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Treatment of waste water from nitrates explosive plant



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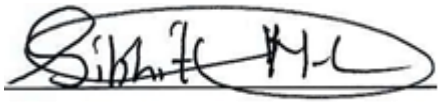
A Dissertation submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Masters of Science.

January 2019, Johannesburg

DECLARATION

I, Sikhitha Ntuweleni Lawrence declare that this Dissertation is my own, unaided work. It is being submitted for the Degree of Masters of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.



_____

(Signature of candidate)

04 day of January 2019 in Johannesburg

DEDICATION

I would like to dedicate this work to my late grandmother Nyamuofhe Mutwautshila; I wish she has lived a little longer than she did and to my late uncle Reuben Muvhango Sikhitha whose departure left wounds in my heart. May their souls rest in peace and arise in heavenly glory.

ABSTRACT

Nitrate waste water usually contains high concentrations of ammonium nitrogen (NH_4^+-N), which is known to hinder nitrification during biological treatment processes.

In this study, removal of ammonium nitrogen from nitrate waste water was studied. Various purification processes such as using coagulation/flocculation and precipitation of magnesium ammonium phosphate was tested. Optimum parameters such as optimum pH, precipitation by pH adjustment and molar ratio were studied and precipitated crystals that formed were characterized.

Sequential flocculation with two cationic flocculants reduced the turbidity of the nitrate waste water from 163 Neupholetric Turbidity units to 15 NTU. An optimum pH of 9 could remove ammonium nitrogen in nitrate waste water, as pointed out by evidence. Mg^{2+}: NH_4^+-N: PO_4^{3-}-P with a 1:1:1.1 molar ratio was found to be the most effective ratio for maximum ammonium nitrogen removal, with quite a low residual concentration of PO_4^{3-}-P. $MgCl_2{\cdot}6H_2O$ + 85% H_3PO_4 combination was found to be more efficient combination for ammonium Nitrogen removal from nitrate waste water, with a low residual concentration of PO_4^{3-}-P. Precipitate crystals formed were found to be pure struvite crystals. Approximately 69.9% of ammonium nitrogen was recovered as struvite. Struvite precipitation is deemed to be an efficient for the treatment of ammonium nitrogen removal from nitrate waste water.

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LIST OF ABBREVIATIONS

AC	Activated Carbon
MAP	Magnesium Ammonium Phosphate (struvite)
CCD	Charged - Coupled Detector
$Cm^3\ min^{-1}$	Cubic centimeter per minute
COD	Chemical Oxygen Demand
cPs	count Per second
EDS	Energy-Dispersive Spectroscopy
Flocs	Flocculated suspended solids
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
IE	Ion Exchange Chromatography
KOH	Potassium Hydroxide
pH	$-\log[H^+]$
RO	Reverse Osmosis
ppb	Parts per billion
rpm:	revolutions per minute
TDS	Total Dissolved Solids
TEM	Transmission Electron Microscopy
TGA	Thermo Gravimetric Analysis
TG-DSC	Thermo Gravimetric- Differential Scanning Calorimetry
TOPAS	Total Phase Analysis
TSS	Total Suspended Solids
WHO	World Health Organization
XRD	X-Ray Diffraction

˚C	Degree Celsius
λ	Lambda

DEFINITIONS

Explosive: Material that causes a sudden, almost instantaneous, release of gas, heat and pressure, accompanied by a loud noise when subjected to a certain amount of shock, pressure or temperature.

Watergels: A wide variety of explosives, all containing water and ammonium nitrate, used for blasting.

Contaminated: Something that is impure or unsuitable by contact or mixture with something unclean, bad, etc.

Waste water: Spent or used water with dissolved or suspended solids, discharged from homes, commercial establishments, farms and industries.

Effluent: Liquid waste discharged into a sewer system or water or anywhere.

Physical & chemical treatment: Process commonly used in large-scale waste water treatment plants. “Physical’’ treatment usually includes air-stripping and filtration; “chemical’’ treatment includes chlorination, coagulation, and ozonization. This term may also refer to the treatment of toxic waste in surface and ground water, oil spills and the soil.

Polyatomic ion: A polyatomic ion, also known as a molecular ion, is a charged chemical species (ion) composed of two or more atoms covalently bonded or of a metal complex that can be considered to be acting as a single unit.

Desorption: A phenomenon whereby a substance is released from or through a surface.

Nitrification: The biological oxidation of ammonia or ammonium to nitrite followed by the oxidation of the nitrite to a nitrate.

Denitrification: A microbially facilitated process where nitrate is reduced and ultimately produces molecular nitrogen through a series of intermediate gaseous nitrogen oxide products. Facultative anaerobic bacteria perform denitrification as a type of respiration that reduces oxidized forms of nitrogen in response to the oxidation of an electron donor such as organic matter.

Dechlorination: The process of removing residual chlorine from disinfected waste water, prior to discharge into the environment.

Struvite (magnesium ammonium phosphate): A phosphate mineral with formula: $NH_4MgPO_4 \cdot 6H_2O$.

CHAPTER ONE

INTRODUCTION

1.1 General Introduction

South Africa can be called a semi – arid country because of its average rainfall of about 480 mm (Shippey *et al*., 2005). This is half of the world's average rainfall (Reeves, 1997). This makes industrial waste water treatment and recycling for re-use essential in South Africa, particularly for the sustainability of the economy. The treatment of waste water is even more important to industry when it carries valuable and recoverable components.

When pollutants are removed through biological, chemical and physical methods, the process is called waste water treatment. Pollutants that might be present, are pharmaceutical, nitrogen (such as nutrients) and phosphate, microorganisms, inorganic substances, such as sand and other contaminants. Waste water treatment reduces the contaminants to levels acceptable for re-use or discharge into the environment (*Tchobanoglous et al*., 2003).

Some of the industries and households create waste water that can be broken down by natural means. In this case, a biological process can be used. Biological treatment plants use bacteria and other biological means to break down waste (*Kornaros et al*., 2006). On the other hand, industrial waste water can contain chemicals that can be harmful to the environment; in this case, a chemical plant is needed to treat that water.

The waste water treatment process, starts by removing the heavier particles followed by the dissolved minerals. This process consists of three end products, i.e. firstly, trash and grid are removed for disposal during the pre-

treatment stage. Secondly, the biological component of the waste water solution, called bio – solids, needs various steps to be separated. Lastly, the receiving stream will receive the treated effluent waste water. The solid substances that are removed during water treatment are called sludge. This sludge can be further re-used as valuable materials like fertilizer, in land reclamation or it will be sent for land filling or incineration (Davis, 2010).

1.2 Background

The Sasol Satellite Ekandustria, manufactures high quality commercial explosives for Southern Africa and abroad. With the growth of mining industries over the years, the production of explosives and explosive components has increased tremendously. The Ekandustria factory is today the largest commercial explosive manufacturer in the world.

The Sasol watergel plant in Ekandustria is one of the Sasol satellite plants which makes use of lots of water during the production of secondary explosives. In the process of watergel manufacturing, ammonium nitrate (NH_4NO_3), calcium nitrate ($CaNO_3$) and sodium nitrate ($NaNO_3$) are used as ingredients. As a result watergel contains a significant amount of nitrogen, but has a different solubility to water and therefore has varying degrees of capacity to introduce its nitrogen into the water system.

Normally, the watergel mixture contains 20% to 30% (by weight) nitrogen (Kindt *et al*., 1994). This nitrogen is in two very water soluble forms, ammonium (NH_4^+) and nitrate (NO_3^-) ions. The water solubility of a watergel mixture is good once the water-soluble gums and gel modifiers like guar has gelled the whole mixture. This gelled gum forms a relatively impermeable barrier between the oxidizing agents and any external water. The long term stability of the gelling agent is finite and the nitrogen can eventually be

exposed to external water. Explosive spillage, leakage and floor washing are a major introduction of nitrogen into the environment as NH_4^+ and NO_3^- (from NH_4NO_3, $CaNO_3$ and $NaNO_3$) (Pommen, 1983).

1.3 Problem statement

Thousands of tons of waste water effluent are produced daily from the Sasol Satellite Ekandustria process during the production of watergel explosives. The production of watergel, does however give rise to a larger amount of ammonium nitrate in the waste water. During watergel production, high levels of ammonium nitrogen (NH_4^+-N), sodium nitrates, calcium nitrates, etc. are found in the waste water as outlined in Table1.1

Table 1.1: Typical composition of waste water sample (All values unless indicated, are in mgL^{-1})

pH value	6.87
Nitrate as N	6188
Ammonium as N	4235
Sulphate as SO_4	19.27
Chloride	585.63
Sodium	106
Calcium	47.42
Magnesium	7.68
Total dissolved solids	13.9
Conductivity	290 μScm^{-1}
Turbidity	154 NTU

The receiving water quality will deteriorate if it receives high levels of ammonium nitrogen. Nitrates and ammonia are generally the compounds of greatest concern for water quality degradation due to potential human health

and aquatic life impacts (Liikanen *et al*., 2003, Reddy-Lopata *et al*., 2006). Before the aquatic systems receive the waste water, NH_4^+-N should be removed, because these components are harmful to the ecology. Currently, waste water are filtered and then pumped to a settling tank, pumped back to the plant and excess effluent is collected in an evaporation dam. The effluent is disposed of in dams along the production facility as shown below Figure 1.1.



Figure 1.1: Waste water effluent disposal dam alongside a watergel production facility in Ekandustria, South Africa

1.4 Justification of the study

More effort has been made in order to minimize plant waste water, by recycling waste water back to plant and excess waste water being pumped into our collection dams for evaporation. A permanent solution is needed to prevent nitrate containing waste water effluent being from discharged into rivers or streams during the rainy season or by runoff from disposal dams

when they are full. This intensifies the need to investigate the alternative nitrate waste water-treatment options that would ultimately eliminate undesirable consequences to the environment. The process of ammonium removal from waste water was investigated by Zaixing *et al*., (2012). In his study it was shown that removal of ammonium from waste water is technically feasible. There is the need to investigate possible treatment options available for the remaining effluent for re-use and for discharge into the streams if possible, provided that they meet the South African Department of Water Affairs and Sanitation Waste Water Discharge Standards as outlined in Table 1.2.

1.5 Objective of the study

The principal objective of waste water treatment is generally to lower pollutant concentrations to be able to dispose of it without danger to human health or unacceptable damage to the natural environment. Waste water from the production of explosives contains a large number of contaminants, some in extremely high concentrations. The explosives industry therefore aims to solve this problem by finding a way of controlling or removing these high concentrations of dissolved inorganic and organic nitro compounds so as to enable the treated waste water to be directly discharged back into production and excess effluent into the overflow dams with minimum hazards to the environment. The main objectives of this research project are:

(1) To determine the contaminants in effluent that are harmful to the environment and living organisms,

(2) To study and apply physico/chemical treatment methods for removing the identified contaminants.

(3) To characterize the removed precipitate and to make sure that the treated effluent meet the South African Department of Water Affairs and Sanitation, Waste Water Discharge Standards before being discharged into receiving streams.

Table 1.2: National Water Act Waste Discharge Standards DWA 2013 Guidelines (All values are in mgL^{-1})

Variables and substances	**Existing general standards**
Chemical oxygen demand	75
Colour, odour or taste	No substance capable of producing the variables listed
Ionized and unionized ammonia (free and saline ammonia)(as N)	3.5
Nitrate (as N)	15
pH	Between 5.5 and 9.5
Phenol index	0.1
Residual Chlorine (as Cl)	0.25
Suspended solids	25
Total Aluminium (as Al)	-
Total Cyanide (as Cn)	0.02
Total Arsenic (as As)	0.02
Total Boron (as B)	1.0
Total Cadmium (as Cd)	0.005
Total Chromium III (as CrIII)	-
Total Chromium VI (as CrVI)	0.05
Total Copper (as Cu)	0.01
Total Iron (as Fe)	0.3
Total Lead (as Pb)	0.01
Total Mercury (as Hg)	0.005
Total Selenium (as Se)	0.02
Total Zinc (as Zn)	0.1
Faecal coliforms (count per 100mL)	1000

CHAPTER TWO
LITERATURE REVIEW

2.1 Introduction

This chapter highlights from the literature, some of the human health and aquatic life impacts associated with excess levels of ammonium nitrogen and other contaminants that may deteriorate the receiving water quality from the nitrate explosive plant discharge. It also highlights some of the technologies which are currently in use for the removal of ammonium nitrogen and other contaminants from aqueous solutions. The advantages and disadvantages associated with these techniques are also discussed. Research work done with respect to the removal of ammonium nitrogen and other dissolved and non-dissolved contaminants in nitrates explosive plant waste water. Studies related to the use magnesium ammonium phosphate (struvite) and other precipitants for the removal of dissolved minerals are also discussed in this chapter.

2.2 Impacts associated with discharge of un-treated waste water from nitrates explosive plant, on receiving water quality

2.2.1 Nitrogen and its derivatives

The forms of nitrogen of great interest in waste waters are ammonia (NH_3), nitrite (NO_2^-), nitrate (NO_3^-) and organic nitrogen (Org-N). All these nitrogen forms as well as nitrogen gas (N_2), are constituents of the nitrogen cycle and are biochemically interconvertible (APHA, 1989).

2.2.1.1 Ammonia (NH_3)

Ammonia is a compound of nitrogen and hydrogen with the formula NH_3 and a molecular mass of 17.031 $gmoL^{-1}$. It is a colourless gas with a characteristic pungent smell. Ammonia may exist as molecular ammonia (NH_3) or as ammonium ions (NH_4^+). Ammonia is lighter than air, with a density of 0.589 times that of air. It is simply liquified due to the strong hydrogen bonding between molecules; the liquid boils at −33.3°C and freezes at −77.7°C to form white crystals (Haynes, 2013).

The ammonia molecule has a trigonal pyramidal shape. The central nitrogen atom has five outer electrons with an extra electron from each hydrogen atom. Bond pairs, such as three of these electron pairs, as well as one single or lone pair of electrons are used. Bond pairs are much less strongly repelled than the single pair of electrons. A base, proton acceptor is coupled of a lone electron pair of a nitrogen atom in the molecule. It is made polar by using the shape that gives the molecule a dipole moments. (Haynes, 2013).

Humans and other mammals have a mechanism that inhibits the build - up of ammonium solutions in their bloodstreams. The enzyme carbamoyl phosphate synthetase converts ammonia to carbamoyl phosphate to be incorporated into amino acids or to be excreted in the urine (Berg *et al*., 2002). However, creatures like amphibians and fish lack this mechanism, as they can frequently eliminate ammonia from their bodies through direct excretion. Even highly diluted concentrations of ammonia is highly poisonous to aquatic animals; for this reason it is categorized as dangerous to the environment. The toxicity of ammonia is believed to be a cause of otherwise unexplained losses in fish hatcheries. Extra ammonia may accumulate and cause modification of metabolism or increases in the body pH of the exposed organism (Oram *et al*., 2014).

Ammonium can be transformed biologically to nitrite, followed by the oxidation of the nitrite to nitrate through a process called nitrification. Nitrogen is removed from waste water by mechanisms such as:

i) Bacterial nitrification and/or
ii) Volatilization of ammonia.

Of these two mechanisms, bacterial nitrification and denitrification have the utmost nitrogen removal abilities. Nitrification is a process of nitrogen compound oxidation and is catalyzed step-wise by a series of enzymes.

$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+$ (Nitrosomonas) 2.1

$2NO_2^- + O_2 \rightarrow 2NO_3^-$ (Nitrobacter, Nitrospira) 2.2

The receiving stream will be contaminated by nitrogen compounds that need to be reduced or removed through nitrification of waste water. Ammonia and other nitrogen compounds can be transformed into nitrites (NO_2^-) by nitrosomonas, nitrites are then transformed to nitrates (NO_3^-) by nitrobacters. This process is called nitrification. For every kilogram of ammonia that is nitrified, 2 kg of molecular oxygen will be used (Kerri *et al*. 2006).

On the other hand, denitrification involves the biological reduction of nitrate and/or nitrite to nitrogen gas in the absence of dissolved oxygen. In the process, bacteria uses the oxygen enclosed in the nitrate or nitrite molecules to metabolize organic carbon (USACE, 2001). Denitrification is done by a wide variety of heterotrophic bacterial species, most of them are commonly found in typical biological treatment. Most of this bacteria are common because they are facultative and can use oxygen, nitrite or nitrate as their oxygen source. These bacteria will normally use oxygen, especially when it is

available, however they can also change and utilize nitrate or nitrite whenever dissolved oxygen is in low supply or absent (USACE, 2001).

Ammonia levels in waste water can also be reduced through a process known as desorption (Patoczka *et al.*, 1984). When ammonia is desorption, it can also be called air stripping. The ammonia molecule is stripped from the waste water solution and released into the atmosphere by surface turbulence. Increased turbulence on the surface of the waste water releases more ammonia to the atmosphere through disc diffuses rays (Monteith *et al*., 2005).

Treated effluent will be discharged into receiving streams by waste water treatment plants. High level of ammonia can be oxidized before it enters a receiving stream. Aquatic organisms may be harmed by levels of molecular oxygen in the receiving streams. The removal of ammonia is therefore essential before the discharge of effluent into receiving streams (Kerri *et al*., 2006).

2.2.1.2 Nitrite (NO_2^-)

Nitrite is an intermediate oxidation state of nitrogen, both in the oxidation of ammonia to nitrate and also the reduction of nitrate to nitrogen gas (APHA, 1989). Naturally, nitrite occurs in fresh waters as a result of nitrification of ammonia and denitrification of nitrate. Nitrite which is intermediate of oxidation of ammonia to nitrate, changes haemoglobin to methaemoglobin that inhibits oxygen transportation and as a result becomes toxic within fish and other aquatic organisms.

Nitrite is unstable and it can be easily oxidized to nitrate. Nitrate exists as an intermediate compound during the oxidation of ammonia to nitrate. When nitrate is present in waste water, the concentration is usually less than 1.0

mgL^{-1}. However, some industrial wastes water may contain nitrite in significant concentrations (Doyle *et al.,* 2002).

2.2.1.3 Nitrates (NO_3^-)

Nitrate is a molecular ion with the molecular formula NO_3^- and a molecular mass of 62.0049 $gmoL^{-1}$. Nitrate (NO_3^-) is a common inorganic form of nitrogen. Chemically, nitrate is an anion with a single negative charge, consisting of one atom of nitrogen and three identically bonded oxygen atoms in a trigonal planar arrangement. The nitrate ion carries a formal charge of −1. This results from a combination of formal charges in which each of the three identical oxygens carries a $-\frac{2}{3}$ charge, although the nitrogen carries a +1 formal charge, all these adding up to formal charge of the polyatomic nitrate ion (He *et al*., 1999). Nitrate ion, similar to the isoelectronic carbonate ion can be represented by resonance structures:

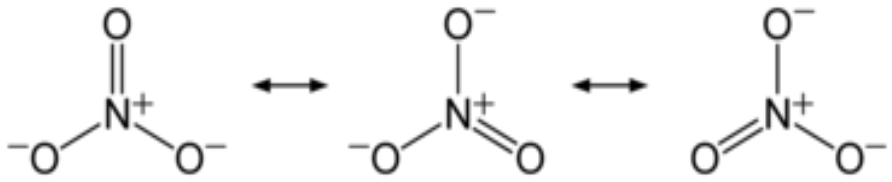

Figure 2.1: Resonance structures for the nitrate ion

Plants normally use nitrates as their source of nitrogen needed by all living organisms; in this case, nitrates are considered to be a nutrient for plants. When nitrate concentrations in streams is in excess or greater than about 5 milligram per liter depending on the volume of water body, it can cause excessive growth of algae and other plants, leading to accelerated eutrophication or “aging'' of water streams or lakes, and occasional loss of dissolved oxygen. If nitrates and nitrites are not removed, discharge of the incompletely treated waste water will cause excess algae growth in rivers and

streams. This excess algae depletes oxygen, it may results in the death of fish and other important organisms and causes odour problems. Humans and animals cannot use inorganic forms of nitrogen; in this case nitrates are not considered a nutrient. Once nitrate-nitrogen exceeds 10 milligram per liter in drinking water, it can cause a condition called methaemoglobinaemia or "blue baby syndrome" in infants. Some recent studies have indicated a possible connection between elevated nitrate concentrations and cancer (He *et al*., 2009).

Human infants, during the first few months, are susceptible to acute nitrate poisoning caused by consuming water with nitrate concentrations of 10 mgL^{-1} or greater. Bacteria in an infant's digestive system will convert nitrates into more toxic nitrites. Nitrites react with haemoglobin and prevents oxygen transport by the blood, turning the oxygen-starved infants into a bluish colour.

Methaemoglobinaemia also occurs in ruminant animals (sheep and cattle) and in infant monogastric animals (chickens and pigs), but at higher nitrate concentrations than in human infants. This is a huge concern to farmers, because the concentrations of nitrates in agricultural drains sometimes reach 20 - 40 mgL^{-1} or more (Kerri *et al.*, 2006).

The nitrates must then be removed from the waste water through a denitrification process, which is anaerobic process. Nitrates are thus reduced and eventually produce molecular nitrogen through a sequence of intermediate gaseous nitrogen oxide products. Nitrates are metabolized by many types of anaerobic and facultative bacteria to obtain oxygen. Under aerobic conditions, this process does not occur (Kerri *et al*., 2006).

$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$ (nitrate reductase) 2.3

$NO_2^- + 2H^+ + e^- \rightarrow NO + H_2O$ (nitrite reductase) 2.4

$2NO + 2H^+ + 2e^- \rightarrow N_2O + H_2O$ (nitric oxide reductase) 2.5

$N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2O$ (nitrous oxide reductase) 2.6

The anoxic zone is an untreated sector of the aeration basin in which denitrification occurs during biological waste water treatment. A percentage of the previously nitrified activated sludge as well as raw waste water were received in the anoxic region. The aerated units of the basin receives the raw waste water from the anoxic region after denitrification of activated sludge and raw waste. The atmosphere gets the denitrified nitrogen gas after aeration discharge. When total nitrogen removal takes place in the waste water, denitrification controls it (Habermayer *et al*., 2005).

Dissolved oxygen, ammonia and nitrate levels are in a close relationship in waste water. Adjustments should be made in the waste water treatment process after the levels are monitored in the waste water. If you fail to monitor the receiving stream can have excessive discharge pollutants.

2.2.2 Chlorides

Chlorides are double constituents of chlorine and are made up of chloride ions combined with metals. Naturally, chloride is formed when hydrochloric acids react with any metal that is present in the water. It is mostly common in the areas with limestone deposits. Chlorine is normally used to sterilize final effluent, but is also useful in controlling odour.

In our households, chloride salts such as sodium chloride are normally used to preserve food. In the petroleum industry, the chlorides are a thoroughly monitored component of the mud system. An increase of the chlorides in the

mud system may be a sign of drilling into a high-pressure saltwater formation system.

Chlorides are also useful and reliable chemical indicators of river or groundwater contamination, because chloride is a non-reactive solute and universal to portable water resources. Many water regulating companies around the globe, utilizes chloride to check the contamination levels of the rivers and potable water sources (Choe *et al*., 2004). However, chloride contaminated water is unhealthy for human consumption and can be deadly to aquatic vegetation and the wildlife that rely on that ecosystems. The normal range for river surface water is 45 -155 mgL^{-1}. Ozonisation is a more effective sterilizer, and leaves no residual chemicals in water (Rutala *et al*., 2002).

Chlorine is a toxic gas which makes it ideal for killing harmful pathogens, but it does not stop there. Once chlorinated water is released into the receiving streams, it can also be harmful to fish, birds, wildlife and any other living organisms it may come into contact with. Before chlorinated water can be released into any streams, the chlorine content must be equal or below the accepted dispatched limit. The presence of chlorides, e.g. in seawater, significantly worsens the conditions for pitting corrosion of most metals (including stainless steel, aluminum, aluminium alloys and high-alloyed materials) by enhancing the formation and growth of the pits through an autocatalytic process.

The majority of dissolved solids are mostly removed from waste water through a precipitation process. However, chloride and other ionic species are difficult to remove due to their high solubility. Chloride can be easily removed from water and waste water by the precipitation process as calcium chloroaluminate making use of an advanced softening process. In the advanced softening process, lime and aluminium are used as reagents (Choe *et al*., 2004).

Chlorine must be removed prior to discharge into receiving water streams, in order to reduce toxicity before entering the receiving water environment. Dechlorination is one of the processes by which some or most of the chlorine is removed prior to discharge into streams. Some of the well-used dechlorination chemicals are sulfite compounds, sulfur dioxide, activated carbon and hydrogen peroxide. In this case sulfur dioxide gas is used as the chemical for the dechlorination process. In the process, before the disinfected water leaves the contact basin, the chlorine content in water is removed with sulfur dioxide. The sulfur dioxide gas reacts so quickly that only a few seconds is essential to turn the chlorine compounds into chloride ions.

A perfect dechlorination chemical is formed when chlorinated compounds react with sulfur dioxide. Once sulfur dioxide (SO_2), is released to atmospheric pressure and temperature, it is colourless, smelling strong, corrosive, non-flammable gas. It will be a colourless liquid when it is cooled and compressed. The following reactions will be formed when the combined chlorine reacts with the free chlorine after hydrogen sulfite (HSO_3^-) ions have reacted with water and sulfur dioxide (Maxwell, 2008):

Free Chlorine Reactions:

$SO_2 + H_2O \rightarrow HSO_3^- + H^+$ 2.7

$HOCl + HSO_3^- \rightarrow SO_4^{2-} + Cl^- + 2H^+$ 2.8

$SO_2 + HOCl + H_2O \rightarrow Cl^- + SO_4^{2-} + 3H^+$ 2.9

Combined Chloramine Reactions:

$SO_2 + H_2O \rightarrow HSO_3^- + H^+$ 2.10

$NH_2Cl + HSO_3^- + H_2O \rightarrow Cl^- + SO_4^{2-} + NH_4^+ + H^+$ 2.11

$SO_2 + NH_2Cl + 2H_2O \rightarrow Cl^- + SO_4^{2-} + NH_4 + 2H^+$ 2.12

In this reaction scheme, chloride (Cl^-) ions has been converted from chlorine. Seawater contains naturally occurring chloride which is crucial for human

metabolism. If the effluent contained hydrogen sulfite ions, it needs to be avoided due to an increased oxygen demand. See the following reaction:

$$HSO_3^- + 0.5O_2 \rightarrow SO_4^{2-} + H^+ \qquad 2.13$$

Once the chlorine content is reduced to the acceptable limits, waste water can be dispatched into receiving streams.

2.2.3 Phosphorus (P)

Phosphorus is a chemical element with symbol P and atomic number 15. Elemental phosphorus occurs in two major forms, red phosphorus and white phosphorus. Phosphorus is vital for life. In water medium, phosphorus appears exclusively as phosphate (PO_4^{3-}). Phosphate normally appears in several forms in nature, which include condensed phosphates (Meta, poly and pyro), orthophosphate and organically bound phosphates. However, although phosphates are not toxic and do not pose any direct health threat to living organisms, they do represent a serious threat to water quality. Phosphates can interfere with the treatment process at concentrations as low as 0.2 mgL^{-1} (Fried *et al.*, 2003).

Enhanced biological phosphorus removal is the process that is used for the removal of phosphorus from water systems. During this process, there is particular bacteria, called polyphosphate, which selectively enriched organisms with phosphorus and as a results, they end up accumulating large amounts of phosphorus inside their cells (up to 20% of their mass). Once, the biomass enriched in these bacteria is separated from the treated water, these bio solids can have a higher fertilizer value. Chemical precipitation is a useful method for phosphorus removal, particularly with aluminium salts (e.g. alum) or iron (e.g. ferric chloride). The drawback of this chemical precipitation is that

the resulting sludge, are difficult to handle and chemicals needed are very expensive. A considerably smaller equipment footprint is needed for chemical phosphorous removal than for biological removal. Some waste water compositions cause difficulty when removing phosphorous biologically, whereas the chemical removal can be more reliable and easier to operate (Hammer, 2004).

2.2.4 Sodium (Na)

Sodium is a chemical element with symbol Na and atomic number 11. Sodium is an important element for all animals and some plants. Sodium compounds are of huge commercial importance and are at the centre of industries that produces soap, paper glass and textiles. The most common sodium compounds are table salt (NaCl), sodium nitrate ($NaNO_3$), caustic soda (NaOH), soda ash (Na_2CO_3) and baking soda ($NaHCO_3$) (Klemm *et al*, 2005).

Sodium is an essential mineral in human beings, because it regulates blood pressure, pH, blood volume and osmotic equilibrium. The physiological minimum required sodium per day is 500 milligrams. Excess sodium in the bloodstream pose a threat to human kidneys. An increased blood volume means more pressure on blood vessels and more work for the heart, which lead to high blood pressure, heart attacks and strokes (Mack *et al*., 2004).

Sodium can be removed from any water body before dispatched into a receiving stream by making use of any of these three treatment options: (i) hydrogen forms a cation exchanger portion of a deionizer (ii) Reverse osmosis can reduce sodium by 94 – 98% (iii) Distillation can also remove sodium.

2.2.5 pH

pH (potential Hydrogen) measures alkalinity and acidity in a water sample. It measures the amount of hydrogen ions present in water. The pH of water used for households and in agriculture, as well as for drinking, should be between 6 and 9 (Aucamp *et al*., 1990). As pH has a direct influence on solubility, it is an important aspects of chemical precipitation. Literature studies regarding struvite precipitation, reveal that struvite precipitation occurs at a pH of 8.5 until 9.5 (Song *et al*., 2007). In order to achieve the maximum removal of ammonium nitrogen (NH_4^+-N) from waste water, the reaction were carried out at a pH range of 7.0 to 11.

2.2.6 Total solids

The solids in water are comprised of dissolved and suspended solids. A water filter sometimes trap suspended solids or they can settle on the stream bottom when stream velocities are low enough. Some of these solids are organic waste, plankton, clay, silt or compounds found in acid mine drainage like inorganic precipitates (Miller, 1996).

Dissolved solids, such as salts, toxins, organic materials as well as inorganic nutrients, are able to pass through a water filter. The water flow in and out of cells of aquatic organisms are determined by concentration of dissolved solids in a water stream that therefore play a crucial role. Some of the important nutrients in life are phosphorous, nitrogen and sulfur that are dissolved inorganic elements. Nutrients deficiencies can cause limited growth of aquatic organisms, due to a low total concentration of solids. An Increase turbidity of eutrophication occurs with increased levels of total solids. The stream water quality is decreased by both increased turbidity and eutrophication.

2.2.6.1 Total dissolved solids

Total dissolved solids (TDS) involve inorganic salts (principally calcium, chlorides, magnesium, potassium, sodium, bicarbonates and sulfates) and small quantities of organic matter that are dissolved in water. Anions and cations ions are responsible for the total dissolved solid concentrations in the water. Water that have a blackish, corrosive or salty taste might has a high concentration of dissolved ions that can also decrease or interfere with the efficiency of hot water heaters. The corroding of plumbing fixtures, deteriorated quality of water and interference with the washing of clothes, can all be caused by the high total number of dissolved solids. The Secondary Drinking Water Standards (Miller,1996), has set of limit of 500mgL^{-1} (milligrams per liter) for aesthetic reasons.

2.2.6.2 Total suspended solids

Domestic waste water mostly contains large amounts of suspended solids that are inorganic and organic in nature. These solids are measured as Total Suspended Solids (TSS) and are expressed as mg TSS/liter of water. Total Suspended Solids (TSS) are solids in water that can be trapped by a filter. Total suspended solids can consist of a wide range of material, such as animal matter, decaying plants and silt, industrial waste and sewage. High concentrations of suspended solids can cause many problems to the receiving water stream's health and aquatic life (Mitchell *et al*., 1992).

When the TSS is high, it can block the light from reaching immersed vegetation. Since the amount of light that could be passing through the water will be reduced, the photosynthesis will also slow down. The reduced speed of photosynthesis may cause little of the dissolved oxygen to be released into the water by plants. When the light is completely blocked from bottom

dwelling plants, the plants will stop producing oxygen and as a result will end up dying. When the plants are decomposed, bacteria will use up even more oxygen from the water. When the dissolved oxygen content is lower, fish can end up dying.

If the TSS content is higher, it can cause an increase in surface water temperature, due to the fact that the suspended particles absorb heat from sunlight. This can make the dissolved oxygen levels fall even further (because warmer water can hold less dissolved oxygen), and can hurt aquatic life in many different ways. (Mitchell *et al*., 1992).

When the water visibility (clearness) decreases because of the amount of total suspended solids, it can affect the ability of fish to see and catch food. TSS can also reduce growth rates, obstruct fish gills, decrease resistance to disease, and prevent egg and larval development. Once TSS has settled at the bottom of a water body, it can oppress the eggs of fish and aquatic insects, as well as suffocate newly hatched insect larvae. Settling suspended solids down at the bottom can fill in spaces between rocks which could have been used by aquatic organisms as their homes (Mitchell *et al*., 1992).

High TSS in a water system can cause higher concentrations of bacteria, nutrients, pesticides and metals in the water body. High TSS can create problems for industrial use, because the solids may clog or scour pipes and machinery (Mitchell *et al*., 1992). Total suspended solids are removed through a number of combination processes. A combination of filtration and sedimentation removes the solids in the sedimentation and filtration tanks. These processes happen in the sedimentation and filtration tanks respectively (Mitchell *et al*., 1992).

2.2.7 Dissolved oxygen (DO)

Dissolved oxygen refers to oxygen freely available in water, which is needed by aquatic organisms, for their respiration. DO is dependent on temperature, cold water holds more dissolved oxygen. A dissolved oxygen level that is too high or too low can harm aquatic life and affect water quality (Wetzel, 2003).

DO is also essential to many aquatic organisms like fish, invertebrates, bacteria and plants. These organisms use oxygen in their respiration, in a similar way to organisms living on land. Waste water from sewage treatment plants often contains organic materials that are decomposed by microorganisms, which make use of oxygen in the process (Wetzel, 2003). The quantity of oxygen used by these organisms in breaking down the waste is referred to as the biochemical oxygen demand (BOD).

2.2.7.1 Biochemical oxygen demand (BOD)

Biochemical oxygen demand measures the amount of oxygen consumed by microorganisms in decomposing organic matter in stream water. The degree of oxygen consumption in a stream is affected by lots of variables like: pH, temperature, the type of organic and inorganic material in the water and the presence of certain kinds of microorganisms (Carter, 2005).

Oxygen concentration is a major controlling factor that influences biochemical changes in receiving water body, as is evident in the changes the receiving water body undergo as described by Wetzel, 2003. The extent of oxygen depletion is determined by the BOD of effluent and the amount of oxygen readily available in the receiving streams. Pollution also play a major role. If the level of pollution is low, the oxygen saturation may never drop to the level

indicated as the zones of decomposition. Reoxygenation occurs more quickly in wild streams than in slow moving streams (Carter, 2005).

BOD directly affects the amount of dissolved oxygen in rivers or streams. The greater the BOD, the more rapidly oxygen is depleted in the stream. This means less oxygen is available to higher forms of aquatic life. The consequences of high BOD are the same as those for low dissolved oxygen: aquatic organisms become stressed, suffocate and may even die.

Main sources of biochemical oxygen demand includes dead plants and animals, leaves and woody debris, effluents from pulp and paper mills, waste water treatment plants, feedlots and food-processing plants, failing septic systems and urban storm water runoff.

2.2.7.2 Chemical oxygen demand (COD)

Chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. COD is an indicative measure of the amount of oxygen that can be consumed by reactions in a measured solution. COD is also useful in quantifying the amount of oxidizable pollutants found in waste water or surface water. In water quality, COD is useful in providing the effect an effluent will have on the receiving body, particularly biochemical oxygen demand (BOD) (Sawyer *et al*., 2003).

When the chemical oxygen demand in a water sample is higher, it indicates that the amount of pollution in the water sample is higher. For the contaminants that can be oxidized biologically, the biological oxygen demand (BOD) method is used. When the amount of oxygen in the water is not

enough, the aquatic life can die. Under risky conditions, the water may change to black and start producing a foul odour.

COD in a waste water body can be reduced by using a precipitation process (coagulation, like ferric chloride and alum), filtration and as adsorption process with activated carbon, with an oxidator (hydrogen peroxide, ozone), a microbiology process, etc. (Richardson, 2009).

In South Africa, the Department of Water and Sanitation requires effluent to meet the chemical oxygen demand limit before being discharged to receiving streams as follows:

Table 2.1: Department of water and sanitation effluent chemical oxygen demand limit

SUBSTANCE/ PARAMETER	SPECIAL LIMIT ~ WATER TO RIVERS ~ MAXIMUM CONCENTRATION	GENERAL LIMIT ~ WATER TO OTHER AREAS ~ MAXIMUM CONCENTRATION
Chemical Oxygen Demand (COD)	Less than 30 mgL^{-1} after corrective chlorine	Less than 75 mgL^{-1} after corrective chlorine

Companies or industries are required to monitor and control their effluent water. Industries that do not comply with the Department of Water Affairs and Sanitation Waste Water Discharge Standards, can harm the environment and as a result can receive fines, charges or criminal penalties.

2.3 Current technologies for the removal of dissolved and non-dissolved pollutants

Several techniques for the removal of dissolved heavy and light pollutants from waste water are in place. These methods can be divided into three categories, namely biological, chemical and physical techniques.

The removal of dissolved minerals from waste water has been given relatively little attention, because minerals have been considered less pollutional than other constituents, such as organic matter and suspended solids. Chlorides, phosphates, nitrates, ammonium and certain metals are examples of the more common and significant inorganic dissolved solids. This research project will put more effort on all physical-chemical options available, which can be practically applicable for the removal of all un-dissolved and dissolved contaminants from Ekandustria wastewater effluents until they meet the South African Department of Water and Sanitation Waste Water Discharge Standards.

2.3.1 Chemical coagulation/flocculation

Coagulation is a process in which colloidal particles in water are destabilized (i.e. the nature of particles is changed) so that they form flocs through the process of flocculation, that can be separated from the water. This technique is useful for the removal of particles which is difficult to remove by filtration methods. The particles in water or waste water are destabilized by an addition of chemicals (called coagulants) (Schutte, 2006). Fine solid particles dispersed in waste water carry electric surface charges (in their normal stable state), which prevent them from forming larger groups and settling.

Chemical coagulation destabilizes these particles by introducing positively charged coagulants that then reduce the negative particle charge. Once the charge is reduced, the particles freely form large agglomerates. Next, an anionic flocculant is introduced to the mixture. Because the flocculant reacts against the positively charged mixture, it either neutralizes the particle groups or creates bridges between them to bind the particles into larger groups. The objective of coagulation is not only for the formation of readily settleable suspension, but also for the formation of the suspension which is effectively filterable in order to obtain economical operation of the filtration plants (Polasek *et al*., 2002).

Aluminium sulphate normally known as alum and other inorganic aluminium salts as well as inorganic iron salts are commonly used in water treatment to enhance the removal of particulate, dissolved and colloidal impurities through a coagulation process (Srinivasan *et al*., 1999). Although the main purpose of adding coagulants such as alum is for the removal of suspended matter, it has also been reported that these coagulants have a capability of reducing the concentration of dissolved metals such as Cr, Cd, Cu, Mg, As, Ni and Mn in water (Fatoki *et al*., 2002).

2.3.2 Chemical precipitation

Chemical precipitation is the most common method for removing dissolved metals from a waste water solution containing toxic metals. To convert dissolved metals into a solid particle form, a precipitation reagent is added to the mixture. A chemical reaction, triggered by the reagent, causes the dissolved metals to form solid particles. Filtration can then be used to remove the particles from the mixture (*Kornaros et al.,* 2006). How well the process works is dependent upon the kind of metal present, the concentration of the metal and the kind of reagent used. In ammonium nitrogen precipitation,

struvite, magnesium ammonium phosphate ($MgNH_4PO_4{\cdot}6H_2O$) precipitation is an effective technology for the removal of NH_4^+-N from waste water (Zaixing *et al*., 2012).

Struvite, is a white crystalline inorganic mineral (Doyle *et al.*, 2002). Struvite is normally associated with scaling, that affects treatment processes, as it leads to operational failures linked with sludge build-up in pipes, heat exchangers, centrifuges and flow-meters (Neethling *et al.*, 2004). Pig farms, nitrogen works, coke plants, Industrial waste water treatment plants, landfill leachate (Prater, 2014) and sludge liquor (Schulze, 1999), implemented the precipitation of NH_4^+-N as magnesium ammonium phosphate (MAP), which is also called struvite (Zdybiewska *et al*., 1991). The basic reaction is as follows:

$$Mg^{2+} + NH_4^+ + H_nPO_4^{3-n} + 6H_2O \leftrightarrow MgNH_4PO_4{\cdot}6H_2O + nH^+ \ (n=0, 1, 2) \qquad 2.14$$

The water phase can easily separate magnesium ammonium phosphate as it has a low water solubility (0.169 gL^{-1} at 25°C). When 1 g of NH_4^+-N is removed, 17.5 g $MgNH_4PO_4{\cdot}6H_2O$ theoretically formed as precipitate with a molecular weight of magnesium ammonium phosphate of 245 $g.mol^{-1}$. The following (Li *et al*., 1999) reports on the basic chemical reactions of magnesium ammonium phosphate formations:

$$MgCl_2{\cdot}6\ H_2O + Na_2HPO_4 \cdot 12H_2O + NH_4^+ \leftrightarrows MgNH_4PO_4{\cdot}6H2O{\downarrow} + 2NaCl \qquad 2.15$$

$$MgO + H_3PO_4 + NH_4^+ \rightarrow MgNH_4PO_4{\cdot}6H_2O{\downarrow} + H_2O \qquad 2.16$$

$$Ca(H_2PO_4)_2{\cdot}H_2O + MgSO_4{\cdot}7H_2O + NH_4^+ \rightarrow MgNH_4PO_4{\cdot}6H_2O{\downarrow} + CaSO_4{\downarrow} \qquad 2.17$$

For the removal of ammonium from waste water, a useful technology called chemical precipitation, has been used. Another attractive way of waste water

treatment, is the precipitation of NH_4^+-N by forming magnesium ammonium phosphate (struvite, $MgNH_4PO_4 \cdot 6H_2O$). Slow release fertilizer is formed by the recovery of NH_4^+-N as struvite. Equal concentrations of phosphate, ammonium and magnesium form struvite crystals in the form of orthorhombic structure (*Ronteltap et al*., 2007).

The success of struvite precipitation depends on two main factors: Mg^{2+}: NH_4^+-N: PO_4^{3-}-P ratio and pH of the solution as reported (Müch *et al*., 2001). Zaixing *et al*., (2012) investigated the influence of pH, molar ratio and various chemical compositions of magnesium ammonium phosphate. The result indicated that ammonium in waste water can be removed from water body at an optimum pH of 9. To remove ammonium nitrogen and avoid the creation of a higher concentration of PO_4^{3-}-P in the effluent, the Mg^{2+}:NH_4^+-N: PO_4^{3-}-P molar ratio was readily controlled at a ratio of 1:1:1:1. The most efficient combination for NH_4^+-N removal in the effluent were $MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4. The same combination were used for the lowest concentration of residual PO_4^{3-}-P.

2.3.3 Adsorption

Adsorption is the process in which molecular species (solid, gas or liquid) is attached or held together on the surface of solids. The substance that gets adsorbed on the surface is known as adsorbate and the surface on which adsorption occurs is known as adsorbent. Atoms and molecules can held to the surface through a process called a chemisorption or physisorption process. In the chemisorption process, atoms or molecules held or attach to the surface of the adsorbent by forming a chemical (usually covalent) bond, whereas in the physisorption process, the Van Der Waals forces between adsorbate and the adsorbent are responsible for the interaction.

The adsorption process is influenced by a few factors. These factors are:

a) Nature of solvent. The solvent can encourage adsorption by interacting with the solute or surface as results weaken the interaction between solute and surface. The polarity and nature of the chemical are the most important property of the chemical.
b) Nature of adsorbent. The chemical nature surface defines reactivity towards the adsorbate and physical characteristics of solids determine the area available for adsorption. When there is a presence of adsorbed impurities, it can affect the adsorption process.
c) Solute chemical structure and its interaction with solvent. The structure of solute and interaction with solvent, have a great impact on its adsorption.
d) Temperature. Temperature has a huge impact on adsorption by changing the properties of the solvent, solute, surface as well as mutual interaction. Physical adsorption normally decreases with an increase in temperature, possibly due to an increase in the solubility of solute. Chemisorption properties depend on the nature of the chemical reaction taking place on the surface.

Clays are possibly good adsorbents of anions, due to the fact that they contain crystalline minerals such as smectite, kaolinite and amorphous minerals such as allophone and other hydroxides and metal oxides which could adsorb anions (Coetzee *et al*., 2003). Ammonia has a strong affinity with water, therefore activated carbon is considered as ineffective for aqueous phase adsorption although activated carbon (AC) is mostly used in the adsorption of ammonia gas. Bamboo charcoal which is carbonized at 400°C, is used for the adsorption of the aqueous phase of ammonia, after it has been treat with diluted sulfuric acid to enhance its adsorption properties (Asada *et al*., 2006). The formation of chloramines, its corresponding removal

by activated carbon, is well known. Normally, chloramines are formed by adding chlorine or its by-products to waste water with some ammonia content.

The reactions are:

$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$ (monochloramine) 2.18

$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$ (dichloramine) 2.19

$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$ (nitrogen trichloride) 2.20

pH and the molar ratio of Cl_2:NH_4^+ are the determining factor for the formation of specific chloramines (Tchobanogolous *et al*., 2003). The catalytic reaction schemes of activated carbon with residual chlorine and dichloramine are:

$AC + 2Cl_2 + 2H_2O \rightarrow 4HCl + CO_2$ 2.21

$AC + 4NHCl_2 \rightarrow 2N_2 + CO_2 + 8H^+ + 8Cl^-$ 2.22

For the chemical breakdown, activated carbon acts as a catalyst and it does not actually adsorb chloramines. The catalytic reaction includes the formation of oxide of carbon intermediate (CO*). Because of their bigger surface area, fine mesh sizes activated carbon are more efficient in removing chloramines than coarse ones, thus allowing faster access to the catalytic sites.

2.3.4 Ion exchange

Ion exchange is a reversible reaction in which a charged ion in a solution is exchanged with a similarly charged ion which is electrostatically attached to an immobile solid particle. The most common implementation of the ion exchange method in waste water treatment is for softening, where polyvalent cations (e.g. calcium and magnesium) are exchanged with sodium. Waste water is normally introduced into a bed of resin (Clifford, 1999). Sodium is

exchanged with cations in the solution (Mack *et al*., 2004). The bed is shut down when it becomes saturated with the exchanged ions, where it should be regenerated by passing a concentrated solution of sodium back through the bed.

Over years, ion exchange has been mostly used to purify target ions from water and waste water (Koon *et al*., 1975). The reaction normally occurs between two or more phases, typically liquid and solid (Colella, 1996). The transfer of ion is regulated by the ion concentration in both phases and the ion selectivity of a given exchanger (Colella, 1996). The amount of ions exchangeable by a solid exchanger, depending on its structural and chemical features, is referred to as ion exchange capacity. Ion exchange is normally a reversible reaction, even though it can be irreversible (Dyer, 1988).

To remove undesirable anions and cations from waste water, ion exchange is used. During this process anions are exchanged for hydroxyl ions and cations are exchanged for sodium or hydrogen. An inorganic or organic network structure forms ion exchange resins with attached functional groups. If the resins exchange positive ions, it's called cationic and anionic if they exchange negative ions. Anion exchanges resins that have basic functional groups, such as amine, whereas cation exchange resins are comprised of acidic functional groups, for example sulphonic groups. The ability of ionisation of the functional groups forms the strength of its acidic or basic character (Lin *et al.*, 2009).

Most common functional groups are carboxyl (-COOH) for weak acid, quaternary ammonium (R_3 N^+ OH-) for a strong base and amine (-NH_2 or -RNH) for a weak base.

2.3.5 Reverse osmosis (RO)

Reverse osmosis (RO) is a process by which a solvent passes through a porous membrane in the direction opposite to that of natural osmosis when subjected to a hydrostatic pressure greater than the osmotic pressure. RO is the most common technology used to separate dissolved salts and small organics (size less than 1 mm). The technology is normally applied in the production of drinking water from seawater or sea desalination.

RO is the process of forcing a solvent from a region of high solute concentration through a semi-permeable membrane to a region of low solute concentration by applying a pressure in excess of the osmotic pressure as shown on Figure 2.1. However, applied pressure pushes the water through the reverse osmosis membrane by applying pressure that is greater than the naturally occurring osmotic pressure, in order to desalinate (demineralize or deionize) water in the process, allowing pure water through, while holding back a majority of contaminants (Dickson, 1988)

When pressure is applied to the concentrated solution, the water molecules are forced through the semi-permeable membrane and the contaminants are not allowed through.

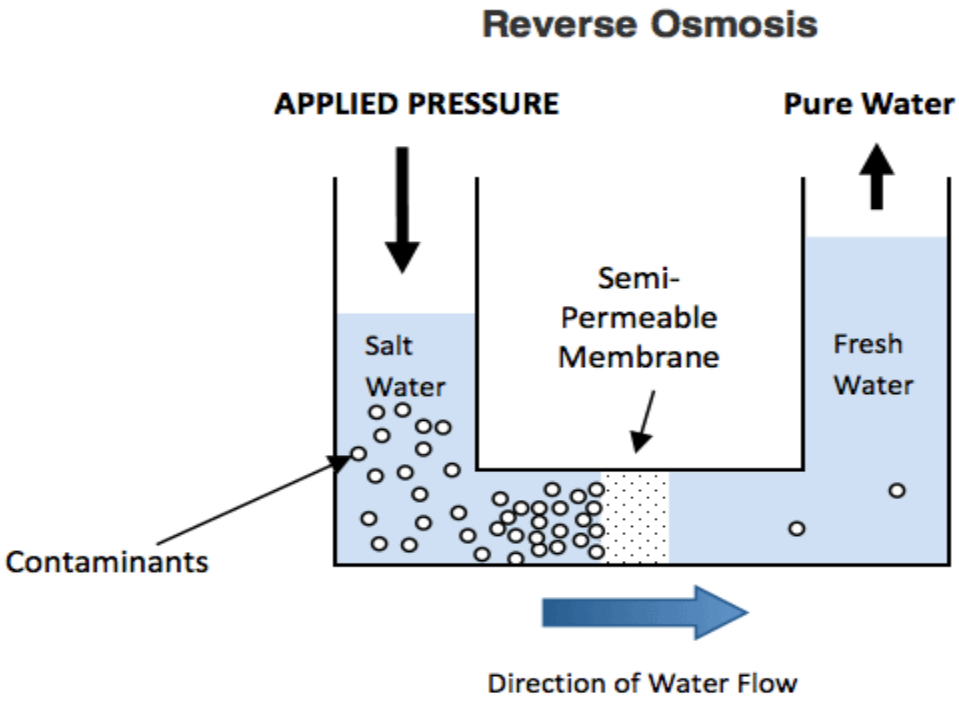

Figure 2.2: Reverse osmosis waste water filtering process (Dickson, 1988)

The feed water permeates the RO membrane under enough pressure to overcome osmotic pressure, the water molecules go through the semi – permeable membrane, salts and other contaminants are stopped from entering and are ejected through the brine, concentrate or reject stream. The stream flows into the drain, if it is fed back to the feed water supply, it might be recycled through the RO system to save water as shown on Figure 2.2. Product or permeate water, is water that has 95 - 99% of dissolved salts removed, it is also water that went through the RO membrane (Dickson, 1988).

The desalinated water that is demineralized or deionized, is called permeate (or product) water (Humplik *et al*., 2011). The water stream that carries the concentrated contaminants that did not pass through the RO membrane is called the reject (or concentrate) stream.

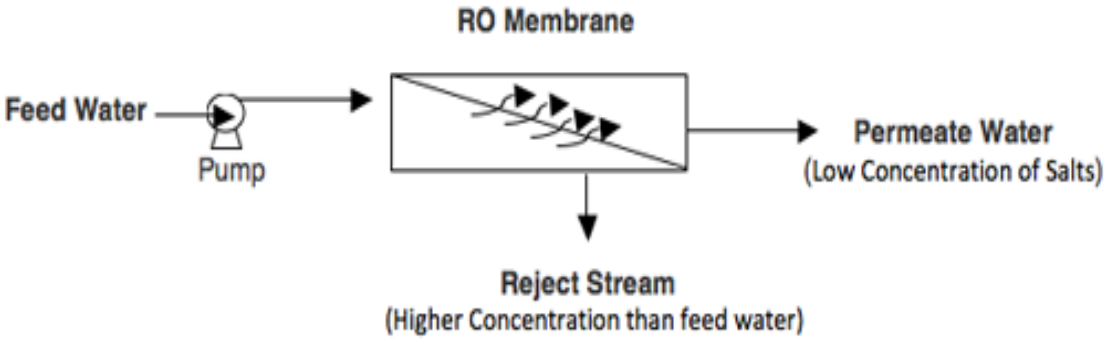

Figure 2.3: Reverse osmosis process flow (Dickson, 1988)

Once the feed water enters the RO membrane under pressure (enough pressure to overcome osmotic pressure) the water molecules pass through the semi-permeable membrane and the salts and other contaminants are not allowed to pass and are discharged through the reject stream (also known as the concentrate or brine stream), which goes to the drain or can be fed back into the feed water supply in some circumstances to be recycled through the RO system to save water. The water that makes it through the RO membrane is called permeate or product water and usually has around 95% to 99% of the dissolved salts removed from it (Dickson, 1988).

2.4 Analytical methods

2.4.1 Inductively coupled plasma – optical emission spectroscopy (ICP – OES)

Inductively coupled plasma optical emission spectroscopy (ICP-OES) also referred to as inductively coupled plasma atomic emission spectrometry (ICP-AES), is an analytical technique used for the detection of chemical elements. ICP-OES involves the emission of electromagnetic radiation of atoms or ions based on a plasma source. ICP-OES is an instrument for analyzing trace metal ions in a complicated sample (Naozuka *et al*., 2011). ICP-OES is

unique due to its high reliability, dynamic range and elevated sensitivity (Morishige *et al*., 2008).

Inductively coupled plasma – optical emission spectroscopy (ICP-OES) involves the emission of electromagnetic radiation of atoms or ions based on a plasma source. The atomic spectra is obtained through an atomization process, in which molecular components of a sample are decomposed and converted to atomic particles. In the process, argon is used as plasma, whereby conducting gaseous mixture and an electrode discharge produces heating.

Atomic spectra are obtained by atomization, a process whereby molecular constituents of a sample are decomposed and converted to atomic particles. The plasma used is argon which is a conducting gaseous mixture and an electrode discharge produces heating. The sample is carried into the hot plasma by argon flowing through the central quartz tube. The sample is nebulized by the flow of argon and the resulting finely divided droplets are carried into the plasma as shown on Figure 2.3. In the region of 10 to 30 cm above the central core of the plasma, it is optically transparent and this is where spectral observations are made. By the time the sample atoms have reached the observation point, they would have resided for about 2 milliseconds at temperatures ranging from 6 000 to 8 000 K (Boss *et al*., 1997).

Furthermore, ICP-OES has several advantages in respect of detection limits and the speed of analyses when compared to various techniques. When comparing different techniques, you will find better detection limits when high temperature use the results of the excitation process or the efficiency of atomization. When using ICP-OES the limitation of quantitation values are in parts per million or parts per billion (Vallapragada *et al*., 2011).

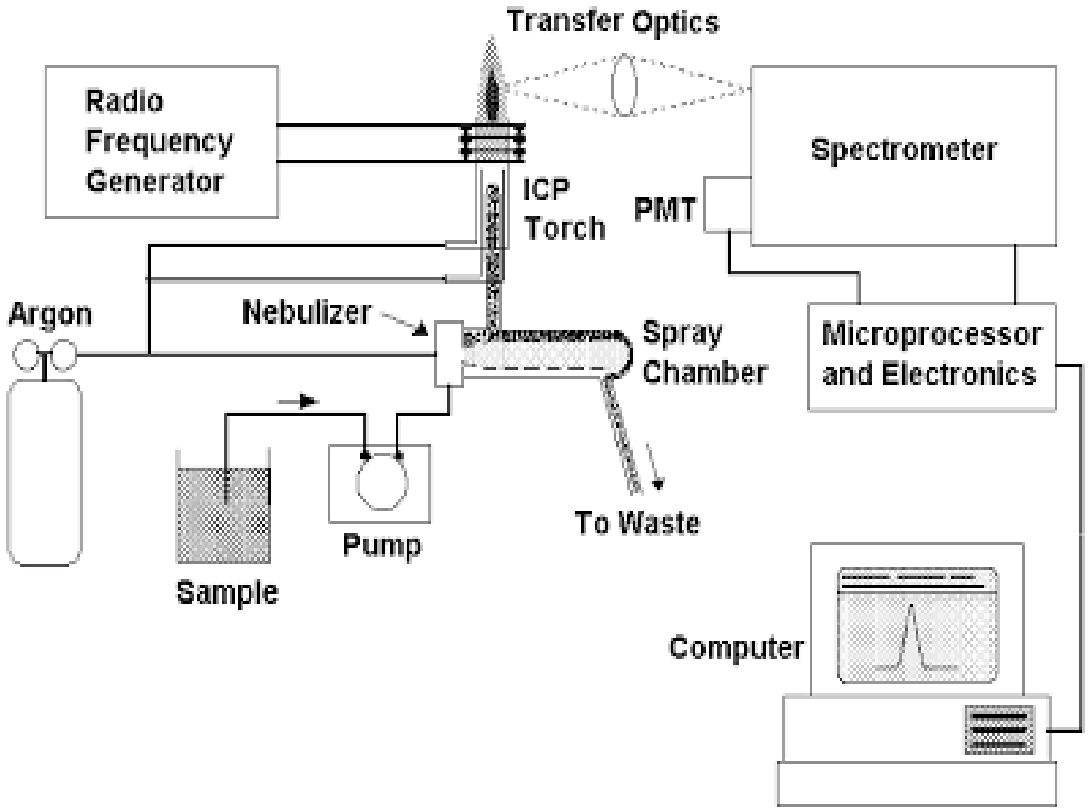

Figure 2.4: Schematic representation of ICP-OES (Ghosh *et al*., 2013)

2.4.2 Ion chromatography (IC)

When separating ions, ion chromatography is one of the most important analytical methods when taking their interactions with eluent (mobile phase) and resin (stationary phase) into account. In ion chromatography there are phase's difference between a column that attracts cations and one that attracts anions (Atkins, 1998). The different columns measure the conductivity of the specific types of ions that are attracted, only. In the ion chromatography different speeds will be used for the ions as they move between the columns, based on their affinity for specific resin and separation from each other depends on the different ion size and charge. As the eluent passes through columns, it will move faster if the ions has a weaker affinity for the resin and

will thus be eluted first. It will move slower through the column if the ion has a stronger affinity for the column. An electrical conductivity detector will measure the ions the moment they exit the column as shown on Figure 2.4. A chromatogram is produced by the detector based on time vs conductivity. A peak on the graph is produced by each ion, relative ion concentration in the injected solution determined by height. An unknown samples concentration of analytes are determined by using those measurements (*Skoog et al*., 2004). Prior to the conductivity measurements, an unwanted electrolyte is removed by using a suppressor, this will eliminate the possibility of interference caused by their ion in the mobile phase. Non - ionic species will replace the eluent ions, when the solution goes through the suppressor. The use suppressor will not be necessary (Harris, 2011) if the eluent is either sufficiently diluted or if it has a low conductivity.

Ion chromatography is normally used in water chemistry analysis. Ion chromatographs are able to measure concentrations of major anions, such as chloride, nitrate, nitrite fluoride and sulfate, as well as major cations such as sodium, ammonium, potassium, calcium, lithium and magnesium in the parts-per-billion (ppb) range. IC can also be used to measure concentrations of organic acids.

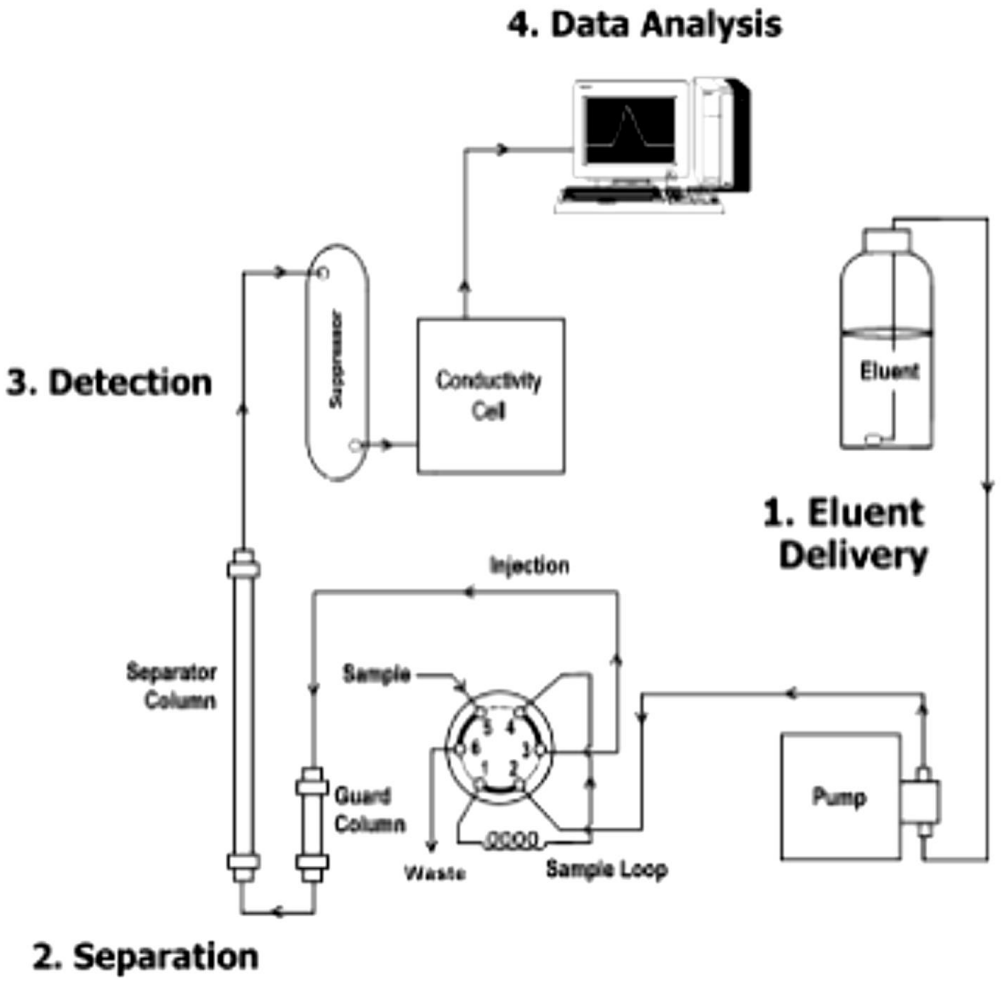

Figure 2.5: Schematic representation of ion chromatograph (Harris *et al*., 2011)

There are a number of operating steps to follow when ion exchange is used in waste water treatment. The contaminant will only appear in the effluent after all the available exchange sites have been filled and the waste water has already passed through the resin. This is called the breakthrough process. The resin has to be re – graded after the bed has been backwashed to remove the dirt; this only happened after the treatment was stopped. The bed will be regenerated at this stage. The residual regenerant will be washed at after the bed is rinsed once the regeneration has taken place.

2.4.3 X-Ray diffraction

X-rays are defined as short wavelength electromagnetic radiation generated by electronic transitions involving electrons in the inners orbital of atoms. Interaction amongst the x-ray radiation and the electrons of the matter through which it passes results in their scattering. When x-rays are scattered by the ordered environment in a crystalline matter, both constructive and destructive interference takes place between the scattered rays. In order to interpret the spectra obtained by this technique, the Bragg equation is used. Consequently, the identification of a species from its diffractogram pattern is centered upon the position of the lines in the spectrum and their relative intensities. The diffractogram angle is determined by the spacing among a particular set of planes. Line intensities depend on the number and kind of atomic inflection centers that exists in each set of planes.

CHAPTER THREE

MATERIALS, ANALYTICAL TECHNIQUES AND METHODS

3.1 Experiment description

Experiments were done to study the objectives of this Dissertation which were to identify the contaminants in effluent that are harmful to the environment and living organisms, to study and apply physico/chemical treatment methods, for removing the identified contaminants and to make sure that the treated waste water meet the South African Department of Water and Sanitation Waste Water Discharge Standards before discharge into streams.

3.2 Materials

The chemicals used in the experiments are listed in Table 3.1.

Table 3.1: Chemicals used in experiment

Supplier	**Chemical Name**	**Chemical Formula**	**Assay**
Sigma Aldrich	Magnesium chloride	$MgCl_2 \cdot 6H_2O$	≥ 99%
Sigma Aldrich	Magnesium oxide	MgO	99.9%
Merck	Sodium hydroxide	NaOH	≥ 99%
Merck	Potassium hydroxide	KOH	≥ 99%
Sigma Aldrich	Ferrous sulphate	$FeSO_4$	≥ 99%
Merck	Aluminium chlorohydrate	$AlCl(OH)_5$	95%
Merck	Ferric chloride	$Fecl_3$	45%

Ultra-pure water

All the water used was produced by the reverse osmosis process to the type 1 standard of ASTM D1193, with a resistivity of 18.2 M

All apparatus, glassware, filter papers and magnetic stirrers were provided by Sigma Aldrich and Merck. Analytical instruments were provided at Sasolburg Infrachem, Sasol Secunda and South African Nuclear Energy Corporation (Soc) Ltd.

3.3 Methods

Several trials were carried out to find out the most efficient coagulant/flocculant and their respective optimum dosage. Two combinations of chemicals were used, ($MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4 and MgO + 85% H_3PO_4) in order to pinpoint what the most efficient combination will be for the removing of ammonium nitrogen, sodium nitrate, calcium nitrate, residual PO_4^{3-}-P in solution, COD and pH change in a waste water sample. Several trials on the influence of pH on the solubility of dissolved species, were investigated.

3.3.1 Coagulation/flocculation of nitrate waste water

A jar test was carried out for the all three flocculants listed in Table 3.2. Optimization of flocculant dosage was only carried out for flocculants that demonstrated promising results from the jar test.

Table 3.2: Flocculants selected for testing and their properties

	$FeSO_4$ (Flocculant1)	$AlCl(OH)_5$ (Flocculant 2)	$FeCl_3$ (Flocculant 3)
Molecular mass ($gmol^{-1}$)	151	174.45	162.2
pH of Flocculant	Not specified	4	2
Ionicity	Cationic	Cationic	Cationic
Viscosity	Not specified	150 cPs	12 cPs
Volume of stock solution (mL)	1000	1 000	1 000
Concentration of stock Solution (mgL^{-1})	0.002	0.002	0.002

Stock solutions of the coagulants with a concentration of 0.002 mgL^{-1} Al or Fe were prepared according to Table 3.2. The flocculated liquor was analyzed by ICP-OES and IC.

3.3.2 Inorganic salts/coagulants addition

Solutions of waste water containing 0.008 mgL^{-1}, 0.016 mgL^{-1}, 0.024 mgL^{-1} and 0.032 mgL^{-1} $FeCl_3$, $AlCl(OH)_5$ and respective $FeSO_4$ were prepared by pippeting 4 mL, 8 mL, 12 mL and 16mL of the stock solutions listed in Table 3.4, into a 1L beaker; each containing 1L of the waste water sample. The solutions were mixed for 2 minutes at a speed of 250 rpm, until the precipitates formed. The solutions were allowed to cool down overnight, allowing the formed precipitate to settle down. The supernatant was filtered and analyzed by IC and ICP-OES. The filtered supernatant was further used for NH_4^+-N precipitation.

3.3.3 Investigation of more efficient reagent for nitrate waste water pH adjustment

Several trials were carried out to find out the most efficient reagent for nitrate explosive waste water pH adjustment between KOH and NH_4OH available.

Table 3.3: Preparation of stock solutions for KOH and NH_4OH for pH adjustment

	KOH	**NH_4OH**
Molecular mass ($gmoL^{-1}$)	56.105	35.04
Acid/base	Strong base	Weak base
Concentration of stock solution	10%	10%

100 mL of flocculated waste water filtrate was poured into two 250 mL Erlenmeyer flasks. The sample was stirred at a very slow speed of 10 rpm. Sample pH of 6.87 was adjusted to a pH of 9 making use of 10% KOH in one flask and 10% NH_4OH in another flask. A sample pH was recorded after 1 hour, 6 hours, 12 hours, 24 hours and 48 hours to determine the stable pH reagent to proceed with.

3.3.4 Precipitation by pH adjustment using 10 % KOH

3.3.4.1 Precipitation of NH_4^+-N from waste water using 1M $MgCl_2 \cdot 6H_20$ and 1M 85% H_3PO_4, by pH adjustment using 10% KOH

Table 3.4: Preparation of stock solutions for 1M $MgCl_2 \cdot 6H_2O$ and 1M 85% H_3PO_4, using 10% KOH for pH adjustment

	$MgCl_2 \cdot 6H_20$	**85% H_3PO_4**
Molecular mass ($gmoL^{-1}$)	203.31	97.994
Mass weight (g) or volume added	20.3 g	6.8 mL
Volume of stock solution (ml)	100	100
Concentration of stock solution	1M	1M

100 mL of flocculated waste water filtrate was poured into a 250 mL Erlenmeyer flask. 20.3 g magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) was added slowly whilst stirring into a 250 mL Erlenmeyer flask containing 100 mL flocculated waste water filtrate. 6.8 mL phosphoric acid (85% H_3PO_4) was then added dropwise into the flocculated sample while stirring. 10% KOH was added dropwise into the flocculated waste water while stirring until the pH was reduced to 9.0 (measured with an electrode). The solution was stirred for 20 minutes. The solutions were allowed to cool down overnight, allowing the formed precipitate to settle down. The precipitate formed was filtered via whatmans 125mm filter paper through gravity, dried overnight and sent for XRD, EDS, Raman and TGA analysis. The supernatants were decanted and analyzed by ICP-OES and IC. The whole experiment was repeated at pH 7, 8, 9, 10 and 11, in order to assess the influence of pH on ammonium nitrogen precipitation while monitoring the residual phosphate and COD.

3.3.4.2 Precipitation of NH_4^+-N from waste water making use of 1M MgO and 1M 85% H_3PO_4 by pH adjustment using 10% KOH

Table 3.5: Preparation of stock solutions for 1M MgO and 1M 85% H_3PO_4, using 10% KOH for pH adjustment

	MgO	**85% H_3PO_4**
Molecular mass ($gmoL^{-1}$)	40.3044	97.994
Mass weight (g) or volume added	14 g	6.8 mL
Volume of stock solution (mL)	100	100
Concentration of stock solution	1M	1M

100 mL of flocculated waste water filtrate was poured into a 250 mL Erlenmeyer flask.14 g of magnesium oxide (MgO) was added slowly while stirring into a 250 ml Erlenmeyer flask containing 100 mL flocculated waste water filtrate. 6.8 mL phosphoric acid (85% H_3PO_4) was then added drop wise into the flocculated sample while stirring. 10% KOH was added drop wise into the flocculated waste water while stirring until the pH was reduced to 9.0 (measured with an electrode). The solution was stirred for 20 minutes. The solutions were allowed to cool down overnight, allowing the formed precipitate to settle down. The precipitate formed was filtered via whatmans 125mm filter paper through gravity, dried overnight and sent for XRD, EDS, Raman and TGA analysis. The supernatants were decanted and analyzed by ICP-OES and IC. The whole experiment was repeated at pH 7, 8, 9, 10 and 11, in order to assess the influence of pH on ammonium nitrogen precipitation while monitoring the residual phosphate and COD.

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3.3.5 Turbidity

Turbidimeter was used to determine the turbidity of waste water samples.
30 mL of waste water sample was measured with a measuring cylinder and poured into a clean cell. The sample cell was cleaned and dried with a paper

towel. The sample cell was then placed into the instrument light cabinet and covered with the light shield. The turbidity of sample was then read.

3.3.6 Inductively coupled plasma-optical emission spectroscopy

The elements in filtered supernatant sample such as Na, Ca and Mg were quantified using ICP-OES. All the samples were pre-treated by the following methods, which were verified to give similar results. A 5 g representative sample of the filtered supernatant was accurately weighed. To this 10 ml HNO3 was added to the solution in order to oxidize all organic species present in the sample. The solution was then heated to near dryness. Another 10 ml of HNO3 was added to the heated solution or solids and the process repeated as above. The resultant solution was made up to 50 ml with the distilled water and subsequently analyzed for selected elements by ICP - OES.

3.3.7 Carl Zeiss microscopic characterization of formed crystals

Carl Zeiss electron microscope was used to characterize crystal morphology precipitate crystals formed through a struvite precipitation reaction. A small quantity of precipitate crystals was scoped using a spatula and spread evenly onto microscope glass slides. A few drops of distilled water were added onto the precipitated crystal sample to suspend and distribute it. The precipitate crystal sample was examined with the stereo microscope under the highest comfortable magnification. A larger magnification was achieved by selecting lens 10/0.22 (460400 – 9904). The precipitate crystals were examined with a 10 kV and 5 nA setting on a Carl Zeiss microscope using 20 µm beam size to counteract any damage that the electron beam will cause to the sample.

3.3.8 X-Ray diffraction

A precipitate sample from waste water precipitation was received as solid powder. A mass of approximately 4 g of sample was further grounded and homogenized by hand in an agate mortar. Approximately 0.5 g of the ground sample was placed in a stainless steel sample holder and the surface was smoothen with a glass plate. The samples were exposed to an x-ray beam to generate the diffraction patterns

3.3.9 Raman spectroscopic analysis of formed crystals

A precipitate sample, from waste water precipitation was received as solid powder. A mortar and pestle was used to finely grind 1g of sample. A Linkam ^{TM} stage TMS 94 was used to control *In situ* Raman measurements in a TS 1500 reactor. A 100 cm^3 min^{-1} continuous nitrogen flow was used for a precipitated white crystal to be heated to 3000°C. A Bruker Raman spectrometer equipped with a charged - coupled device detector (CCD) and a green laser (λ=532) was used to take Raman scans of the sample that was heated up at a rate of 20°C min^{-1} to set temperatures after it has been quenched. Blank runs from struvite samples were also carried out under the same conditions.

3.3.10 Thermal analysis of formed crystals

Thermo gravimetric measurements were done making use of a TG-DSC Analyzer SDT Q600 instrument in a continuous nitrogen flow of 100 cm^3 min^{-1}. A constant flow of nitrogen (100cm^3 min^{-1}) was used to heat 8mg of sample from an ambient temperature to 600°C at 20, 25 and 30°C min^{-1}.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

In this chapter the results obtained during the treatment of waste water from a nitrate explosive plant, are presented and discussed.

4.1 Coagulation/flocculation

The jar test results shown in Figure 4.1 reveal that one flocculant tested (flocculant 1) was ineffective in removing the turbidity of the waste water. Flocculant 2 and 3 showed promising results in reducing the turbidity. Both flocculants are cationic. Flocculant 2 reduced the turbidity of nitrate waste water from 168 to 32 and 28 NTU respectively at the dosage of 100 mgL^{-1}

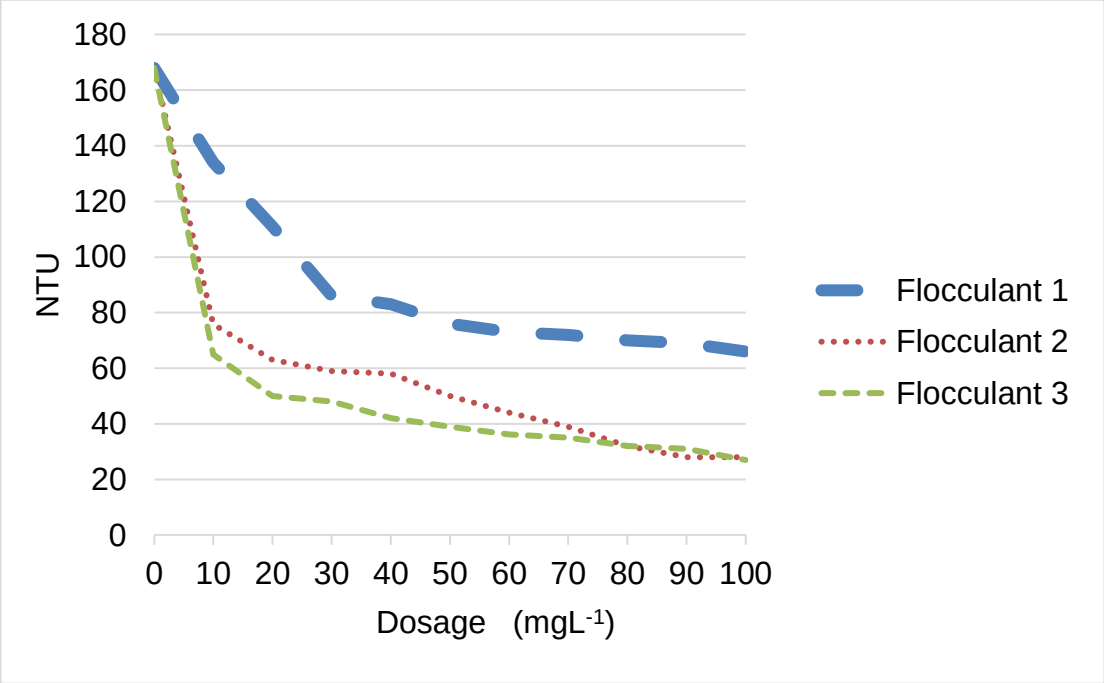

Figure 4.1: Turbidity of waste water before and after coagulation/flocculation

The sequential addition of the two cationic flocculants (Flocculant 2 and 3) to the waste water sample greatly improved the floc formation and reduced turbidity of treated waste water significantly. The results obtained during the optimization of the quantity of the flocculants are given in Table 4.1.

Table 4.1: Turbidity of waste water before and after sequential addition of coagulation/flocculation

Blend number	Flocculant 2 (mgL^{-1})	Flocculant 3 (mgL^{-1})	Turbidity of flocculated waste water (NTU)
1	0	0	168
2	10	6	34
3	20	6	18.1
4#	30	6	15.4
5	40	6	13.2
6	50	6	12.4
7	60	6	11.7
8	70	6	11.3

Optimal dosage

A measure of up to 25 mgL^{-1} of Flocculant 2 which was conditioned for 2 minutes, followed by an addition of 6 mgL^{-1} of flocculant 3 reduced the turbidity of waste water from 168 to 15 NTU. The increase in the dosage of Flocculant 3, up to 70 mgL^{-1}, improved the turbidity reduction slightly (15 to 11 NTU). A blend of a ratio of 30:6: Flocculant 2: Flocculant 3 was selected as an optimal dosage of the flocculants for the treatment of waste water. The waste water treated with Flocculant 2 and 3 was allowed to settle down and

the supernatant was analyzed by ICP-OES. Flocculants 2 and 3 were then used sequentially and the supernatant of the settled waste water was analyzed by ICP-OES and IC. Table 4.2 shows the results.

Table 4.2: Concentration of elements in waste water sample before and after flocculation (mgL^{-1})

Elements	Untreated waste water	Waste water treated with 50 mgL^{-1} Flocculant 2	% Reduction	Waste water treated with a blend of flocculant 2 and 3	% Reduction*
Ca	47.72	8.9	81	6.54	86
Mg	7.68	1	86	< 0.10	98.7
Na	106	98	7.54	75.11	29
Cl	585	47	92	61	89
Sulphate as SO_4	19.27	< 1	94	< 1	94
Ammonium as N	4235	3644	13.96	3518	16.93
Nitrate as N	6188	5941	4	5836	5.68

* % Reduction= $\frac{(C_i - C_f) \times 100\%}{C_i}$

Where C_i = concentration of element in waste water before flocculation

C_f = concentration of an element in the flocculated waste water.

The concentration of sodium was reduced by 8% and that of the dissolved nitrates by 4%. These results show that although the turbidity of the flocculated waste water was significantly reduced from the original turbidity, there was no corresponding reduction in the concentrations of the dissolved sodium and nitrates. The sequential addition of Flocculant 2 and 3, resulted in a reduction of the concentration of sodium, ammonium nitrogen and nitrates by 29%, 16% and 5% respectively. The concentration of calcium and magnesium in the flocculated waste water was reduced by 86% and 99%. Coagulation/flocculation of the waste water did not result in the improved removal of the nitrates. The pH of the waste water was measured to be 7.2, compared to the pH of 6.8 before saturation. The pH of 7.2 is possibly not low enough to precipitate nitrates of waste water into suspended colloids that could then be removed by the coagulation/flocculation process.

Sodium and nitrates are the two major impurities identified in the flocculated waste water. Based on the coagulation/flocculation results in this study, it can be assumed that it is unlikely that sodium and nitrates are present in the suspended or stabilized colloidal species, but they are probably present as dissolved species, hence the reduction of turbidity was not accompanied by the reduction of their concentrations in the treated waste water. Precipitation by pH adjustment was considered as a next step.

4.2 Stable reagent for nitrate waste water pH adjustment

Two readily available reagents were tested in order to determine the more effective stable reagent for adjusting nitrate waste water to a desired pH 9 over a variety time of frames. pH stability results shown in Figure 4.2, reveal that 10% NH_4OH was ineffective in stabilizing the nitrate waste water to desired pH of 9. 10% KOH showed promising results in maintaining the desired pH of 9 over an extended period of 48 hours.

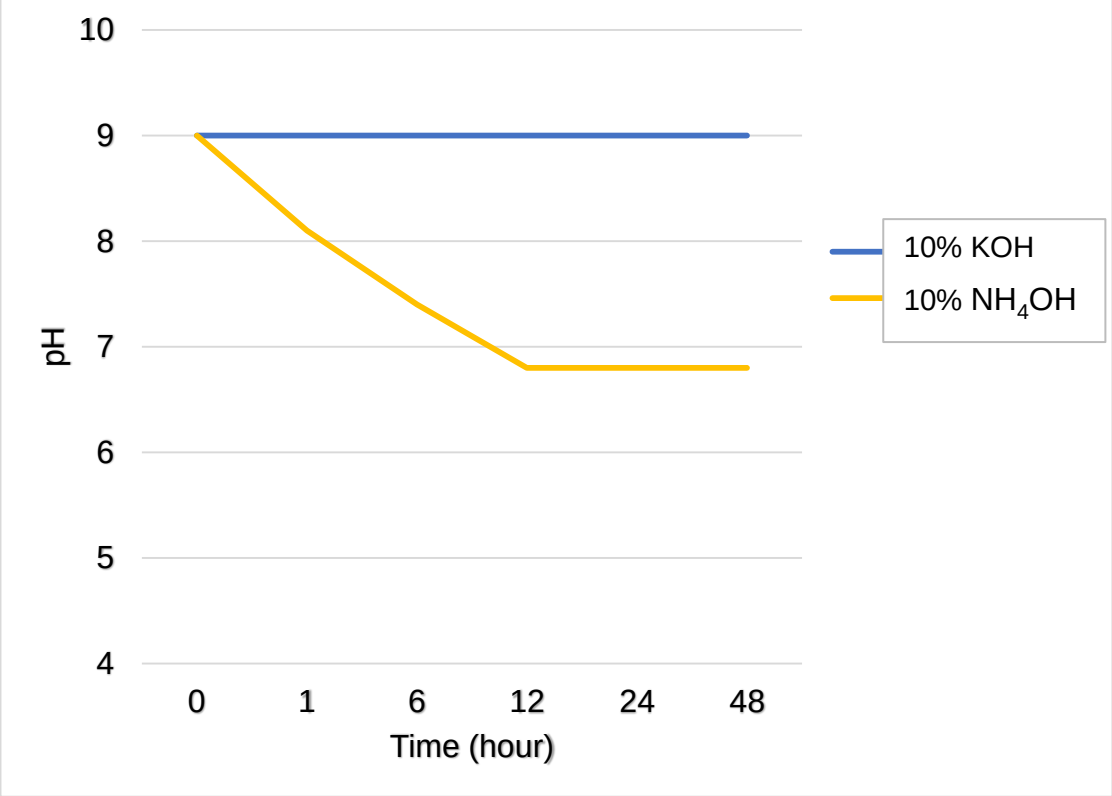

Figure 4.2: Stability of 10% KOH and 10% NH_4OH at desired pH 9 over a period of 48 hours

10% KOH was more efficient in adjusting the pH of waste water when compared to 10% NH_4OH**.** This low efficiency of 10% NH_4OH can be based on to the fact that ammonia is a week base. Ammonia itself obviously doesn't contain hydroxide ions, but it reacts with water to produce ammonium ions and hydroxide ions. Apart from that, the reaction is also reversible, and at any given time about 99% of the ammonia will still be present as ammonia molecules and can easily evaporate out of the solution. KOH was more efficient in adjusting waste water pH. This is due to the fact that KOH is highly basic and is able to form strong alkaline solutions in water and other polar solvents. These solutions are capable of deprotonating many acids, even weak ones. Another advantage of using potassium hydroxide to adjust pH in

this research, is that it does not re-introduce ammonia into the solution when compared to ammonium hydroxide. The major uses of potassium hydroxide applicable to this research work, is that the supernatant can also be used as liquid fertilizers.

4.3 Ammonium nitrogen precipitation as struvite

Two reaction schemes denoted R was used, in order to decide which combination will be efficient to use in order to remove of ammonium nitrogen (NH_4^+-N) from waste water, while monitoring residual PO_4^{3-}-P in the solution, COD removal and pH change.

$MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4	R1
MgO+ 85% H_3PO_4	R2

4.3.1 Struvite precipitation by pH adjustment

Two reaction schemes indicated as R1 and R2 were applied to precipitate ammonium nitrogen (NH_4^+-N) out from flocculated waste water. The initial concentration of NH_4^+-N was 3 518 mgL^{-1}. Depending on the stoichiometry of the struvite precipitation (Mg^{2+}: NH_4^+-N: PO_4^{3-}-P =1:1:1), the amount of chemicals that is needed will be calculated and added to the flocculated waste water. The overall performance of the precipitation reaction in relation to NH_4^+-N removal, residual PO_4^{3-}-P in solution, COD removal and pH change is shown in Figures 4.3 and 4.4.

In the first experiment indicated as R1, $MgCl_2 \cdot 6H_2O$ and 85% H_3PO_4 were used as an alternative source of Mg^{2+} and PO_4^{3-}.

$$MgCl_2 \cdot 6H_2O + H_3PO_4 + NH_4^+ \rightarrow MgNH_4PO_4 \cdot 6H2O\downarrow + 2NaCl \quad (4.1)$$

The molar ratio of Mg^{2+}: NH_4^+-N: PO_4^{3-} was at a stoichiometric ratio of 1:1:1. After adding phosphoric acid into the solution, the pH drops from 7.2 to 2.3. 10% KOH was then used to adjust the pH to 9, which was accompanied by a white layer formation of precipitate settled at the bottom of the vessel as shown in Figure 4.3.

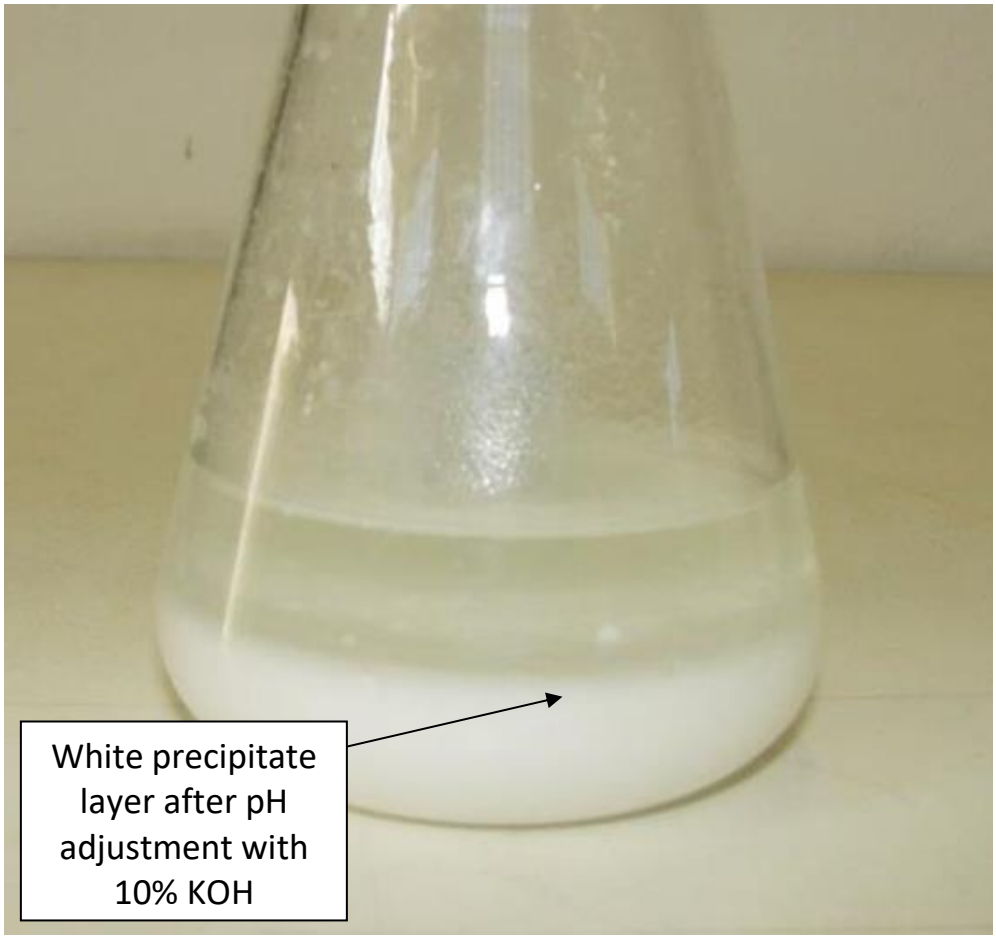

Figure 4.3: Flocculated waste water treated with $MgCl_2 \cdot 6H_2O$ and 85% H_3PO_4, pH 9 adjusted with 10% KOH, at 25°C

In the experiment indicated as R2 (reaction scheme, Magnesium Oxide (MgO) MgO and 85% H_3PO_4 were used as an alternative source of Mg^{2+} and PO_4^{3-}.

$$MgO + H_3PO_4 + NH_4^+ \rightarrow MgNH_4PO_4 \cdot 6H_2O\downarrow + H_2O \quad 4.2$$

The molar ratio of Mg^{2+}: NH_4^+-N: PO_4^{3-} was also kept at a stoichiometric ratio of 1:1:1. After adding phosphoric acid into the solution, the pH drops from 7.2 to 2.7. 10% KOH was used to adjust the pH to 9, accompanied by a white layer formation of precipitate settled at the bottom of vessel as shown Figure 4.4.

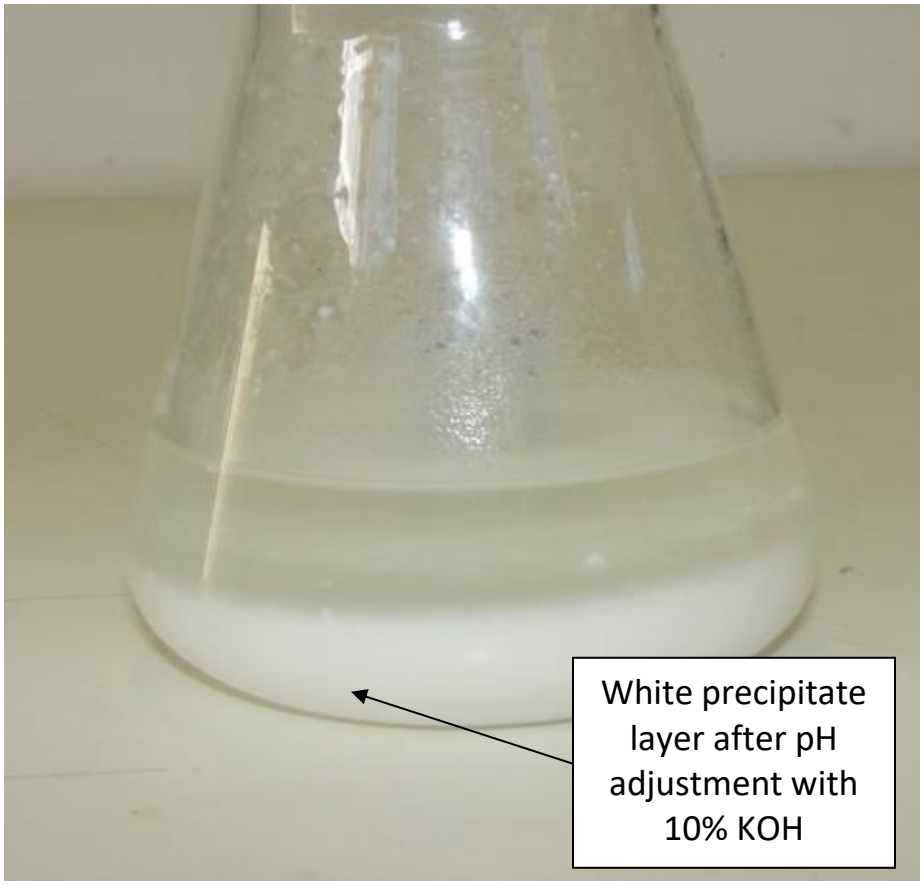

Figure 4.4: Flocculated waste water treated with MgO and 85% H_3PO_4, pH 9 adjusted with 10% KOH, at 25°C

The precipitation of ammonium nitrogen from waste water through a combination of $MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4 reaction scheme, followed by a pH

adjustment using10% KOH was a more effective combination. When Mg^{2+} was added as MgO (experiment R2), the efficiency of NH_4^+-H removal was lower than 40%. MgO is not totally soluble in water, therefore this low efficiency. Furthermore, after the reaction, the concentrations of PO_4^{3-}-P were high, that can cause problems, as the residual PO_4^{3-}-P can cause further pollution in the marine ecosystems. On the other hand, the addition of $MgCl_2{\cdot}6H_2O$ (experiment R1) as an alternative source of Mg^{2+}, the efficiency of NH_4^+-H removal up to 76.29% of the total removal. Moreover, the residual concentration of PO_4^{3-}-P was very low when compared to the previous experiment. The supernatant was filtered through a Whatman filter paper (size 40) and the filtrate was analyzed by ICP-OES and IC. The results are shown in Table 4.3.

Table 4.3: Concentration of elements in waste water sample before and after Precipitation (mgL^{-1})

Elements	Untreated waste water	Waste water after precipitation	% Reduction
pH	6.87	8.5	
Ca	47.72	9.29	80.53
Mg	7.68	<0.10	98.69
Na	106	85.11	57.44
Cl	585	47	91.96
Turbidity (NTU)	168	11.3	93.2
Ammonium as N	4 235	98.7	97.66
Nitrate as N	6 188	4275	30.91

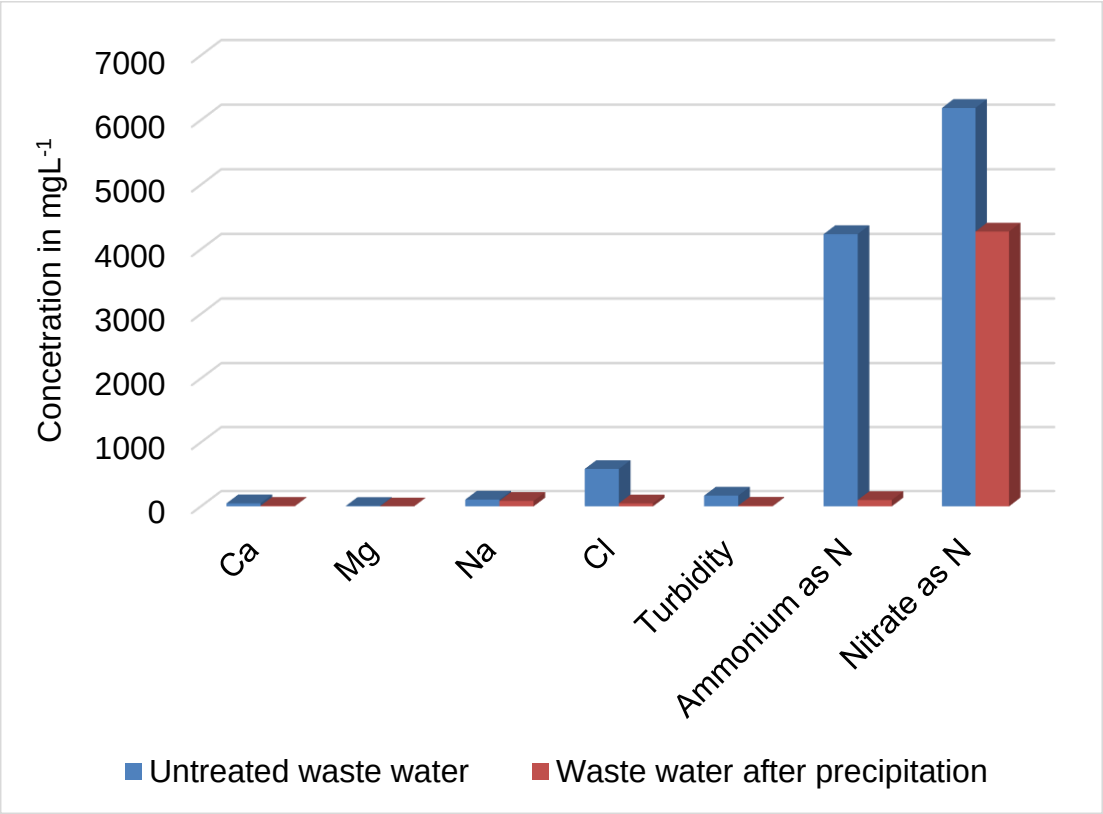

Figure 4.5: Concentration of elements in waste water sample before and after precipitation (mgL^{-1})

The precipitation of ammonium nitrogen, while increasing in pH from 7.2 to 11, using 10% KOH resulted in the reduction of the concentration of dissolved Ca (47.72 mgL^{-1} to 9.29 mgL^{-1}), Mg (7.68 mgL^{-1} to <0.10 mgL^{-1}), NH_4^+-N (4235 $mg.L^{-1}$ to 98.7 mgL^{-1}), Cl (585 mgL^{-1} to 47 mgL^{-1}) and Na (106 mgL^{-1} to 85 mgL^{-1}). The concentration of dissolved sodium and nitrates was not reduced significantly by a pH increase. The concentration of dissolved ammonium nitrogen was reduced significantly from 4 235 mgL^{-1} to 9.87 mgL^{-1} by struvite precipitation. This amounts to a 97.66% reduction. The results indicate that struvite precipitation is effective when removing ammonium nitrogen from nitrate explosive waste water. The most efficient combination to remove NH_4^+-N from waste water, is $MgCl_2$ + 85% H_3PO_4. Consequently,

$MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4 was selected as the best condition to remove ammonium nitrogen form nitrate explosive waste water.

The filtered precipitate crystals were allowed to dry overnight. To evaluate the quality of the precipitated struvite, the crystals formed by precipitation were analyzed by XRD, electron microscope, EDS, thermal analysis and Raman spectroscopy as displayed below (Figures 4.9 to 4.17). The XRD pattern created from the sample match published database model of struvite.

4.3.2 Influence of Mg^{2+}: NH_4^+-N: PO_4^{3-}-P molar ratio on struvite precipitation

The influence of a different Mg^{2+}: NH_4^+-N: PO_4^{3-}-P molar ratio on NH_4^+-N removal, residual PO_4^{3-}-P and COD reduction in explosive waste water, were investigated for various molar concentrations as shown in Figure 4.6. There was no real improvement in NH_4^+-N removal while molar concentration increased. It might be because of other precipitates that formed at higher molar ratios. When there is for example, excessive concentrations of Mg^{2+} in alkali conditions, precipitation might occur in solid $Mg(OH)_2$. The amount of readily available magnesium might affect the removal of NH_4^+-N in the struvite precipitation reaction (Lee *et al*., 2003).

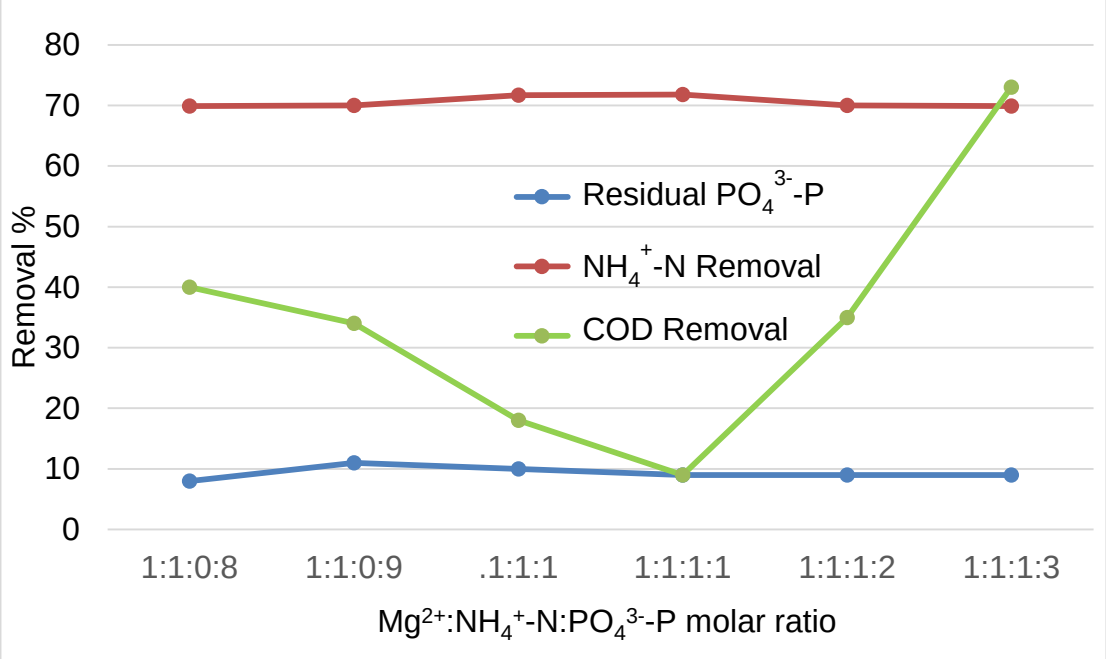

Figure 4.6: Influence of molar ratio of Mg^{2+}: NH_4^+-N: PO_4^{3-}-P on NH_4^+-N, and residual PO_4^{3-}-P, at pH 9, mixing time 20 min

On the other hand, the COD removal increased with an increasing magnesium ions concentration. The efficiency of COD removal reached 18 % at the 1:3:1 Mg^{2+}:NH_4^+-N molar ratio. When removing particulate organic matter in nitrate explosive waste water, the flocculant used is generally magnesium ion. The concentration of residual PO_4^{3-}-P at first decreased and then increased with an increasing Mg^{2+}:NH_4^+-N molar ratio, which indicated that they were a presence of an optimum Mg^{2+}:NH_4^+-N molar ratio to remove PO_4^{3-}-P.

A fixed 1:1 Mg^{2+}:NH_4^+-N ratio was used to determine the influence of PO_4^{3-}-P: NH_4^+-N molar ratio. The effectiveness of the removal of NH_4^+-N was 69.9% when the PO_4^{3-}-P: NH_4^+-N molar ratio was 1:1. The efficiency of NH_4^+-N removal increased by 1.8% at PO_4^{3-}-P: NH_4^+-N molar ratio of 1.1:1 and then declined with PO_4^{3-}-P: NH_4^+-N molar ratio slightly above 1.1:1, whereas the

theoretical value was higher than that of the removal efficiency. The adding of excess concentrations of PO_4^{3-}-P to improve the recovery of NH_4^+-N might be promising when looking at the characteristics of nitrate explosive waste water and selected operating conditions.

4.3.3 Influence of pH on struvite precipitation

Experiment R1, $MgCl_2 \cdot 6H_2O$ and 85% H_3PO_4 was repeated in order to monitor the influence of pH changes, in the degree of supersaturation during the precipitation process. The molar ratio of Mg^{2+}: NH_4^+-N: PO_4^{3-} was at a stoichiometric ratio of 1:1:1. After adding phosphoric acid into the solution, pH drops from 7.2 to 1.8. 10% KOH was then used to adjust the pH to a pH of 7, 8, 8.5, 9, 10 and 11 which was accompanied by a white layer formation of precipitate settled at the bottom of the vessel as shown in Figure 4.7.



Figure 4.7: Waste water treated with $MgCl_2 \cdot 6H_2O$ and 85% H_3PO_4, pH, 7, 8, 9, 10 and 11 adjusted with 10% KOH, at 25°C

The degree of supersaturation that occurs during the precipitation process is impacted by an increase in pH changes as shown in Figure 4.8.

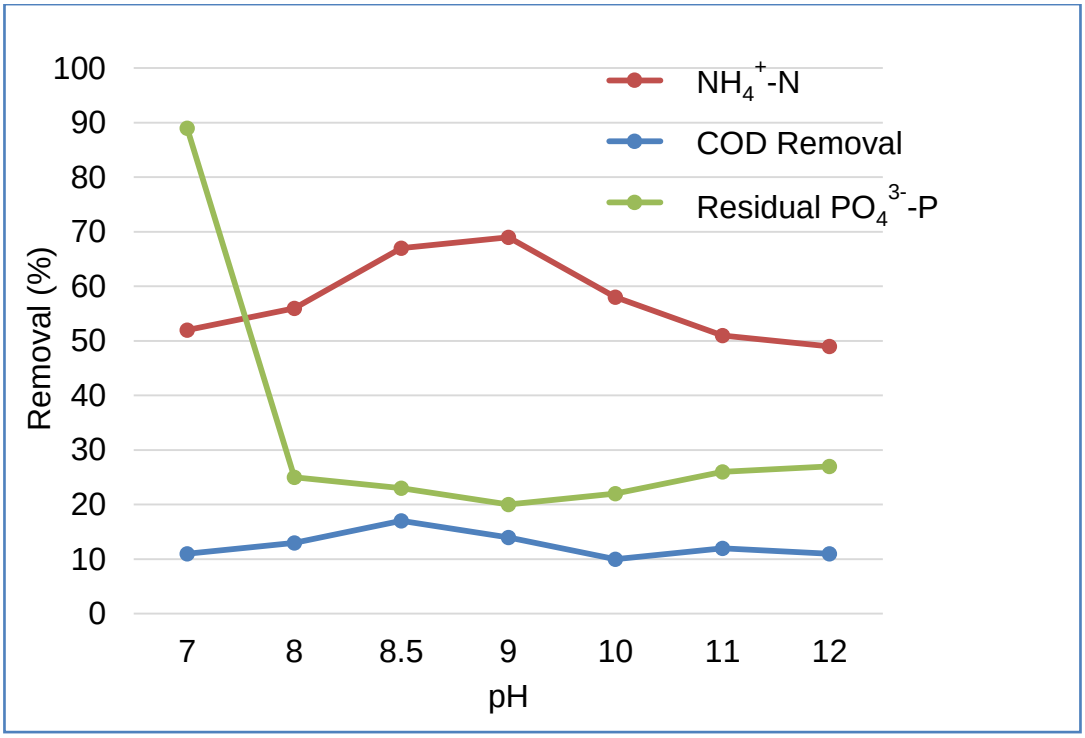

Figure 4.8: Influence of pH on NH_4^+-N, residual PO_4^{3-}-P at Mg^{2+}: NH_4^+-N: PO_4^{3-} : PO_4^{3-}-P 1:1:1 molar ratio, COD removals and 20 min mixing time

Figure 4.8 shows that the removal of NH_4^+-N increases as the pH increase from 8 to 9. At a lower pH of 7, no NH_4^+-N removal was detected and at pH 8 a slightly quantity of crystals was detected. With a slightly increase of pH to 9, the precipitation at the bottom of the beaker increased and the growth of the crystals improved with a pH higher than 8. When stirring was concluded at pH of 9, the crystals formed quickly and settled rapidly on the beakers bottom. However, the quantity and the rate of crystal formation reduced significantly at a pH of 10 and 11. The optimum range observed for the removal of

ammonium nitrogen in these research projects was found to be between pH 8.5 and 9.3, which is consistent with what is reported by (Booker *et al*., 1999).

4.4 Characterization of precipitate crystals

The filtered precipitate crystals from reaction R1 ($MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4) and R2 (MgO+ 85% H_3PO_4) as shown in Figures 4.9 and 4.10, were allowed to dry overnight and characterized by XRD, Raman, EDS and electron microscope. The precipitate crystals formed from reaction R1 were very clear snow white in colour, whereas precipitate crystals from the R2 reaction were creamy white colour.

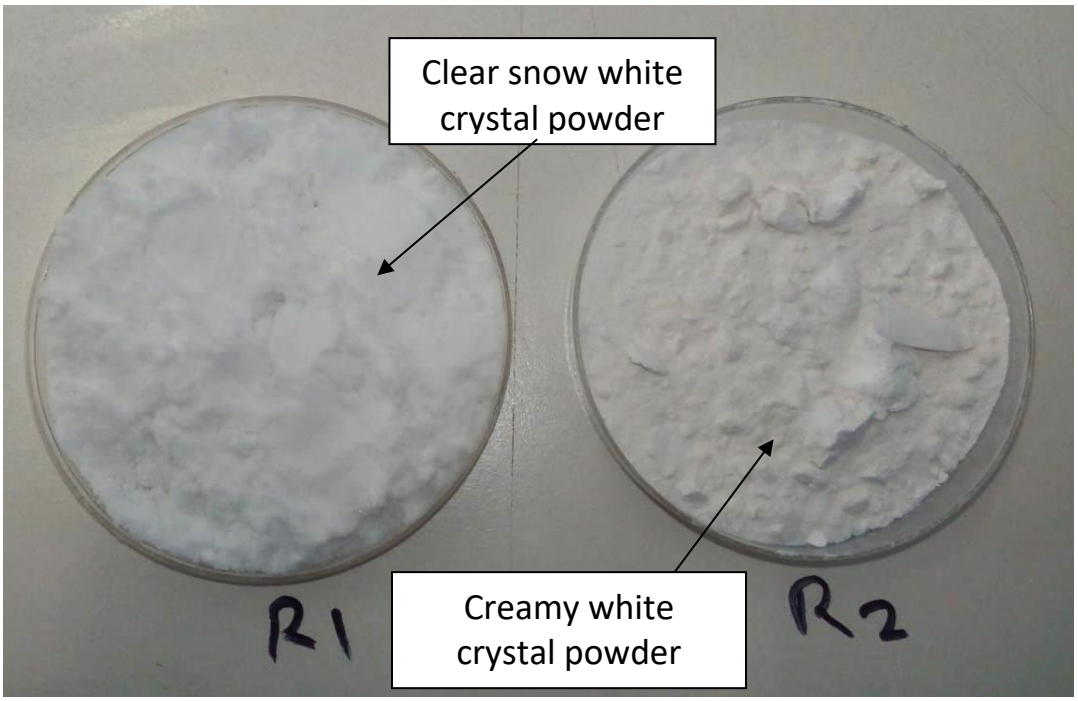

Figure 4.9: Colour comparison between R1 and R2 reaction crystalline powder formed through struvite precipitation

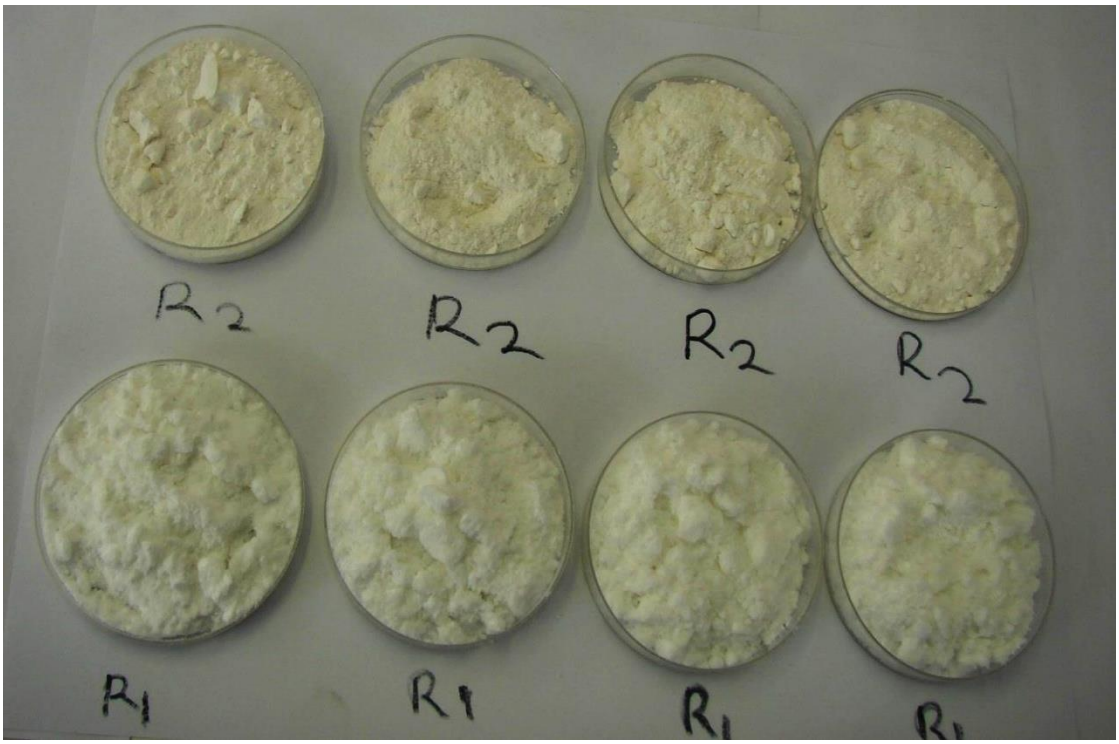

Figure 4.10: R1 and R2 reaction powder formed after struvite precipitation

4.4.1 Carl Zeiss electron microscope analysis of precipitate crystals

The Carl Zeiss electron microscope was used to examine the crystalline morphology of precipate crystals formed through struvite precipitation. To minimize sample damage by electron beams, the precipitate crystals were examined with a Carl zeiss microscope at 5 nA and 10 kV with a 20 μm beam size. An electron microscope analyzed the morphology of struvite precipitations for two different chemical combinations (R1 and R2) at pH 9 and a Mg^{2+}: NH_4^+-N: PO_4^{3-}-P 1:1:1 molar ratio.

$MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4 R1

MgO+ 85% H_3PO_4 R2

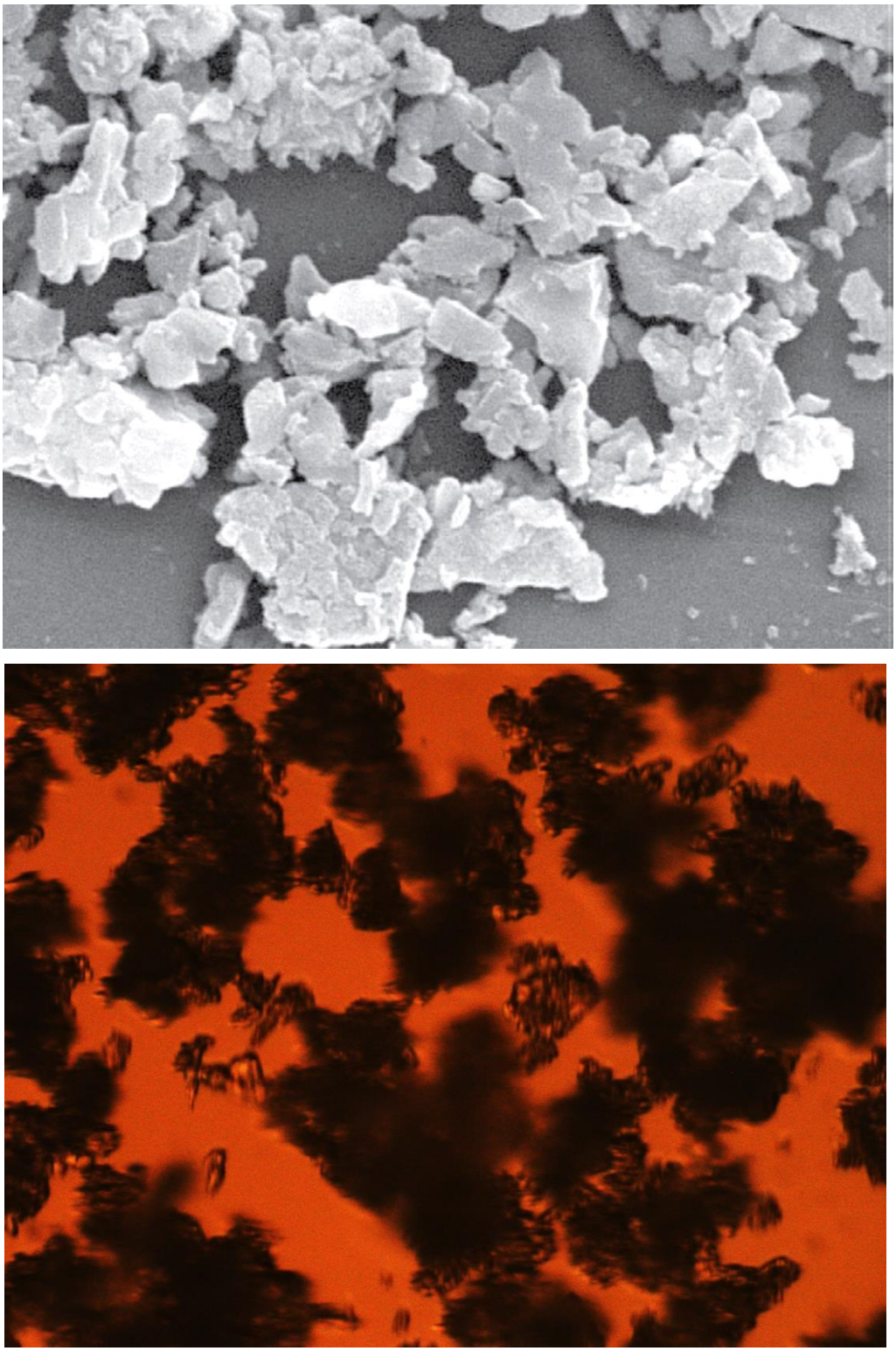

Figure 4.11: The crystals formed through struvite precipitation using the R1 reaction scheme

Figure 4.11 shows that the crystals formed through reaction scheme R1 **(**$MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4) was more discrete and its size was consistent (radius 25 - 30 nm). The crystals have a prominent white orthorhombic shape, expected for pure struvite.

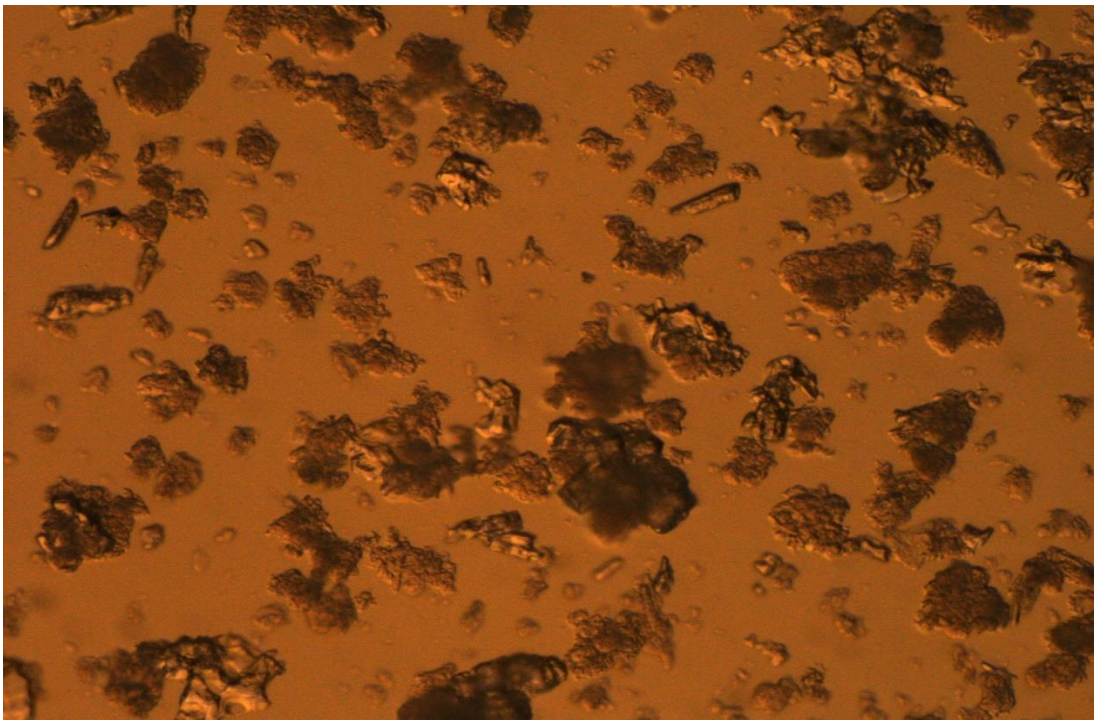

Figure 4.12: The crystals formed through struvite precipitation using the R2 reaction scheme

The results obtained from a Karl Zeiss electron microscope morphological analysis for both chemical combinations represented as R1 and R2, were compared with XRD and corresponding EDS analysis. As shown in Figures 4.9 and 4.10, the needle-shaped spherical crystal precipitate of $MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4 was more distinct than the corresponding MgO+ 85% H_3PO_4 with a more regular size (radius 25 - 30 nm). Consequently, $MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4 is suggested as the best condition for the removal of ammonium nitrogen form nitrate explosive waste water.

4.4.2 XRD analysis of precipitate crystals

XRD analysis was performed on the sample of the precipitate removed from waste water to access the quality of struvite ($MgNH_4PO_4$) formed through precipitation. An XRD diffractogram of precipitates for two chosen chemical combinations (represented as R1 and R2) at pH 9 and a Mg^{2+}: NH_4^+-N: PO_4^{3-}-P molar ratio of 1:1:1

$MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4	R1
MgO+ 85% H_3PO_4	R2

Sample was analyzed as received and the diffraction patterns obtained are shown in Figures 4.13, 4.14 and 4.15. The database model for struvite was similar to the XRD pattern generated from the samples. The crystalline phases identified in the sample from chemical combinations $MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4 was pure struvite – $(NH_4)Mg(PO_4)(H_2O)_6$, (Figure 4.13). The corresponding EDS results from chemical combinations $MgCl_2 \cdot 6H_20$ + 85% H_3PO_4 (R1) shown in Figure 4.14, also confirm that the crystalline structure is indeed a pure struvite ($(NH_4)Mg(PO_4)(H_2O)_6$) crystal. The elements identified in the sample are: magnesium (Mg), phosphorus (P) and chlorine (Cl) only. The crystalline phases identified in the sample from chemical combinations MgO+ 85% H_3PO_4 (R2) contain different magnesium phosphates, magnesium oxide and struvite (Figure 4.15). The crystal identified is not pure struvite. The crystalline phases identified in the sample are:

- Struvite – $(NH_4)Mg(PO_4)(H_2O)_6$
- Periclase – MgO
- Brucite – $Mg(OH)_2$
- Graphite – C
- Dolomite – $CaMg(CO_3)_2$
- Magnesium phoshate – $Mg_2P_4O_{12}$

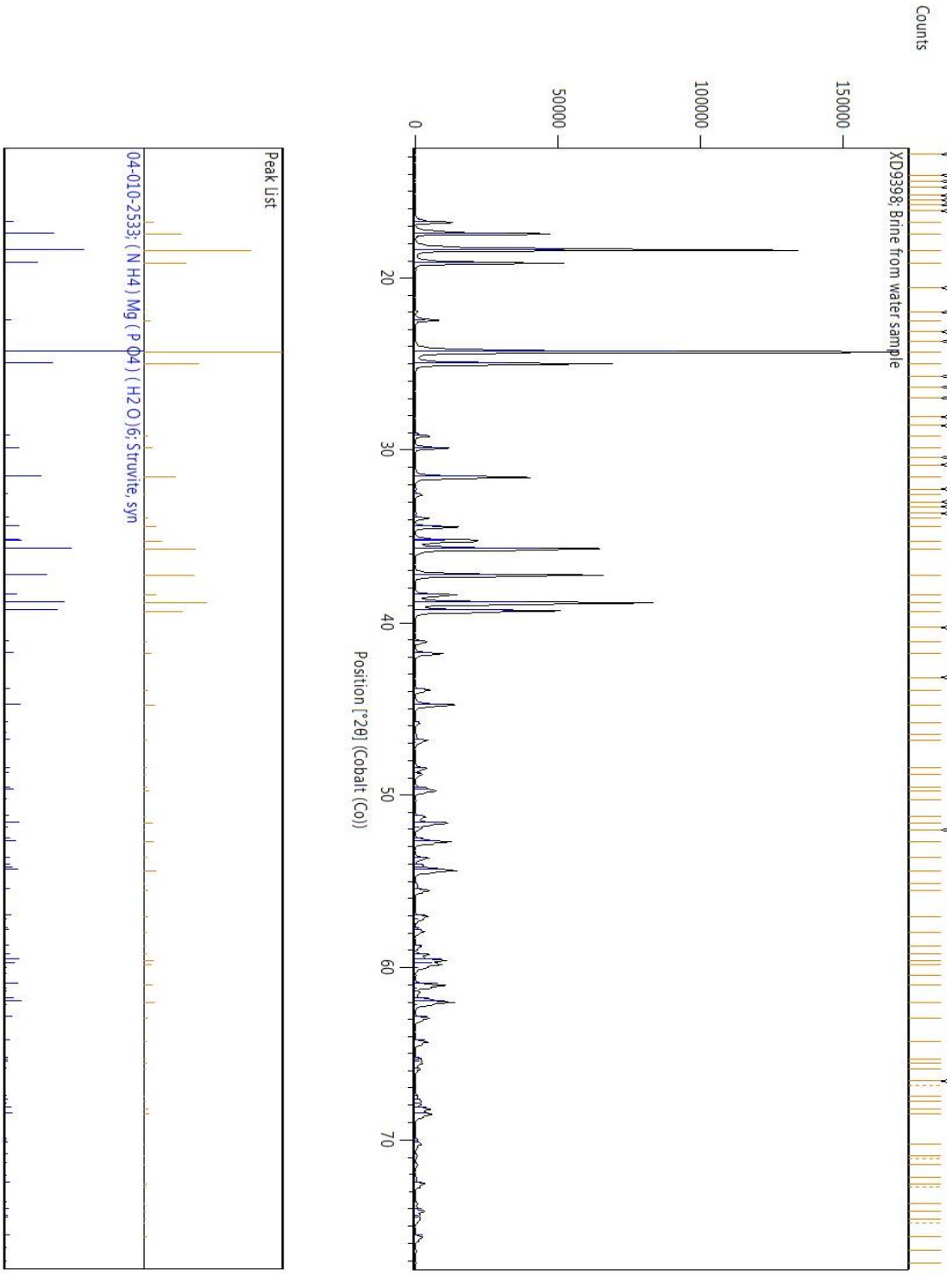

Figure 4.13: XRD diffractogram of precipitates for chemical combinations of $MgCl_2{\cdot}6H_2O$ + 85% H_3PO_4, at pH 9 and a Mg^{2+}: NH_4^+-N: PO_4^{3-}-P molar ratio of 1:1:1

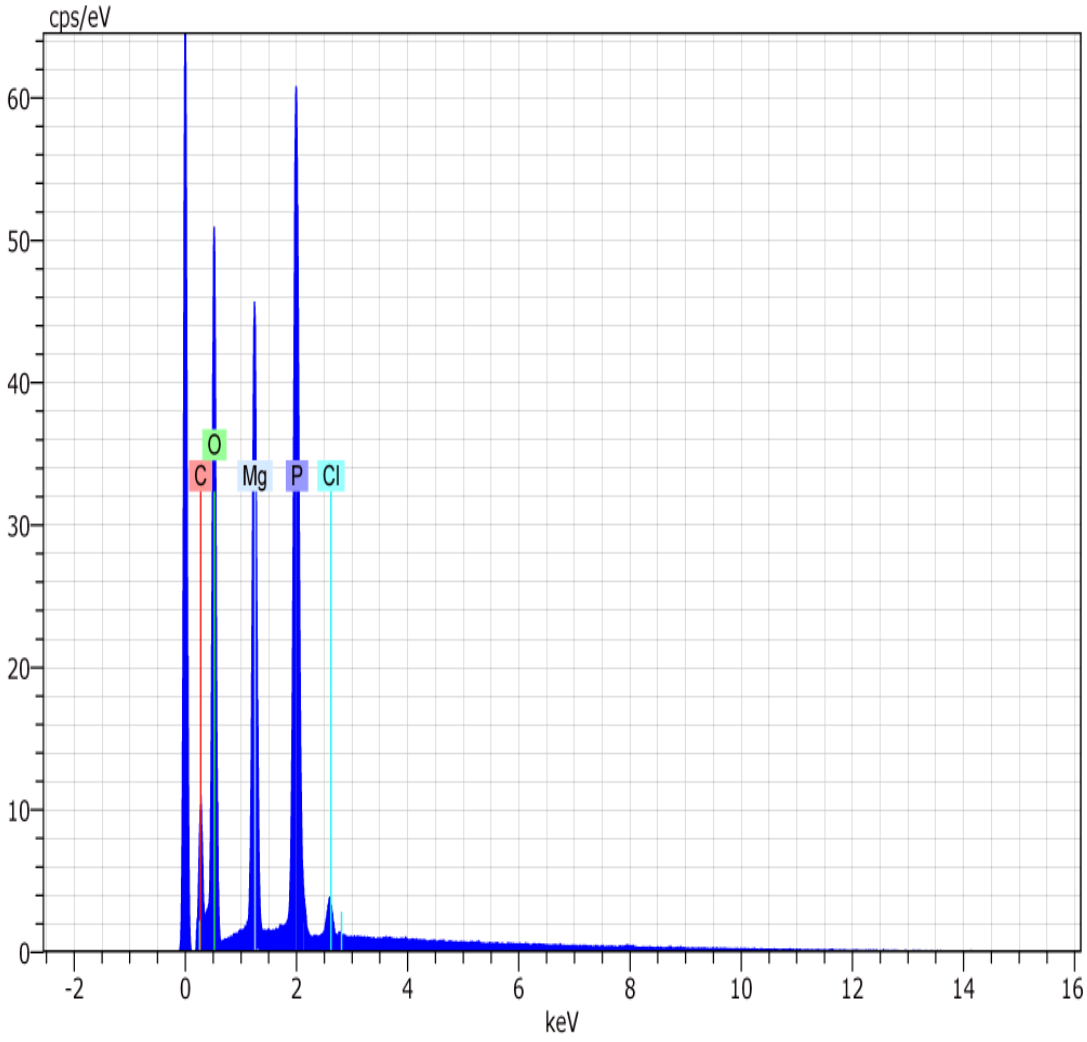

Figure 4.14: EDS spectrum of the elements identified from struvite precipitates from chemical combinations of $MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4, at pH 9 and a Mg^{2+}: NH_4^+-N: PO_4^{3-}-P 1:1:1 molar ratio

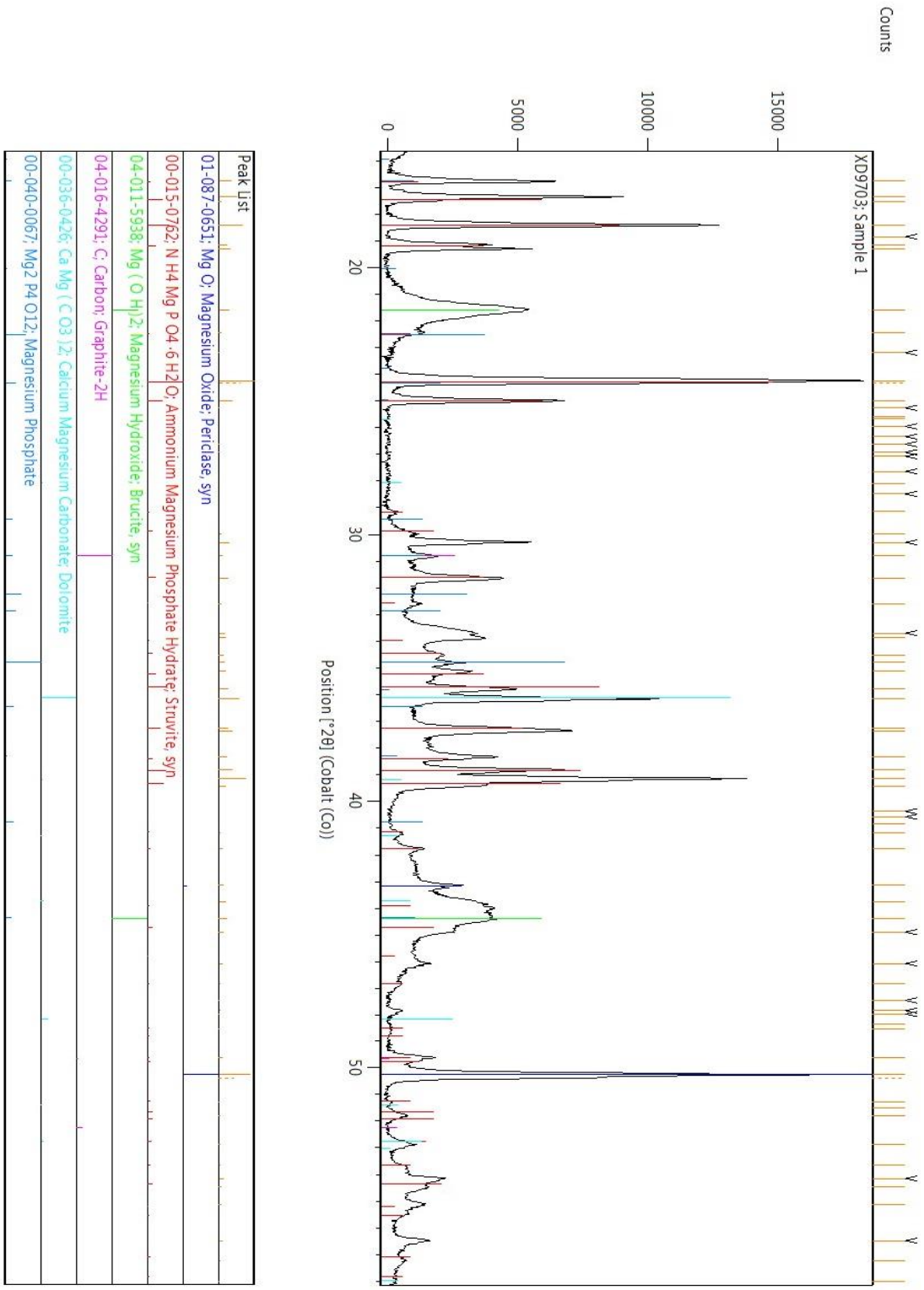

Figure 4.15: XRD diffractogram of precipitates for chemical combinations of MgO + 85% H_3PO_4, at pH 9 and a Mg^{2+}: NH_4^+-N: PO_4^{3-}-P molar ratio of 1:1:1

The total phase analysis on the crystalline sample reveals that the sample from chemical combinations $MgCl_2 \cdot 6H_20$ + 85% H_3PO_4 (R1) contains only struvite ($(NH_4)Mg(PO_4)(H_2O)_6$).

The volume weighted average crystallite sizes (L_{Vol}) of the crystalline phases that are reported were calculated as follow:

$$L_{Vol} = k / Voigt_IB$$

Where:

L = Lorentzian half width of phase reflections after deconvolution from the instrumental broadening

k = Shape factor, fixed to 1

Voigt_IB = Integral breadth of the Pseudo-Voigt profile used to fit the reflections

The volume weighted mean column height result (L_{Vol}) should be compared to the crystallite sizes as measured by TEM.

The XRD shape generated from 85% H_3PO_4 + $MgCl_2 \cdot 6H_2O$ samples matched the database of a model of struvite. The crystalline phases identified in the sample are pure struvite – (NH_4) Mg $(PO_4)(H_2O)_6$. This confirms that the combination of 85% H_3PO_4 + $MgCl_2 \cdot 6H_2O$ matched strongly indicating that you can create a relatively pure precipitate of struvite using 85% H_3PO_4 + $MgCl_2 \cdot 6H_2O$. The study also showed that, nitrates waste water could be considered as an ammonium source in a formation of struvite products. The quantitative XRD analysis technique is an effective and powerful tool to determine the content of struvite products. Consequently, $MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4 is proposed as the best chemical reaction for precipitating ammonium nitrogen out from nitrate explosive waste water.

4.4.3 Raman spectroscopic analysis of precipitate crystals

A Raman scan was performed on the sample of the precipitate removed from waste water to access the structural fingerprint of struvite ($MgNH_4PO_4$) formed through precipitation. The Raman spectra of precipitates for chosen chemical combinations (denoted as R1) at pH 9 and a Mg^{2+}: NH_4^+-N: PO_4^{3-}-P molar ratio of 1:1:1 is shown in Figure 4.16.

$MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4 R1

A Raman scan was performed on the sample of the precipitate removed from waste water. The sample was analyzed as received and the spectrum obtained is shown in Figure 4.16.

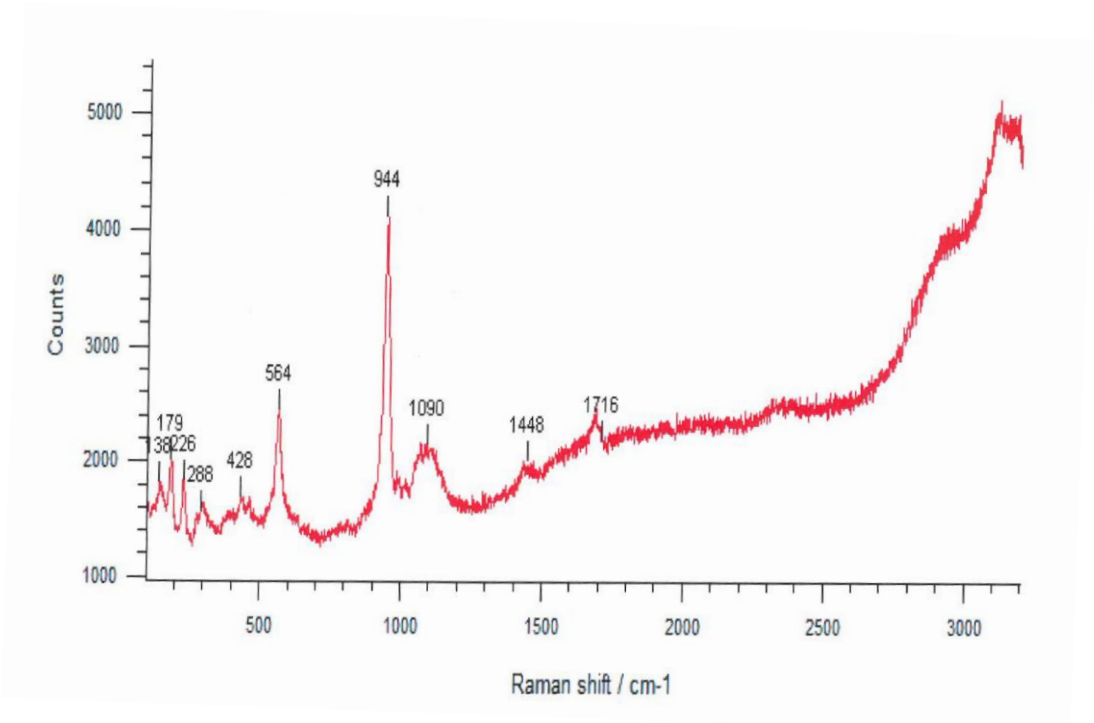

Figure 4.16: Raman spectra of struvite precipitates from chemical combinations of $MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4, at pH 9 and a Mg^{2+}: NH_4^+-N: PO_4^{3-}-P molar ratio of 1:1:1, heating under continuous N_2 flow to 3 000°C

Seven main peaks were observed at Raman spectra from precipitates from waste water. A single band at 944 cm^{-1} denotes the presence of a phosphate ion. The 1 716 cm^{-1} band could be an indication of H_2O bonding. 1 448 is the N-H-N bending vibration for struvite. The 564 cm^{-1} and below may be Mg related vibrations.

Two distinctive groups of bonds can be seen when NH_4^+ in crystals occurs. The one at ~1 448 cm^{-1} is due to the H-N-H bending vibrations and the other at ~3 100 cm^{-1} is due to the N-H stretching vibrations. The local symmetry of NH_4^+ and the bonding environments change the positions of bond in each group and the actual numbers will differ. Six O atoms coordinate NH_4^+ with a range of 2.800 - 3.498 Å N – O distances and a 3.136 Å average N – O distances. The marked distortion of its A site primarily causes the large separation between the two H-N-H bending modes (1 468 – 1 432 = 36 cm^{-1}) for precipitate from waste water. The longer average N – O distances can explain the greater wave numbers of the two bonding bonds in precipitate. The H-N-H bending is made more interesting for the N-H…O bond, when a larger N-O distance means stronger N-H and weaker H…O bonding.

The Raman spectra closely resemble those struvite Raman spectra published (Banks *et al*., 1975). Given the strong resemblances between crystals obtained from nitrate waste water and the published structure struvite and chemistry thereof, precipitation of struvite from nitrate waste water can become very attractive as it may present a potential route for magnesium ammonium phosphate also known as struvite precipitation.

4.4.4 Thermo gravimetric analysis of precipitate crystals

Thermo gravimetric analysis (TGA) was performed on the sample of the precipitate removed from waste water to access the structural fingerprint of

struvite ($MgNH_4PO_4$) formed through precipitation. The TGA spectra of precipitates for chosen chemical combinations (represented as R1) at pH 9 and a Mg^{2+}: NH_4^+-N: PO_4^{3-}-P molar ratio of 1:1:1 is shown in Figure 4.17.

$MgCl_2 \cdot 6H_2O$ + 85 % H_3PO_4 R1

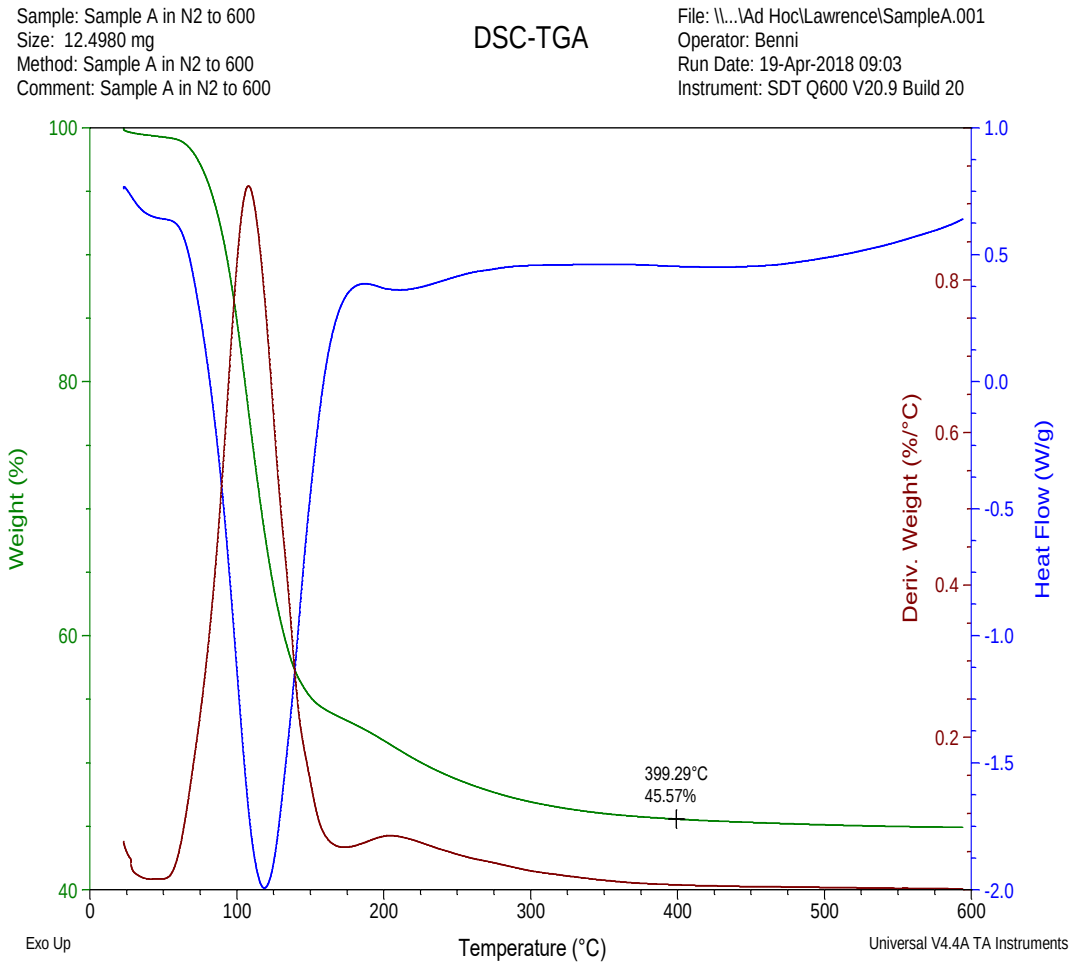

Figure 4.17: Thermo gravimetric spectra of struvite precipitates formed from chemical combinations of $MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4, at pH 9 and a Mg^{2+}: NH_4^+ -N: PO_4^{3-}-P molar ratio of 1:1:1

The thermal composition of struvite has been studied many times before. The decomposition of struvite has been found to be dependent on the conditions of decomposition (Liptay *et al*., 1975). The decomposition is different in a moist atmosphere or in nitrogen. The theoretical mass loss of struvite, also known as magnesium ammonium phosphate ($NH_4MgPO_4.6H_2O$) is 52.42%. This is due to a mass loss of water at 44.08%, followed by ammonia at 7.34% as displayed in Figure 4.17.

These three thermal events observed are between 80°C and 400°C. The first step shows the evolved gas mass gain for the thermal decomposition of precipitated crystals.
The TGA spectra (Figure 4:17) shows that struvite starts decomposing at 58°C and the whole decomposition process finishes at about 550°C. In the process of decomposition, two different stages were observed. The first stage between 112 and 180°C shows the evolved gas mass gain for the thermal decomposition of precipitated crystals. This shows that, by using a heating rate of 2 degrees per minute and a resolution of 4, water and ammonia are lost concurrently and continue up to 180°C. In this studies, the decomposition has been found to be depended on the heating rate.

The second stage is between 190 and 600°C, in this step, $2MgHPO_4{\cdot}3H_2O$ molecules are observed, which resulted in the elimination of seven water molecules; as a result $Mg_2P_2O_7$ was formed. Magnesium pyrophosphate ($Mg_2P_2O_7$) is very stable.

The proposed sequence for struvite decomposition is as follows:

$$MgNH_4PO_4{\cdot}6H_2O \xrightarrow{112 - 180°C} MgHPO_4{\cdot}3H_2O + NH_3 + 3H_2O$$

$$2MgHPO_4 \cdot 3H_2O \xrightarrow[7H_2O]{190 - 600^\circ C} Mg_2P_2O_7$$

The XRD and EDS analyses confirm that the precipitate crystals formed from chemical combinations of $MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4, is the struvite crystals. The thermal decomposition of precipitate crystals also confirms that the crystals is indeed struvite. It has been observed that struvite has two thermal decomposition stages. The first stage is the dehydration of three water molecules and deamination of an ammonia molecule. The second stage is the dehydration stage, which resulted in the loss of seven water molecules. Thermo gravimetric analysis is in agreement with the proposed structure of struvite ($NH_4MgPO_4 \cdot 6H_2O$).

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The overall goal of this study was generally to develop a method to remove the pollutants in waste water. Physico-chemical processes have been applied on the nitrate waste water in order to lower pollutants concentration. Major pollutants were ammonium nitrates and sodium nitrates. Physico-chemical processes were used to remove ammonium nitrogen from waste water and the characterization of crystals formed. Among them includes coagulation/flocculation, sedimentation, filtration, pH adjustment, Chemical precipitation and characterization of struvite formed with XRD, EDS, TOPAS, TGA, Raman, etc. In general, the objective of the study was a success. The main outcome of the study are summarized as follows:

5.1.1 Coagulation/flocculation

When neutral synthetic polymers were used as coagulation /Flocculation, flocs did not form. Continuous coagulation/flocculation with two cationic flocculants reduced the turbidity of nitrate waste water from 168 to 15 NTU. Although the turbidity of the flocculated nitrate waste water was reduced, the concentrations of sodium and nitrates in the flocculated waste water were not significantly reduced. The concentration of calcium and magnesium in the flocculated waste water was reduced by 86 and 99% respectively. Coagulation/flocculation of the waste water did not result in the improved removal of the nitrates. From these results it could be concluded that iron and

aluminium coagulants/flocculants can be used as a treatment option for nitrate waste water turbidity reduction.

5.1.2 Precipitation by pH adjustment

Struvite ($NH_4MgPO_4 \cdot 6H_2O$) precipitation was applied for the removal of ammonium nitrogen (NH_4^+-N) from nitrates waste water. The two combinations of chemical reagents that were used are $MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4 (R1) and MgO+ 85% H_3PO_4 (R2) to decide what would be the best combination to remove ammonium nitrogen. The influence of pH and molar ratio's on struvite precipitation were also investigated. From the experimental results obtained, the following could be concluded:

- $MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4 was the most effective combination to remove ammonium nitrogen as compared to the MgO+ 85% H_3PO_4 combination studied. The residual phosphate (PO_4^{3-}-P) on the $MgCl_2 \cdot 6H_2O$ + 85% H_3PO_4 combination was very low.
- pH was a very crucial factor in the removal of ammonium nitrogen removal from nitrate waste water. The best pH observed for the optimum removal of ammonium nitrogen was at a pH of 9, whereas a slightly elevated pH was good for the maximum residual phosphate removal.
- Mg^{2+}: NH_4^+-N: PO_4^{3-}-P molar ratio of 1:1:1.1 was appropriate for the efficient removal of ammonium nitrogen from nitrate waste water with acceptable minimum levels of residual phosphate remaining in nitrate waste water.

5.1.3 Characterization of precipitate crystals

The crystals formed from two combinations of chemicals used, were characterized by the Carl Zeiss electron microscope, XRD, EDS, Raman and TGA. Two combinations of chemical reagents that were used are $MgCl_2{\cdot}6H_20$ + 85% H_3PO_4 (R1) and MgO+ 85% H_3PO_4 (R2) to decide on the most effective combination to remove ammonium nitrogen. Both analyses confirm that the crystalline phases identified in the sample from chemical combinations of $MgCl_2{\cdot}6H_2O$ + 85% H_3PO_4 were pure struvite – $(NH_4)Mg(PO_4)(H_2O)_6$. The Carl Zeiss electron microscope reveals that the crystals formed via $MgCl_2{\cdot}6H_2O$ + 85% H_3PO_4, has a needle shaped spherical crystal precipitate, which is more discrete; its size was consistent (radius 25 - 30 nm). It also reveals that the crystals have a prominent orthorhombic shape, expected for pure struvite.

The XRD shape obtained from these samples was similar to the database of the struvite model. The crystalline phases identified in the sample are struvite – $(NH_4)Mg(PO_4)(H_2O)_6$. This confirms that the combination of 85% H_3PO_4 + $MgCl_2.6H_2O$ indicate the strongest match, showing that you can create a relatively pure struvite precipitate using 85 % H_3PO_4 + $MgCl_2{\cdot}6H_2O$.

EDS results from chemical combinations $MgCl_2{\cdot}6H_2O$ + 85% H_3PO_4 (R1), also confirm that the crystalline structure indeed consists of pure struvite ($(NH_4)Mg(PO_4)(H_2O)_6$) crystals. The elements identified in the sample are: magnesium (Mg), phosphorus (P) and chlorine (Cl) only. The Raman spectra closely resemble those struvite Raman spectra published by Banks (Banks *et al*., 1975).

The thermal decomposition of precipitate crystals also confirm that the crystals are indeed struvite. It has been observed that struvite has two

thermal decomposition stages. The first stage is the dehydration of three water molecules and the deamination of ammonia molecules. The second stage is the dehydration stage, which resulted in the loss of seven water molecules. Thermo gravimetric analysis is in agreement with the proposed structure of struvite ($NH_4MgPO_4.6H_2O$).

The total phase analysis of crystalline samples reveal that the sample from chemical combinations $MgCl_2{\cdot}6H_2O$ + 85% H_3PO_4 (R1) contains only struvite ($(NH_4)Mg(PO_4)(H_2O)_6$).

5.2 Recommendations

The following recommendations for the future can be made:

- It would be recommended to recover nitrates from waste water using bio-leaching where bacterials can be used to recover metals instead of ion exchange to cut down on costs.
- The technical feasibility of struvite precipitation has been proven in these studies. In order to ascertain the goal of reducing the capital layout, it is recommended that a comparative economic feasibility study be carried out.
- Sodium nitrate has been used as one of the ingredients in the production of watergel explosives. In order to cut down cost and generate revenue out of waste water, it would be recommended to replace sodium nitrates with potassium nitrates as reagents, which is more essential in farming as fertilizer.

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