitoring and Assessment, 192(3), pp.1-18.

Jafaripour, A., Rowson, N.A. and Ghataora, G.S., 2015. Utilisation of residue gas sludge (BOS sludge) for removal of heavy metals from acid mine drainage (AMD). International Journal of Mineral Processing, 144, pp.90-96.

Jiang, L., Wang, Q., Zhou, M., Liang, L., Li, K., Yang, W., Lu, X. and Zhang, Y., 2020. Role of adsorption and oxidation in porous carbon aerogel/persulfate system for non-radical degradation of organic contaminant. Chemosphere, 241, pp.125066.

Jiang, S., Jin, W., Wang, Y.N., Pan, H., Sun, Z. and Tang, R., 2017. Effect of the aggregation state of amorphous calcium phosphate on hydroxyapatite nucleation kinetics. RSC advances, 7(41), pp.25497-25503.

Jin, D., Wang, X., Liu, L., Liang, J. and Zhou, L., 2020. A novel approach for treating acid mine drainage through forming schwertmannite driven by a mixed culture of Acidiphilium multivorum and Acidithiobacillus ferrooxidans prior to lime neutralization. Journal of Hazardous Materials, pp.123108.

Jooste, S. and Thirion, C., 1999. An ecological risk assessment for a South African acid mine drainage. Water Science and Technology, 39(10-11), pp.297-303.

Jouini, M., Rakotonimaro, T.V., Neculita, C.M., Genty, T. and Benzaazoua, M., 2019. Stability of metal-rich residues from laboratory multi-step treatment system for ferriferous acid mine drainage. Environmental Science and Pollution Research, 26(35), pp.35588-35601.

Kapp, K.J. and Miller, R.Z., 2020. Electric clothes dryers: An underestimated source of microfiber pollution. Plos one, 15(10), pp.165.

Kaur, G., Couperthwaite, S.J. and Millar, G.J., 2018. Performance of bauxite refinery residues for treating acid mine drainage. Journal of Water Process Engineering, 26, pp.28-37.

Kaur, G., Couperthwaite, S.J., Hatton-Jones, B.W. and Millar, G.J., 2018. Alternative neutralisation materials for acid mine drainage treatment. Journal of Water Process Engineering, 22, pp.46-58.

Lei, Y., Du, M., Kuntke, P., Saakes, M., van der Weijden, R. and Buisman, C.J., 2019. Energy efficient phosphorus recovery by microbial electrolysis cell induced calcium phosphate precipitation. ACS Sustainable Chemistry & Engineering, 7(9), pp.8860-8867.

Lei, Y., Saakes, M., van der Weijden, R.D. and Buisman, C.J., 2020. Electrochemically mediated calcium phosphate precipitation from phosphonates: Implications on phosphorus recovery from non-orthophosphate. Water Research, 169, pp.115206.

Lei, Y., Song, B., Saakes, M., Van Der Weijden, R.D. and Buisman, C.J., 2018. Interaction of calcium, phosphorus and natural organic matter in electrochemical recovery of phosphate. Water Research, 142, pp.10-17.

Li, H., Ge, W., Zhang, J., Kasomo, R.M., Leng, J., Weng, X., Chen, Q., Gao, Q., Song, S., Xiao, L. and Tian, C., 2020. Control foaming performance of phosphate rocks used for wet-process of phosphoric acid production by phosphoric acid. Hydrometallurgy, 195, pp.105364.

Liu, H., Zhu, L., Tian, X. and Yin, Y., 2017. Seasonal variation of bacterial community in biological aerated filter for ammonia removal in drinking water treatment. Water Research, 123, pp.668-677.

Liu, J., Zhou, L., Dong, F. and Hudson-Edwards, K.A., 2017. Enhancing As (V) adsorption and passivation using biologically formed nano-sized FeS coatings on limestone: Implications for acid mine drainage treatment and neutralization. Chemosphere, 168, pp.529-538.

Magagane, N., Masindi, V., Ramakokovhu, M.M., Shongwe, M.B. and Muedi, K.L., 2019. Facile thermal activation of non-reactive cryptocrystalline magnesite and its application on the treatment of acid mine drainage. Journal of Environmental Management, 236, pp.499-509.

Mahmoud, M.E., Allam, E.A., Saad, E.A., El-Khatib, A.M. and Soliman, M.A., 2019. Remediation of Co/Zn ions and their 60Co/65Zn radioactive nuclides from aqueous solutions by acid activated nanobentonite. Environmental Nanotechnology, Monitoring & Management, 12, pp.100277.

Marshall, J.A., Morton, B.J., Muhlack, R., Chittleborough, D. and Kwong, C.W., 2017. Recovery of phosphate from calcium-containing aqueous solution resulting from biochar-induced calcium phosphate precipitation. Journal of Cleaner Production, 165, pp.27-35.

Masindi, V., Akinwekomi, V., Maree, J.P. and Muedi, K.L., 2017. Comparison of mine water neutralisation efficiencies of different alkaline generating agents. Journal of Environmental Chemical Engineering, 5(4), pp.3903-3913.

Masindi, V., Chatzisymeon, E., Kortidis, I. and Foteinis, S., 2018. Assessing the sustainability of acid mine drainage (AMD) treatment in South Africa. Science of the Total Environment, 635, pp.793-802.

Masindi, V., Gitari, M.W., Tutu, H. and De Beer, M., 2015. Passive remediation of acid mine drainage using cryptocrystalline magnesite: A batch experimental and geochemical modelling approach. Water SA, 41(5), pp.677-682.

Masindi, V., Osman, M.S. and Shingwenyana, R., 2019. Valorization of acid mine drainage (AMD): A simplified approach to reclaim drinking water and synthesize valuable minerals–Pilot study. Journal of Environmental Chemical Engineering, 7(3), pp.103082.

Mavhungu, A., Foteinis, S., Mbaya, R., Masindi, V., Kortidis, I., Mpenyana-Monyatsi, L. and Chatzisymeon, E., 2021. Environmental sustainability of municipal wastewater treatment through struvite precipitation: Influence of operational parameters. Journal of Cleaner Production, 285, pp.124856.

Mavhungu, A., Masindi, V., Foteinis, S., Mbaya, R., Tekere, M., Kortidis, I. and Chatzisymeon, E., 2020. Advocating circular economy in wastewater treatment: Struvite formation and drinking water reclamation from real municipal effluents. Journal of Environmental Chemical Engineering, 8(4), pp.103957.

Mavhungu, A., Mbaya, R., Masindi, V., Foteinis, S., Muedi, K.L., Kortidis, I. and Chatzisymeon, E., 2019. Wastewater treatment valorisation by simultaneously removing and recovering phosphate and ammonia from municipal effluents using a mechano-thermo activated magnesite technology. Journal of Environmental Management, 250, pp.109493.

Mitrogiannis, D., Psychoyou, M., Baziotis, I., Inglezakis, V.J., Koukouzas, N., Tsoukalas, N., Palles, D., Kamitsos, E., Oikonomou, G. and Markou, G., 2017. Removal of phosphate from aqueous solutions by adsorption onto Ca (OH) 2 treated natural clinoptilolite. Chemical Engineering Journal, 320, pp.510-522.

Monballiu, A., Ghyselbrecht, K., Pinoy, L. and Meesschaert, B., 2020. Phosphorous recovery as calcium phosphate from UASB effluent after nitrification with or without subsequent denitrification. Journal of Environmental Chemical Engineering, 8(5), pp.104119.

Muratoglu, A., 2020. Grey water footprint of agricultural production: An assessment based on nitrogen surplus and high-resolution leaching runoff fractions in Turkey. Science of The Total Nowińska, K. and Adamczyk, Z., 2021. Effect of galena contained in dust from Zn–Pb metallurgical processes on environment. Environmental Earth Sciences, 80(8), pp.1-7. Environment, 742, p.140553.

Naidu, G., Ryu, S., Thiruvenkatachari, R., Choi, Y., Jeong, S. and Vigneswaran, S., 2019. A critical review on remediation, reuse, and resource recovery from acid mine drainage. Environmental Pollution, 247, pp.1110-1124.

Núñez-Gómez, D., Lapolli, F.R., Nagel-Hassemer, M.E. and Lobo-Recio, M.Á., 2020. Optimization of Fe and Mn removal from coal acid mine drainage (AMD) with waste biomaterials: Statistical modeling and kinetic study. Waste and Biomass Valorization, 11(3), pp.1143-1157.

Othman, A., Sulaiman, A. and Sulaiman, S.K., 2017, May. The use of hydrated lime in acid mine drainage treatment. In AIP Conference Proceedings (Vol. 1847, No. 1, p. 040001). AIP Publishing LLC.

Park, I., Tabelin, C.B., Jeon, S., Li, X., Seno, K., Ito, M. and Hiroyoshi, N., 2019. A review of recent strategies for acid mine drainage prevention and mine tailings recycling. Chemosphere, 219, pp.588-606.

Parkhurst, D.L. and Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-Resources Investigations Report, 99(4259), pp.312.

Pereira, T.C.B., dos Santos, K.B., Lautert-Dutra, W., de Souza Teodoro, L., de Almeida, V.O., Weiler, J., Schneider, I.A.H. and Bogo, M.R., 2020. Acid mine drainage (AMD) treatment by neutralization: Evaluation of physical-chemical performance and ecotoxicological effects on zebrafish (Danio rerio) development. Chemosphere, pp.126665.

Qureshi, A., Jia, Y., Maurice, C. and Öhlander, B., 2016. Potential of fly ash for neutralisation of acid mine drainage. Environmental Science and Pollution Research, 23(17), pp.17083-17094.

Ramontja, T., Eberle, D., Coetzee, H., Schwarz, R. and Juch, A., 2011. Critical challenges of acid mine drainage in South Africa’s Witwatersrand gold mines and mpumalanga coal fields and possible research areas for collaboration between South African and German researchers and expert teams. In The New Uranium Mining Boom (pp. 389-399). Springer, Berlin, Heidelberg.

Roveri, V., Guimarães, L.L. and Correia, A.T., 2020. Spatial and temporal evaluation of the urban runoff water flowing into recreational areas of Guarujá, São Paulo State, Brazil. International Journal of River Basin Management, pp.1-17.

Ryu, S., Naidu, G., Johir, M.A.H., Choi, Y., Jeong, S. and Vigneswaran, S., 2019. Acid mine drainage treatment by integrated submerged membrane distillation–sorption system. Chemosphere, 218, pp.955-965.

Šabanović, E., Memić, M., Sulejmanović, J. and Selović, A., 2020. Simultaneous adsorption of heavy metals from water by novel lemon-peel based biomaterial. Polish Journal of Chemical Technology, 22(1), pp.46-53.

Saha, S., Sarkar, S. and Sinha, A., 2019. Use of Basic Oxygen Furnace (BOF) Steel Slag for Acid Mine Drainage Treatment: A Laboratory Study. Mine Water and the Environment, 38(3), pp.517-527.

Sahoo, H., Senapati, D., Thakur, I.S. and Naik, U.C., 2020. Integrated bacteria-algal bioreactor for removal of toxic metals in acid mine drainage from iron ore mines. Bioresource Technology Reports, 11, p.100422.

Sahoo, P.K., Tripathy, S., Panigrahi, M.K. and Equeenuddin, S.M., 2013. Evaluation of the use of an alkali modified fly ash as a potential adsorbent for the removal of metals from acid mine drainage. Applied Water Science, 3(3), pp.567-576.

Salama, A. and Hesemann, P., 2020. Synthesis and characterization of N-guanidinium chitosan/silica ionic hybrids as templates for calcium phosphate mineralization. International Journal of Biological Macromolecules, 147, pp.276-283.

Samimi, M. and Moghadam, M.S., 2018. Optimal conditions for the biological removal of ammonia from wastewater of a petrochemical plant using the response surface methodology. Global Journal of Environmental Science and Management, 4(3), pp.315-324.

Sebogodi, K.R., Johakimu, J.K. and Sithole, B.B., 2020. Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa. Journal of Cleaner Production, 246, pp.118979.

Seo, E.Y., Cheong, Y.W., Yim, G.J., Min, K.W. and Geroni, J.N., 2017. Recovery of Fe, Al and Mn in acid coal mine drainage by sequential selective precipitation with control of pH. Catena, 148, pp.11-16.

Shajib, M.T.I., Hansen, H.C.B., Liang, T. and Holm, P.E., 2020. Rare earth elements in surface specific urban runoff in Northern Beijing. Science of The Total Environment, 717, pp.136969.

Shen, Y., Li, M., Liu, K., Xu, X., Zhu, S., Wang, N., Guo, W., Zhao, Q., Lu, P., Yu, F. and Xu, X., 2020. Integrated bioinformatics analysis of aberrantly-methylated differentially-expressed genes and pathways in age-related macular degeneration. BMC Ophthalmology, 20, pp.1-12.

Sithole, N.T., Ntuli, F. and Okonta, F., 2020. Synthesis and evaluation of basic oxygen furnace slag based geopolymers for removal of metals and sulphates from acidic industrial effluent-column study. Journal of Water Process Engineering, 37, p.101518.

Skousen, J.G., Ziemkiewicz, P.F. and McDonald, L.M., 2019. Acid mine drainage formation, control and treatment: Approaches and strategies. The Extractive Industries and Society, 6(1), pp.241-249.

Slavov, L., Abrashev, M.V., Merodiiska, T., Gelev, C., Vandenberghe, R.E., Markova-Deneva, I. and Nedkov, I., 2010. Raman spectroscopy investigation of magnetite nanoparticles in ferrofluids. Journal of Magnetism and Magnetic Materials, 322(14), pp.1904-1911.

Sun, R., Li, Y., Lin, N., Ou, C., Wang, X., Zhang, L. and Jiang, F., 2020. Removal of heavy metals using a novel sulfidogenic AMD treatment system with sulfur reduction: Configuration, performance, critical parameters and economic analysis. Environment International, 136, p.105457.

Tanaka, Y., Hasegawa, T., Sugimoto, K., Miura, K., Aketo, T., Minowa, N., Toda, M., Kinoshita, K., Yamashita, T. and Ogino, A., 2014. Advanced treatment of swine wastewater using an agent synthesized from amorphous silica and hydrated lime. Environmental Technology, 35(23), pp.2982-2987.

Tolonen, E.T., Sarpola, A., Hu, T., Rämö, J. and Lassi, U., 2014. Acid mine drainage treatment using by-products from quicklime manufacturing as neutralization chemicals. Chemosphere, 117, pp.419-424.

Torres, E., Lozano, A., Macías, F., Gomez-Arias, A., Castillo, J. and Ayora, C., 2018. Passive elimination of sulfate and metals from acid mine drainage using combined limestone and barium carbonate systems. Journal of Cleaner Production, 182, pp.114-123.

Tutu, H., McCarthy, T.S. and Cukrowska, E., 2008. The chemical characteristics of acid mine drainage with particular reference to sources, distribution and remediation: the Witwatersrand Basin, South Africa as a case study. Applied Geochemistry, 23(12), pp.3666-3684.

Vadapalli, V.R.K., Sakala, E., Dube, G. and Coetzee, H., 2020. Mine Water Treatment and the Use of Artificial Intelligence in Acid Mine Drainage Prediction. Recovery of Byproducts from Acid Mine Drainage Treatment, pp.23-48.

Van Deventer, H. and Cho, M.A., 2014. Assessing leaf spectral properties of Phragmites australis impacted by acid mine drainage. South African Journal of science, 110(7-8), pp.1-12.

Wang, X., Jiang, H., Fang, D., Liang, J. and Zhou, L., 2019. A novel approach to rapidly purify acid mine drainage through chemically forming schwertmannite followed by lime neutralization. Water research, 151, pp.515-522.

Woo, H.E., Tran, T.V., Lee, I.C., Kim, J.O., Hibino, T., Nohara, H. and Kim, K., 2019. Remediation of contaminated sediment originating from wastewater at harbor areas using slaked lime–fly ash–cement mixture. Estuarine, Coastal and Shelf Science, 227, pp.106340.

Wu, Z. and Ye, Q., 2020. Water pollution loads and shifting within China's inter-province trade. Journal of Cleaner Production, 259, pp.120879.

Yahya, N., Qureshi, S., ur Rehman, Z., Alqasem, B. and Kait, C.F., 2017. Green urea synthesis catalyzed by hematite nanowires in magnetic field. Journal of Magnetism and Magnetic Materials, 428, pp.469-480.

Yousefi, M., Nabizadeh, R., Alimohammadi, M., Mohammadi, A.A. and Mahvi, A.H., 2019. Removal of phosphate from aqueous solutions using granular ferric hydroxide process optimization by response surface methodology. Desalin. Water Treat, 158, pp.290-300.

Yuan, Z., Zhang, G., Ma, X., Yu, L., Wang, X., Wang, S. and Jia, Y., 2019. Rapid abiotic As removal from As-rich acid mine drainage: Effect of pH, Fe/As molar ratio, oxygen, temperature, initial As concentration and neutralization reagent. Chemical Engineering Journal, 378, p.122156.

Zhang, M., Gu, P., Yan, S., Liu, Y. and Zhang, G., 2020. Effective removal of radioactive cobalt from aqueous solution by a layered metal sulfide adsorbent: Mechanism, adsorption performance, and practical application. Separation and Purification Technology, p.117775.

Zhou, K., Wu, B., Su, L., Xin, W. and Chai, X., 2018. Enhanced phosphate removal using nanostructured hydrated ferric-zirconium binary oxide confined in a polymeric anion exchanger. Chemical Engineering Journal, 345, pp.640-647.

CHAPTER SIX

OVERALL CONCLUSIONS AND RECOMMENDATION

6.1 Conclusions

This study was proposed with an attempt to answer the following questions relating to the synthesis of calcium phosphate from municipal wastewater and its subsequent application for for acidity neutralization and attenuation of chemical species concentration from acidic effluents.

- What are the physico-chemical properties of municipal effluents and acid mine drainage (AMD)?
- What are the physicochemical and mineralogical properties of calcium hydroxide and calcium phosphate?
- What are the optimum of the conditions that are suitable for the synthesis of calcium phosphate from municipal effluents using hydrated lime as the feedstock?
- What are the optimum conditions that are suitable for the treatment of acidic and metalliferous mine effluent using the synthesized calcium phosphate as feedstock?
- What is the chemistry of processed water and the resultant solid residues after interacting municipal wastewater with the calcium hydroxide?
- What is the chemistry of the processed water and the resultant solid residues after interacting AMD with calcium phosphate?
- How does the quality of treated water compare with the South African water quality guidelines?

6.1.1 Characterization of aqueous solution

Analysis of chemical composition of MWW by IC revealed that MWW from Rietvlei contains on average of 55.68 mg L^{-1} sulphate, pH 6.67, TDS of 884 mg L^{-1}, EC of 1473 µS cm^{-1}, 14.87 mg L^{-1} of F^-, 81.91 mg L^{-1} of Cl^-, 1736 mg L^{-1} of NO_3^- and 41.33 mg L^{-1}. Consequently, analysis of chemical composition of AMD by ICP-OES suggest that AMD from Mpumalanga comprises of TDS of 14900 mg L^{-1}, EC of 1605 µS cm^{-1}, pH 9.70, Fe 96.239 mg L^{-1}, Mn of 74.892 mg L^{-1}, Co of 33.821 mg L^{-1}, Cu of 25.959 mg L^{-1}, Ni of 39.744 mg L^{-1}, Al of 59.601 mg L^{-1} and Zn of 115.158 mg L^{-1}. This results proves that MWW and AMD streams are highly polluted water that can pose hazardous impact to living organisms on exposure.

6.1.2 Characterization of calcium hydroxide and calcium phosphate

Calcium hydroxide was reported to contain CaO as the mineral phases. After interacting with MWW, new mineral phase were observed. This could be explained by the decrease of in chemical species from MWW. The FTIR showed the availability of OH and carbonate stretches on raw calcium hydroxide. After interaction of MWW with raw calcium hydroxide, PO_4^{3-} stretches were observed indicating that phosphate ion were adsorbed by Ca hence indicating the formation of new mineral phase, whitlokite ($Ca_3(PO_4)_2$. SEM-EDS showed that the morphology of calcium hydroxide comprise of irregular rough surface with abundant pore structure hence indicating that the material is homogeneous. EDS revealed high levels of Ca, C and O with traces of Mg hence confirming that it is calcium hydroxide. After contacting MWW with calcium hydroxide, the octagonal nano-sheets with a flower like structure and smashed with molded smooth surface were observed hence indicating the dissolution of calcium hydroxide on contact with MWW. Furthermore, after contacting calcium phosphate with AMD, Fe-OH group was observed from the FTIR spectrum indicating the precipitation of Fe^{3+} from AMD. EDS revealed the presense of Al, Fe and Mn indicating that the was attenuation of those chemical speces from AMD. SEM-EDS showed the triangular sheets with homogenous arrangement onto the surface of AMD-reacted with calcium phosphate.

6.1.3 Treatment of MWW with calcium hydroxide

In this study, hydrated lime was utilized as a feedstock for the removal of nitrate and phosphate from municipal wastewater. The addition of this feed into the wastewater had an effect of elevating the pH of the wastewater, hence increasing the removal performance of phosphate whereas nitrate was being difficult to be removed at all pH levels tested. Moreover, at all-times, nitrate-to-phosphate ratios in solution, the ratio of nitrate to phosphate removed was always lower which suggested that the phosphate had a higher selectivity for being removed than nitrate. This suggested that chemical precipitation was the predominant mechanism. Phosphate was recovered as calcium phosphate after the addition of hydrated lime to municipal wastewater solution at solid liquid ratio of 0.06 g: 100 mL. The XRD and SEM analysis confirmed the presence of new mineral phases in the precipitate. Furthermore, PHREEQC geochemical model confirmed the precipitation of calcium phosphate as whitlokite and hydroxyapatite based on these results, it was concluded that the prepared calcium phosphate could serve as alternative sources of phosphorus, and used as slow fertilizers to relieve future shortages of phosphorus. Furthermore, calcium phosphate was able to be applied for the treatment of acid mine drainage.

6.1.3 Treatment of AMD with calcium phosphate

Interaction of AMD with calcium phosphate led to an increase in pH and a notable attenuation of metal ions concentrations. Maximum removal of Al, Fe and Mn was attained after 60 min of contact time for a solid liquid ratio of 1 g: 100 mL. Under these conditions, the pH achieved was > 10, which is suitable enough for attenuation of chemical species from AMD. Using geochemical modelling, it was shown that Al, Fe, and Mn were precipitated as metal oxide and hydroxide. From modelling simulations, the formation of these phases were precipitated at the a selective precipitation sequence with Al^{3+} at pH < 6, Fe^{3+} at pH > 6, Fe^{2+} at pH > 8, Mn^{2+} at pH >10. This study has pointed to the efficiency of calcium phosphate in neutralizing and attenuating metals from AMD and metalliferous industrial effluents. A disadvantage of this technology is that most of earth alkali and alkaline earth metals remain in solution which means a post treatment processes such as ion exchange or reverse osmosis might be required for polishing the product water.

6.1.4 Overall significance of the study

This study confirmed that calcium hydroxide showed some good performances for the removal on nitrate from municipal wastewater however it were not fully effective whereas it proved to be a better candidate for the synthesis of calcium phosphate from municipal wastewater. The synthesized calcium phosphate managed to reclaim water to usable standards as specified by the water quality guidelines hence making it a replacement for conventional methods that are used for AMD treatment.

6.2 Recommendations

The application of calcium phosphate for the treatment of AMD presented a potential AMD treatment method and remediated water to almost within SANS Water Quality Guidelines standards. However, additional research studies are required in this area if this technology is to be applied on a larger scale process. Therefore, this study recognized various research gap that could be pursued:

- Assessing the efficacy of the synthesized material for the removal of sulphate and other chemical components from acid mine drainage (AMD).
- The potential of calcium phosphate to neutralize and remove heavy metals ion from AMD was investigated against one type of AMD from a coal mine in Mpumalanga. More investigations are required to be carried out to corroborate the effectiveness of the calcium phosphate to treat AMD from different sources including neutral drainage.
- This study only focused on batch laboratory experiments and validation of experimental results using a geochemical model. The generation of AMD is a natural process that can take place in abandoned underground workings as well as surface tailings dumps. In light to that, fixed bed column studies that can mimic natural processes under the force of gravity must be also carried out in attempts to explore the effectiveness of calcium phosphate to alleviate tailings dumps, neutralize acidity and remove heavy metals ions from tailings leachates.
- Calcium phosphate has been successfully utilized for the neutralization of acidic solution from metalliferous mine drainage.
- Further research can be pursued with the aim to explore the ability of using calcium phosphate for the treatment of AMD, stabilization of gold- and coal-mine tailings and recovery of metals.
- Pilot assessment and large-scale assessment requires to be established and executed to determine the efficiency of the material at a large scale set up.
- Hybrid systems that can be utilized in integration with calcium phosphate need to be fabricated to refine water quality that meet the required standards for many of defined uses

APPENDIX

Appendix A

Figure A1: An image showing MWWTP where sample are collected

Appendix B: Experimental results

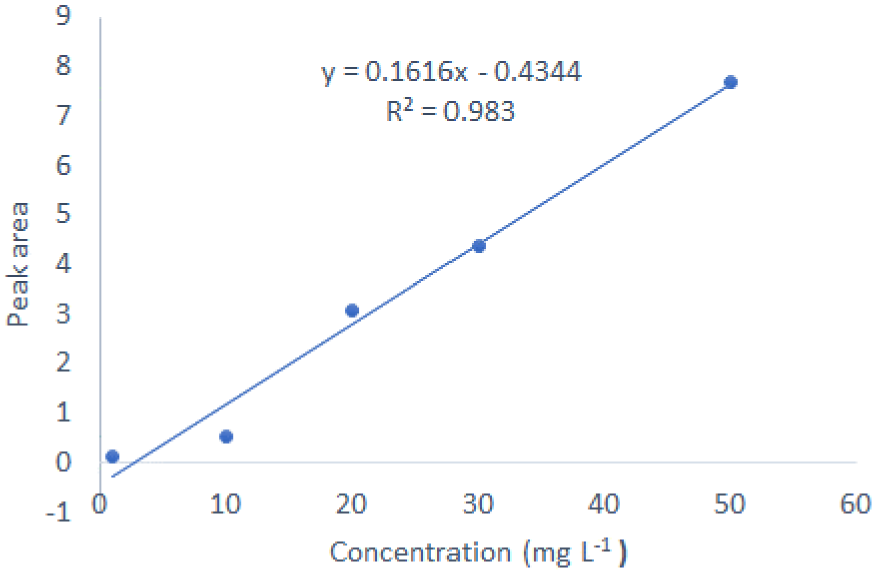


Figure B1: Calibration curve for nitrate obtained from ion chromatography (IC)

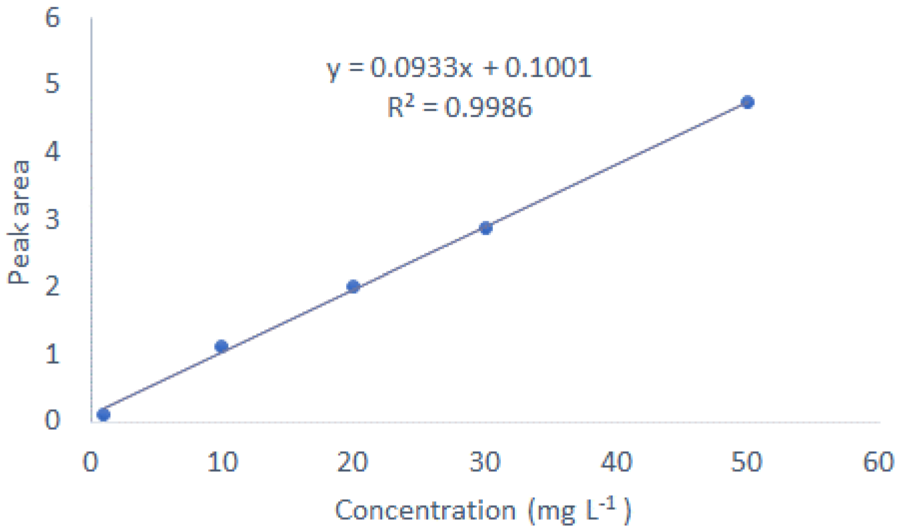


Figure B2: Calibration curve for phosphate obtained from ion chromatography (IC)

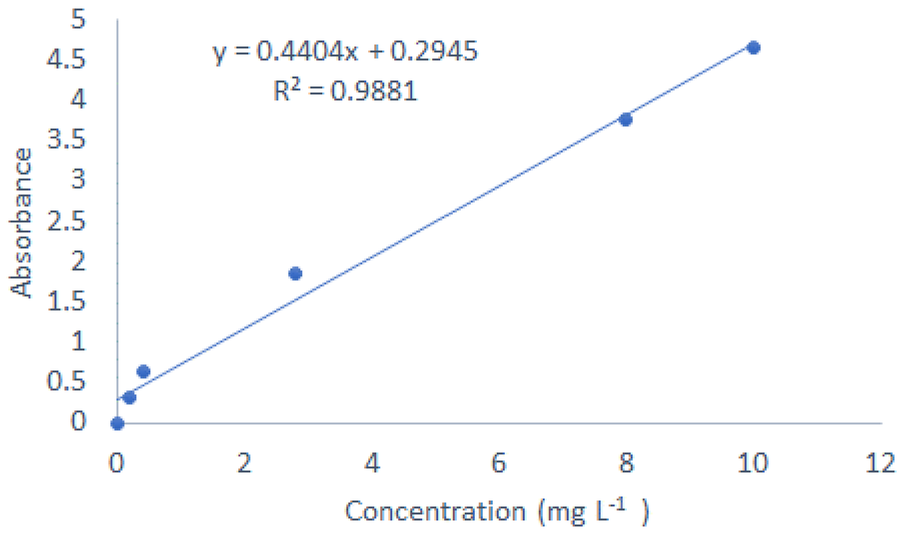


Figure B3: Calibration curve for aluminium obtained from the graphite furnace atomic absorption spectroscopy (GFAAS)

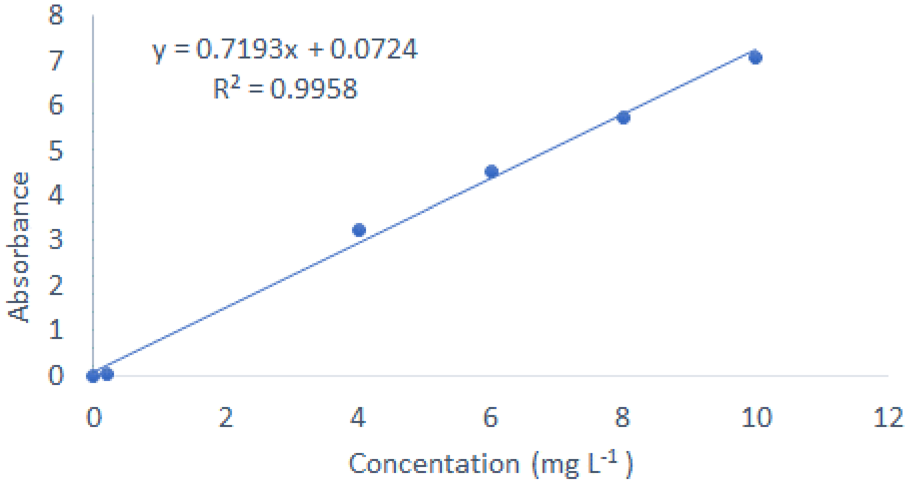


Figure B4: Calibration curve for iron obtained from the graphite furnace atomic absorption spectroscopy (GFAAS)

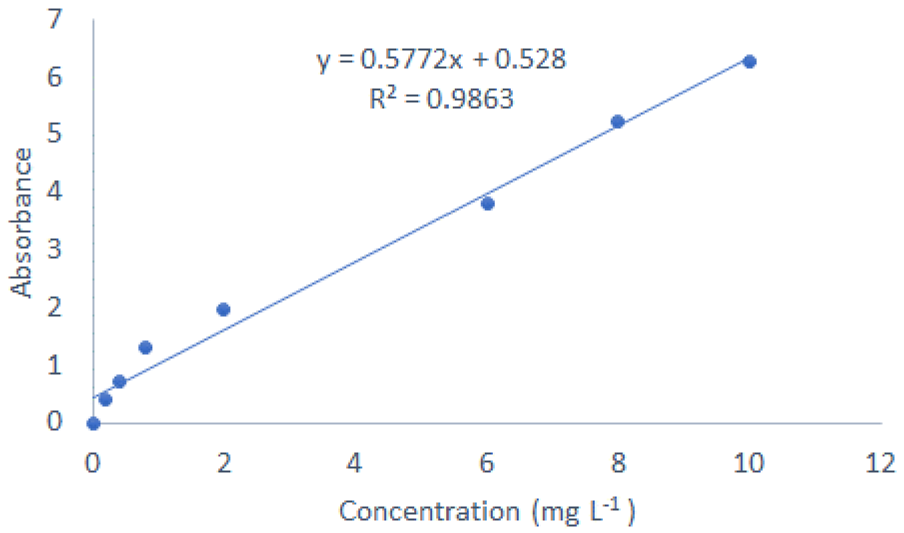


Figure B5: Calibration curve for iron obtained from the graphite furnace atomic absorption spectroscopy (GFAAS)

Table B1: Effect of pH on the treatment of MWWTPs using hydrated lime

pH	Nitrate removal (%)	SD	RSD (%)	Phosphate removal (%)	SD	RSD (%)
2	7.67	0.668	49.50	94.03	0.068	9.37
3	7.52	0.643	38.41	99.99	0.090	6.22
4	9.40	0.244	55.52	94.48	0.082	3.26
5	1.79	0.211	66.64	64.19	0.415	39.64
6	3.09	0.316	38.81	36.64	0.124	32.10
7	2.14	0.360	34.44	34.96	0.271	46.12
8	6.85	0.594	65.08	62.09	0.683	43.99
9	1.39	0.634	69.91	45.77	0.511	28.76
10	6.15	0.719	56.01	46.49	0.288	33.76
11	39.85	0.221	38.10	69.85	0.214	21.16

Table B2: Effect of dosage on the treatment of MWWTPs using hydrated lime

Dosage (g)	Nitrate removal (%)	SD	RSD (%)	Phosphate removal (%)	SD	RSD (%)
0.01	9.48	0.481	39.09	39.83	0.388	46.06
0.02	7.94	0.300	37.08	26.68	0.461	58.10
0.03	9.83	0.212	26.11	39.39	0.200	37.74
0.04	10.57	0.210	37.02	35.14	0.028	31.98
0.05	9.47	0.119	45.26	59.92	0.591	37.23
0.06	29.43	0.380	19.70	73.34	0.044	18.22

Table B3: Effect of chemical species concentration on the treatment of MWWTPs using hydrated lime

Concentration (mg L^{-1})	Nitrate removal (%)	SD	RSD (%)	Phosphate removal (%)	SD	RSD (%)
20	10.78	0.192	27.09	98.66	0.307	11.35
30	7.73	0.343	30.91	71.94	0.556	12.22
50	4.54	0.414	46.39	57.92	0.501	18.47
60	4.12	0.103	69.53	28.14	0.318	34.43
80	5.59	0.879	67.55	23.62	0.264	38.17
100	8.76	0.212	45.00	31.88	0.415	37.10

Table B4: Effect of contact time on the treatment of MWWTPs using hydrated lime

Contact time	Nitrate removal (%)	SD	RSD (%)	Phosphate removal (%)	SD	RSD (%)
5	5.37	0.911	67.8	27.9	0.507	38.47
25	6.29	0.454	59.80	57.3	0.401	22.21
45	6.96	0.400	52.31	99.97	0.204	9.73
120	7.11	0.329	36.30	99.91	0.232	11.21
150	7.34	0.293	41.01	99.89	0.311	17.14
180	7.82	0.363	38.17	99.94	0.201	4.61

Table B5: Effect of pH on treatment of acid mine drainage using calcium phosphate

pH	Al removal (%)	SD	RSD	Fe removal (%)	SD	RSD (%)	Mn removal (%)	SD	RSD
2	73.92	0.059	3.93	99.74	0.003	2.87	99.40	0.002	2.05
3	63.42	0.429	20.02	99.49	0.013	11.89	99.23	0.001	0.83
4	75.98	0.778	23.21	99.48	0.004	3.35	97.73	0.028	3.33
5	64.40	0.067	1.74	89.40	0.031	3.68	98.61	0.012	1.76
6	72.73	0.178	6.73	99.77	0.054	60.49	97.76	0.002	1.38
7	54.89	0.479	14.59	97.32	0.022	8.44	98.21	0.020	3.09
8	34.79	0.119	2.77	95.39	0.006	1.40	97.89	0.028	2.27
9	65.09	0.311	16.68	99.19	0.019	14.90	96.81	0.012	21.16
10	41.62	0.030	1.65	99.99	0.056	49.04	99.88	0.002	3.71
11	26.03	0.138	3.88	99.33	0.120	40.23	94.51	0.003	1.04
12	19.52	0.009	0.22	95.50	0.026	6.74	91.94	0.008	2.27

Table B6: Effect of dosage on treatment of acid mine drainage using calcium phosphate

Dosage (g)	Al removal (%)	SD	RSD (%)	Fe removal (%)	SD	RSD (%)	Mn removal (%)	SD	RSD (%)
0.1	10.78	0.036	3.48	96.51	0.034	2.57	83.17	0.034	6.11
0.2	35.02	0.018	3.18	98.96	0.008	1.94	87.95	0.049	4.06
0.3	46.60	0.231	2.16	97.17	0.007	3.85	92.27	0.077	7.62
0.4	64.57	0.246	38.81	97.71	0.014	5.01	97.98	0.014	2.12
0.8	69.21	0.019	1.12	99.86	0.066	40.23	99.74	0.023	5.29
1	71.28	0.130	6.81	99.99	0.021	7.71	99.88	0.048	5.81

Table B7: Effect of contact time on treatment of acid mine drainage using calcium phosphate

Contact time	Al removal (%)	SD	RSD (%)	Fe removal (%)	SD	RSD (%)	Mn removal (%)	SD	RSD (%)
10	80.26	0.333	19.16	88.29	0.155	39.64	88.03	0.017	3.81
30	69.51	0.332	18.84	89.49	0.028	3.26	94.21	0.014	1.46
50	73.23	0.157	14.26	91.46	0.029	5.77	95.34	0.069	9.38
90	78.41	0.423	28.48	89.63	0.086	9.87	94.70	0.026	2.27
120	78.98	0.097	8.49	94.19	0.029	6.22	97.75	0.185	4.77
150	83.37	0.073	7.51	93.38	0.035	4.26	96.23	0.032	2.73
180	79.36	0.145	10.37	96.27	0.013	2.05	98.13	0.024	2.09

Table B8: Effect of chemical species concentration on treatment of acid mine drainage using calcium phosphate

Concentration (mg L^{-1})	Al removal (%)	SD	RSD (%)	Fe removal (%)	SD	RSD (%)	Mn removal (%)	SD	RSD (%)
5	76.63	0.056	55.72	99.12	0.007	18.22	84.73	0.006	7.23
10	88.97	0.050	11.31	98.87	0.086	55.70	98.84	0.012	10.22
15	72.84	0.149	12.07	96.54	0.051	12.32	95.11	0.009	9.69
20	77.89	0.021	6.54	98.34	0.100	32.10	96.51	0.017	12.91
30	85.17	0.059	5.94	93.53	0.004	8.94	93.73	0.038	35.55
50	86.31	0.068	4.99	96.39	0.004	9.09	96.31	0.006	6.57

Table B9: Effect of temperature on treatment of acid mine drainage using calcium phosphate

Temperature (°C)	Al removal (%)	SD	RSD (%)	Fe removal (%)	SD	RSD (%)	Mn removal (%)	SD	RSD (%)
25	77.87	0.023	2.14	94.17	0.001	2.42	96.98	0.025	6.19
30	91.21	0.246	37.81	94.12	0.050	65.56	97.72	0.038	4.87
40	96.78	0.030	1.69	94.89	0.003	10.48	99.50	0.036	4.61
50	82.72	0.085	9.70	97.21	0.002	3.11	97.54	0.010	0.81
60	90.43	0.058	5.92	97.98	0.004	6.59	99.89	0.083	11.70
70	91.78	0.039	3.24	95.66	0.005	8.71	98.71	0.033	3.91
80	87.64	0.032	5.04	98.12	0.018	2.35	99.73	0.021	3.33