Reduction of ammonia from wastewater effluent using modified activated clay

by

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DECLARATION

I, Mr Wighens Ngoie Ilunga, declare that the content of this thesis represents my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed

Date

ABSTRACT

It has been noticed that effluent from wastewater treatment plants in South Africa does not comply with the minimum requirements of environmental standards of wastewater effluent for discharge into the environment. This is due to the presence of soluble, persistent organic pollutants (POPs) and other related pollutants, in particular ammonia (PakWaterCare Services, 2011).

To rectify this situation, this study sought to treat wastewater effluents, initially using natural clay (bentonite and Montmorillonite). Secondly, clay was activated by sulphuric acid to increase its adsorptive properties. The concentration of sulphuric acid ranged from 0.5M to 18.4M so that the effective concentration could be reached. Tests were carried out to evaluate the conditions (mixing and flocculation stirring speeds, durations, and settling times) and dosages required to achieve optimum in terms of ammonia removal. Due to difficulties encountered the experiment was performed in two ways: 1) at first only bentonite was used and 2) samples were subsequently activated with H_2SO_4 (6M; 8M and 11M). The dosage of the coagulant into the jar tester beakers per litres of water was 0.5; 1; 1.5; 3; 5 and 10g. And then, by keeping the mixing speed (rapid mixing at 150rpm for 1min and slow mixing at 20rpm for 20min) and settling time constant (30min), clay was activated by H_2SO_4 (0.5M; 3M; 5M; 11M and 18.4M).

It was noticed that for an increase in coagulant dosage, a decrease in pH of water was observed, and this was due to an augmentation in acid dosage. The achieved results for wastewater effluents indicated that using activated clay (bentonite) as a coagulant with an optimum removal and maximum surface area for acid activation attained at 5M concentration of sulphuric acid used for activation of clay. The combinations of 5M bentonite clay with ZINPs(zero valent iron nano particles), in a mass ratio of 99:1 respectively, reduced ammonia up to 96.85% with a dosage of 61.6mg coagulant, a reduction from the raw water 277mg/L to 8.71mg/L. Most of the sample pH ranged from 6.5 to 9 as required by the Department of Water Affairs and Forestry. The samples' conductivities were below the standard 2500µs/cm; the 5M+ZVINPs at 60.1mg had a conductivity of 259µs/cm. Hence, this treatment is not only effective, but also ecologically acceptable.

ACKNOWLEDGEMENTS

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DEDICATION

I would like first of all to dedicate this final dissertation to The Most High, my God who gave me life and necessary strength, hope and intelligence to accomplish this work by His Love and Grace.

Secondly, I dedicate my dissertation work to my family, friends, and colleagues.

Special feeling of gratitude to my loving parents, Felix and Marie-Jeanne Ngoie, whose words of encouragement and push for tenacity still ring in my ears, to my sister Lisette Kaunda and brothers Gusthalaure Lenge, Radelphe Malango, Guemraphel Kyombwa who have never left my side and are very special.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS AND SYMBOLS

POPs = Persistent organic pollutants

BOD = biochemical oxygen demand

TOC = total organic carbon

COD = chemical oxygen demand

ZVINPs = zero valent iron nanoparticles

PAC = poly-aluminium chloride

MPWWTP = Mitchells Plain wastewater treatment plant

BWWTP = Bellville wastewater treatment plant

PPAC = polymeric phosphate-aluminium chloride

NPP = nano pre-treatment process

MMP = modified membrane process

μm = micro-meter

NaOH = sodium hydroxide

$NaBH_4$ = sodium borohydride

$FeSO_4.7H_2O$ = iron sulphate seven times hydrated

NOM = natural organic matter

MM = molar mass (g/mol)

M = molarity

V = volume (ml)

m = mass (g)

ρ = density (g/ml)

CHAPTER ONE

INTRODUCTION

1.1 Introduction

The presence of pollutants in wastewater in recent years has resulted in a crucial anxiety in so many countries according to Zawaidah and Zhang (1998). Suwannee Junyapoon declares that "water pollution by anthropogenic sources is the largest environment problems in several countries" (KMITL Sci. Tech. J., 2005).

In particular, industrial wastewater effluent in South Africa does not meet the minimum requirements of environmental standards of wastewater effluent to be discharged into the environment, primarily due to the presence of soluble, persistent organic pollutants (POPs) and other related pollutants (ammonia sulphate, humic acid, peptones, and tannic acid)(Katsoyiannis & Samara, 2004).

Current South Africa water quality guidelines state that wastewater plant effluent should not, for example, exceed a range of 0-0.025 mg of ammonia/kg as high concentrations of ammonia may affect blood pH, osmo-regulation, increase urine flow and/or may adversely affect the oxygen-binding capacity of haemoglobin. The wastewater should also not exceed a pH level of between 6.5-9.0 and turbidity less than 25 NTU and concerning the ammonia level in the wastewater effluents to be released in the environment, it should not exceed 10 mg/L (South Africa, Department of Water Affairs, 2010).

1.2 The research problem

Wastewater effluents, containing a certain amount of persistent organic pollutant, are released daily from the plants and discharged into the environment. They are undeniably harmful to the entire ecosystem. "Ion exchange and reverse osmosis have failed to destroy efficiently the ammonia content from industrial wastewater effluents, due to inherent limitations" (Chang et *al*, 1999); (See Figure 2.12).

The appearance of ammonia related to Persistent Organic Pollutants (POPs) in wastewater is likely to continue into the future if the problem is not addressed with urgency.

As it can be noticed, on the picture below (Figure 1.0) showing the quality of wastewater exiting the Mitchells Plain Wastewater Plants to the Indian Ocean, its quality is really a matter of concern.

Figure 1.0: Final effluent discharged into Blue Waters Indian Ocean, Cape Town (Effervescent Effluent Consulting Engineers [EECE], 2012)

Wastewater or sewage water results from household wastes, human and agricultural wastes, industrial effluents, storm run-off and ground water infiltration. Wastewater is extremely hazardous both to health and to the environment; if not well-treated, this wastewater can seriously alter the total ecosystem of the planet.

Thus, the motivations for treating wastewater include the following:

- Pollution reduction; so that the environment can be safe and clean to live;
- industrial reuse of the reclaimed water;
- Recreational and environmental uses, lakes, rivers, stream flow augmentation, fisheries.

1.3 The research question

This project is proposing a way of treating wastewater effluent and reducing the contamination, and thereby to make it comply with required standards prior its release back to the natural environment. Hence, the following are questions this study will attempt to answer:

- Can natural clay (Bentonite, Montmorillonite) as coagulant efficiently remove ammonia in the wastewater effluents?
- Will the addition of nano materials such as zero valent iron nanoparticles into the mixture containing natural clay effectively play a role in the removal of POPs including ammonia from the wastewater effluent?

1.4 Wastewater treatment technologies

South Africa currently produces a large amount of sewage and industrial wastewater. These wastewaters and leachate are treated by conventional wastewater treatment technologies, which consist of aerobic and anaerobic biological processes and physical and chemical processes.

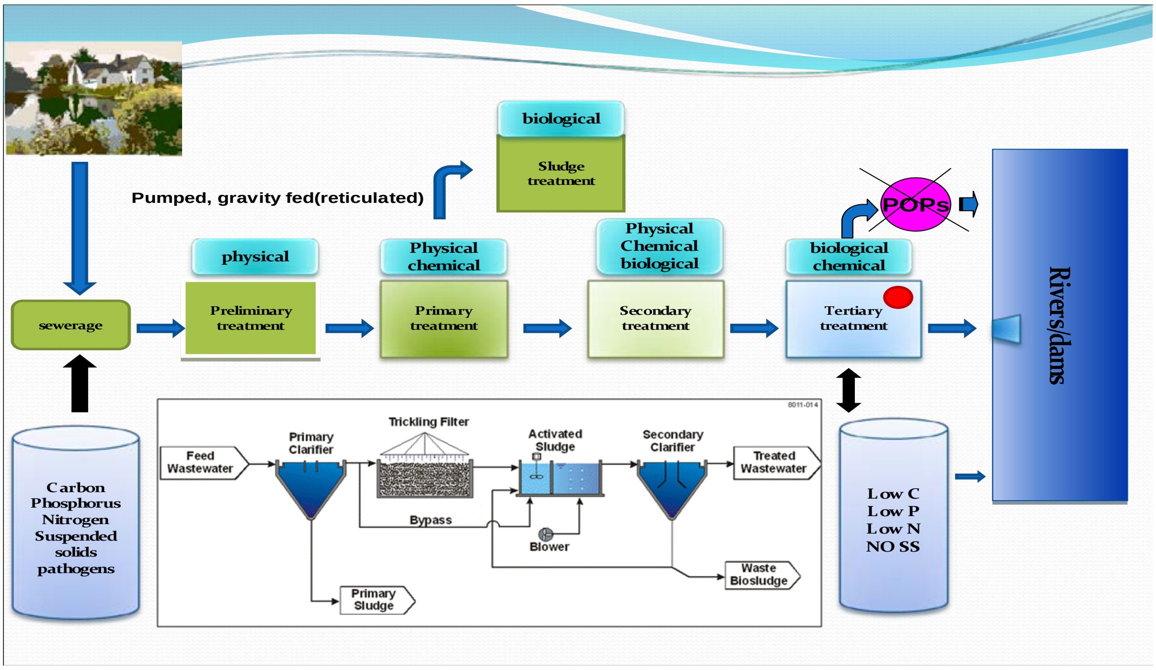


Figure 1.1: Schematic of conventional wastewater treatment facilities (Maiti, 2011).

After analysis of the water leaving the specific point at the final stage of the process, there are still excessive organic pollutants in the effluent produced from the process shown on the figure above (Figure 1.1), consequently deteriorating the quality of wastewater, and resulting in effluent that will not comply with the environmental standards and will thus be considered harmful to the environment.

1.5 Aims and objectives

The aim of this project is to develop an implementable system to improve the quality of the wastewater effluent intended to be discharged into the environment by decreasing as much as possible, the ammonia contents in the final wastewater effluent, thereby ensuring that it complies with environmental standards of South Africa.

This project will discuss the preliminary results found from using two coagulants: (1) activated, non-activated bentonite (clay); and (2) zerovalent iron nanoparticles (ZVINPs) for the modification of the clay to improve its adsorptive properties with the intention of achieving a higher yield of ammonia reduction from wastewater plant effluent. This process is referred to as the ‘nano pre-treatment process’ (NPP).

Objectives to be achieved:

- to prepare the coagulant, mainly the activated clay;
- to prepare the zero valent iron nanoparticles;
- to treat wastewater effluents using activated clay-ZVINPs system as removal agent and assess the ammonia removal efficiency.
- To determine whether or not the final product successfully meets the requirements of South African water quality regulations.

Outcomes:

- to understand the quality and characteristics of the types of wastewater effluents;
- to reach maximum efficiency of system (bentonite + ZVINPs) in the treatment of wastewater effluents;
- to find optimum conditions for the removal of ammonia from sewage wastewater; and
- To reach optimum conditions in terms of scaling-up the technology.

CHAPTER TWO

LITERATURE REVIEW AND THEORY

2.1 Overview on wastewater treatment

Wastewater can be classified as domestic, industrial, or storm, according to its origin. Domestic sources include water used for normal activity in homes, businesses and institutions, domestic water is readily treatable.

Generally, technologies for treating industrial wastewaters can be divided into three categories:

- chemical methods;
- physical methods; and
- Biological methods.

Chemical methods include chemical precipitation, chemical oxidation or reduction, formation of an insoluble gas followed by stripping, and other chemical reactions that involve exchanging or sharing electrons between atoms. Physical methods include sedimentation, flotation, filtering, stripping, ion exchange, adsorption, and other processes that accomplish removal of dissolved and undissolved substances without necessarily changing their chemical structures. Biological methods are those that involve living organisms using organic or, in some instances, inorganic substances for food. In so doing, the chemical and physical characteristics of the organic and/or inorganic substance are changed (Maiti, 2011).

The character of industrial wastewater depends on the type of industry using the water. Some industrial wastewaters can be treated the same as domestic wastes without difficulty. Others may contain toxic substances or high percentages of organic materials or solids which make treatment difficult. In such cases, the industrial plant may have to pre-treat its wastewater to remove these pollutants or reduce them to treatable levels before they are accepted into a publicly-owned treatment facility (Abdel-Magid, 1995).

The general principle in wastewater treatment is to remove pollutants from the water by getting them either to settle or to float, and then removed. Some pollutants are easily removable. Others must be converted to a settleable form before they can be removed.

Figure 2.1 is showing treatment facilities and stages in wastewater treatment plants. Each stage either removes particles from the wastewater or changes dissolved and suspended material to a form that can be removed. A modern wastewater treatment plant may include these stages:

- Influent;
- primary treatment;
- secondary treatment;
- tertiary treatment;
- Disinfection and effluent discharge.

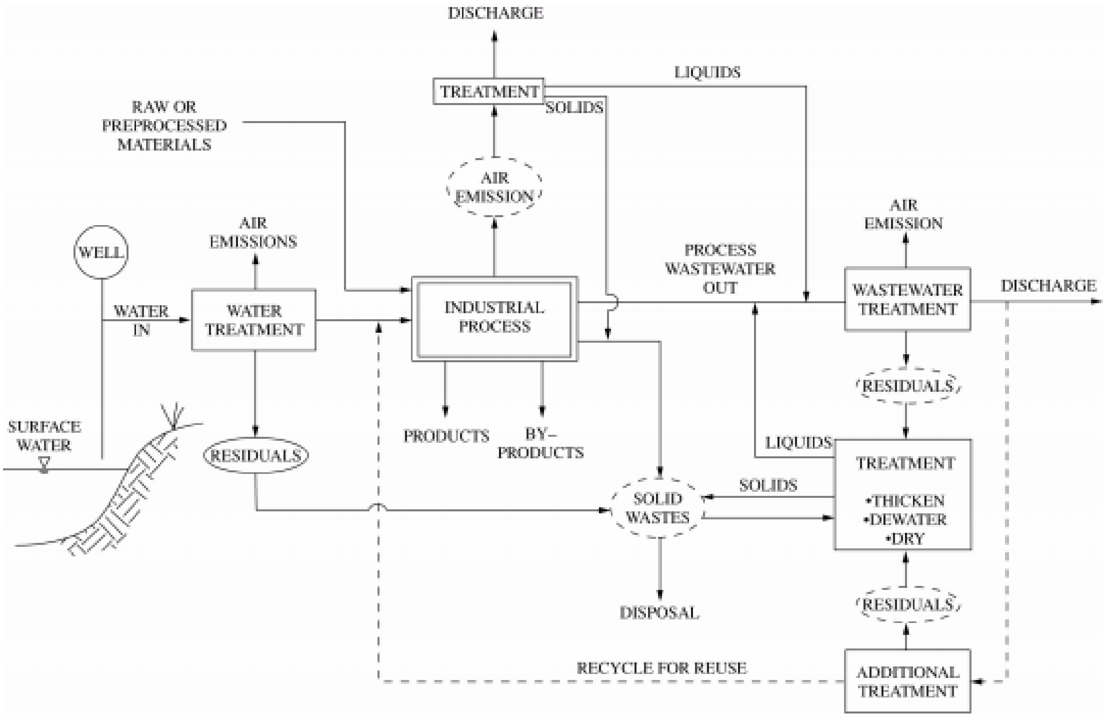


Figure 2.1: The industrial waste system (PakWaterCare Services, 2011).

The figure above represents a schematic of “the industrial waste system,” showing that raw materials, water, and air enter the system, and, as a result of the industrial processes, products and by-products exit the system, along with airborne wastes, waterborne wastes, and solid wastes. Since discharge permits are required for each of the waste-bearing discharges, treatment systems are required. Each of the treatment systems has an input, the waste stream, and one or more outputs. The output from any of the treatment systems could be an air discharge, a waterborne discharge, and, or a solid waste stream.

2.1.1 Primary treatment

Primary Settling Tank (PST)

To prevent damage to pumps and clogging of pipes, raw wastewater passes through mechanically raked bar screens to remove large debris, such as rags, plastics, sticks, and cans. Smaller inorganic material, such as sand and gravel, is removed by a grit removal system (Abdel-Magid, 1995).

- Sludge is driven towards hopper in base of tank;
- Sludge settles;
- Grease and oil are scraped off;
- 30-50% Suspended Solids (SS) removal; and
- 30-35% Chemical Oxygen Demand (COD) removal.

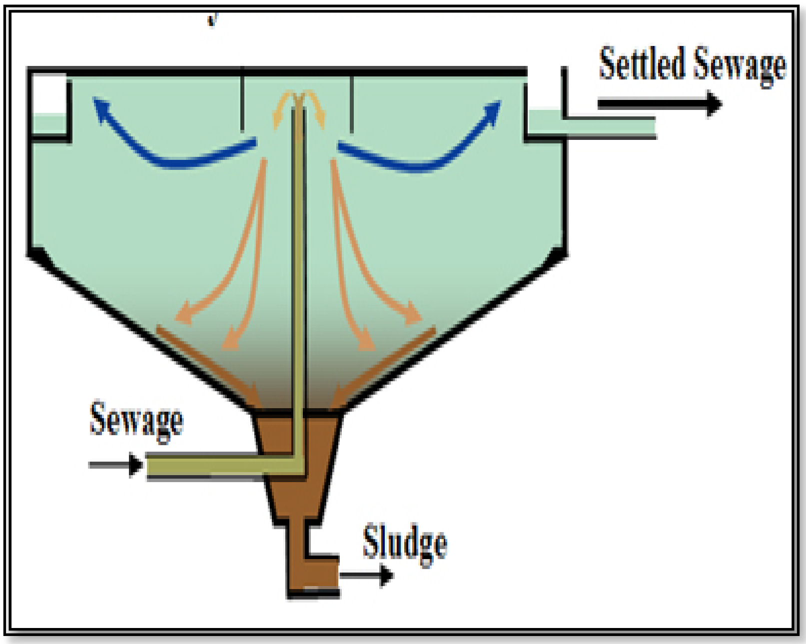


Figure 2.2: Primary treatment (MPWWTP, 2012)

These settled solids, called primary sludge, are removed along with floating scum and grease and pumped to anaerobic digesters for further treatment (Abdel-Magid, 1995).

2.1.2 Secondary treatment

The primary effluent is then transferred to the biological or secondary stage. Here, the wastewater is mixed with a controlled population of bacteria and an ample supply of oxygen. The microorganisms digest the fine suspended and soluble organic materials, thereby removing them from the wastewater. The effluent is then transferred to secondary clarifiers, where the biological solids or sludges are settled by gravity.

Aeration

- Anaerobic zone: no oxygen present and phosphorus are removed;
- Anoxic Zone: nitrate is reduced to gaseous nitrogen; and
- Aeration Zone: oxygen present and oxidation of ammonia to diminish the amount of ammonia in water.

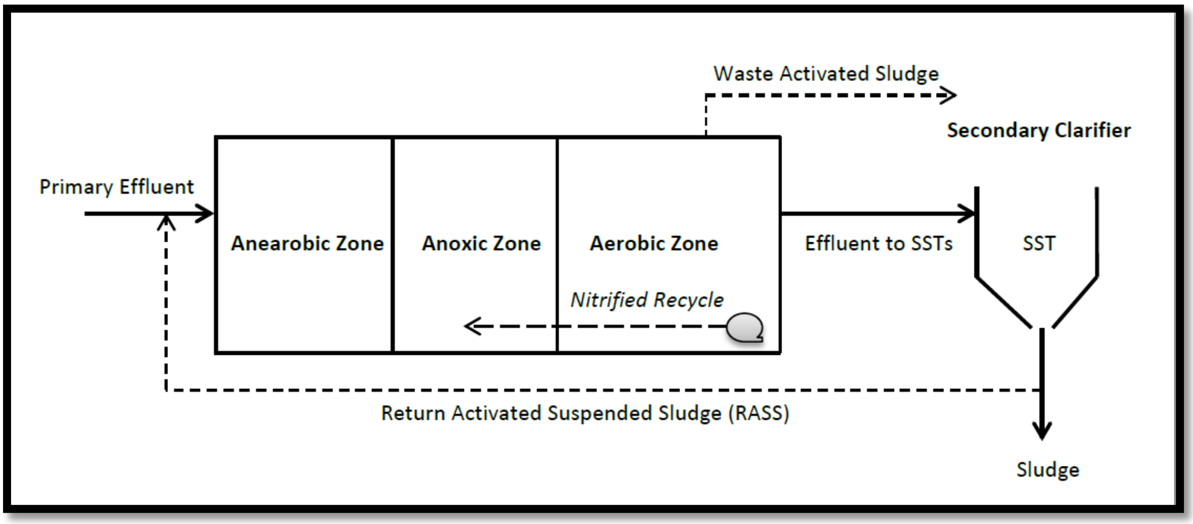


Figure 2.3: Biological reactor zone (MPWWTP, 2012).

2.1.3 Secondary settling tanks

- Eliminates biomass formed during biological treatment; and
- Performs thickening of accumulated biological sludge.

Figure 2.4: Secondary settling tank (MPWWTP, 2012)

As with the primary clarifier, these sludges are pumped to anaerobic digesters, and the clear secondary effluent may flow directly to the receiving environment or to a disinfection facility prior release. There are several variations of secondary treatment, including:

- activated sludge;
- trickling filtration;
- rotating biological contactors (RBC);
- Lagoons and ponds.

2.1.4. Tertiary treatment

The tertiary treatment can be performed in three different stages using ponds:

Stage One:

- First pond solids are accumulated;
- Solids are removed as much as possible to make it easier for Stage Two.

Figure 2.5: Sludge from the secondary treatment (MPWWTP, 2012)

Stage Two: Oxidation pond and lagoons

Here, the sludge undergoes oxidation and after a certain period of time will settle and then will later be filtered. The solid particles can be sold to farmers for agricultural applications or can be recycled into the plant to reduce taxes (Boari et *al*., 1997:262).

Stage Three:

At this stage, lime is added and odour is removed from the filtrate remaining from Stage Two. It is the mutation and final stage before the final effluent can be discharged into the blue water (Boari et *al*., 1997:264-269).

At the end of the process the wastewater treated must be discharged into the environment which is the blue sea, as it can be noticed on the pictorial on figure 2.6 illustrating the Indian Ocean shoreline nearby the wastewater outlet pipe from the Mitchells Plain WWTPs, situated at approximately 16.6km from the Muizenberg beach (Cape Town). But the main important question is about its safety: “is this final product safe enough to be released to the?”

Figure 2.6: Discharge from the tertiary treatment (MPWWTP, 2012)

In order to operate the treatment process correctly and safely, it is important to perform a certain number of studies according to the literature and be able to understand the characteristics of wastewater (Table 2.1). This enables to know the types of chemical used in the processes, the standard procedure to be applied, what the purpose of each is, and the safety precautions required in the use of each.

Table 2.1: General characteristics of industrial wastewater effluents (EPA, 2004)

Oxygen-Demanding Substances	Dissolved oxygen is a key element in water quality that is necessary to support aquatic life. A demand is placed on the natural supply of dissolved oxygen by many pollutants in waste-water. This is called biochemical oxygen demand, or BOD, and is used to measure how well a sewage treatment plant is working. If the effluent, the treated wastewater produced by a treatment plant, has a high content of organic pollutants or ammonia, it will demand more oxygen from the water and leave the water with less oxygen to support fish and other aquatic life. Organic matter and ammonia are “oxygen-demanding” substances. Oxygen-demanding substances are contributed by domestic sewage and agricultural and industrial wastes of both plant and animal origin, such as those from food processing, paper mills, tanning, and other manufacturing processes. These substances are usually destroyed or converted to other compounds by bacteria if there is sufficient oxygen present in the water, but the dissolved oxygen needed to sustain fish life is used up in this break down process.
Pathogens	Disinfection of wastewater and chlorination of drinking water supplies has reduced the occurrence of waterborne diseases such as typhoid fever, cholera, and dysentery, which remain crucial problems in underdeveloped countries. Infectious micro-organisms, or pathogens, may be carried into surface and groundwater by sewage from cities and institutions, by certain kinds of industrial wastes, such as tanning and meat packing plants, and by the contamination of storm runoff with animal wastes from pets, livestock and wild animals, such as geese or deer. Humans may come in contact with these pathogens either by drinking contaminated water or through swimming, fishing, or other contact activities. Modern disinfection techniques have greatly reduced the danger of water borne disease.
Nutrients	Carbon, nitrogen, and phosphorus are essential to living organisms and are the chief nutrients present in natural water. Large amounts of these nutrients are also present in sewage, certain industrial wastes, and drainage from fertilized land. Conventional secondary biological treatment processes do not remove the phosphorus and nitrogen to any substantial extent. In fact, they may convert the organic forms of these substances into mineral form, making them more usable by plant life. The release of large amounts of nutrients, primarily phosphorus but occasionally nitrogen, causes nutrient enrichment which results in excessive growth of algae. Uncontrolled algae growth blocks out sunlight and chokes aquatic plants and animals by depleting dissolved oxygen in the water at night. The release of

	nutrients in quantities that exceed the affected water body's ability to assimilate them results in a condition called eutrophication or cultural enrichment.
Inorganic and Synthetic Organic Chemicals	Vast arrays of chemicals are included in this category. Examples include detergents, house-hold cleaning aids, heavy metals, pharmaceuticals, synthetic organic pesticides and herbicides, industrial chemicals, and the wastes from their manufacture. Many of these substances are toxic to fish and aquatic life and many are harmful to humans. Some are known to be highly poisonous at very low concentrations. Others can cause taste and odour problems, and many are not effectively removed by conventional wastewater treatment.
Thermal	Heat reduces the capacity of water to retain oxygen. In some areas, water used for cooling is discharged to streams at elevated temperatures from power plants and industries. Even discharges from wastewater treatment plants and storm water retention ponds affected by summer heat can be released at temperatures above that of the receiving water, and elevate the stream temperature. Unchecked discharges of waste heat can seriously alter the ecology of a lake, a stream, or estuary.

The following table (Table 2.2) depicts the investigation results of a comparative study that was done by several American scientists:

Table 2.2: Comparative summary of different biological wastewater treatments (EPA, 2004)

Technology	Applications	Advantages	Disadvantages
Activated sludge	low concentration organics some inorganic	removal of dissolved constituents low maintenance destruction process relatively safe low capital costs relatively easy to operate	volatile emissions waste sludge disposal high energy costs susceptible to seasonal changes
Trickling filters **fixed films reactors**	low concentration organics some inorganic	removal of dissolved constituents low maintenance	volatile emissions susceptible to shocks and toxins

		destruction process relatively safe reduced sludge generation	susceptible to seasonal changes relatively high capital costs relatively high operating costs
Aerated lagoons **Stabilization ponds**	low concentration organics some inorganic	removal of dissolved constituents low maintenance destruction process relatively safe low capital costs low energy costs easy to operate infrequent waste sludge	volatile emissions susceptible to shocks and toxins susceptible to seasonal changes high land requirement no operational control
Anaerobic degradation (septic systems)	low concentration organics some inorganic	removal of dissolved constituents destruction process treatment of chlorinated wastes methane generation reduced sludge generation	susceptible to shocks and toxins susceptible to seasonal changes relatively high capital costs relatively high operating costs

As the main objective of this project is to transform the wastewater effluents from the current WWTPs into a wastewater which is acceptable to the environmental South African standards, here is a quick and general overview of the South Africa water act (Table 2.3).

Table 2.3: National water act discharge standards (South Africa, Department of Water Affairs, 2010)

Variables and substances	**Existing SA General standards**	**Existing SA special standards**
Chemical oxygen demand	75mg/L	30mg/L
Colour, odour or taste	No substance capable of producing the variables listed	-
Ionized and unionized ammonia (NH_4^+, NH_3)	3mg/L	2mg/L
Nitrate	15mg/L	1.5mg/L
pH	5.5-9.5	5.5-7.5
Suspended solids	25mg/L	10mg/L
Phosphorous (orthophosphate)	10mg/L	1mg/L
Residual chlorine (Cl)	0.25mg/L	0

Since this project deals with the South African wastewater effluents, the efficiency of the current technology of treating wastewater was investigated in order to understand where exactly the problem is coming from, problem that might be responsible of the persistence of ammonia throughout the whole system (Table 2.4 through Table 2.9).

Table 2.4: Range of wastewater treatment technologies employed in South Africa (South Africa, Department of Water Affairs, 2010)

Treatment technology	**Percentage (%)**
Oxidation ponds	16
Biological filtration	23
Activated sludge with biofiltration	6
Activated sludge	35
Not specified	20

Activated sludge (biological denitrification) is the most widely used method for treating wastewater; this process makes use of a nitrification/denitrification process to reduce nitrate/nitrite contamination from wastewater. Denitrification process is the biological reduction of nitrate to nitrogen gas under anaerobic and anoxic conditions when dissolved oxygen concentration is under 0.2mg/L. This process is being performed by means of the heterotrophic bacteria group (Krupa, 2003:199-221). During this process the nitrates become nitrite, nitrogen oxide, nitrogen monoxide then to nitrogen hemi oxide, in the following sequence:

$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2.$

The complete denitrification process can be express as a redox reaction, and nitrogen which constitutes almost 79% by volume of the earth's atmosphere, inert, odourless and tasteless in its gaseous state will escape naturally to the atmosphere at the end of the denitrification process (Smet et *al*., 2000:187-190).

Water pollution is really a serious matter of concern, in the whole South Africa (DWA, 2010) it can be observed that most of wastewater effluents are unable to comply with the required government standards (Figure 2.3). It obviously depends on the original province where the treatment technology is performed as it can be noticed in figure 2.7 how the bacteriological quality is varying comparatively to the standards and the chemical oxygen demand as well (Figure 2.9).

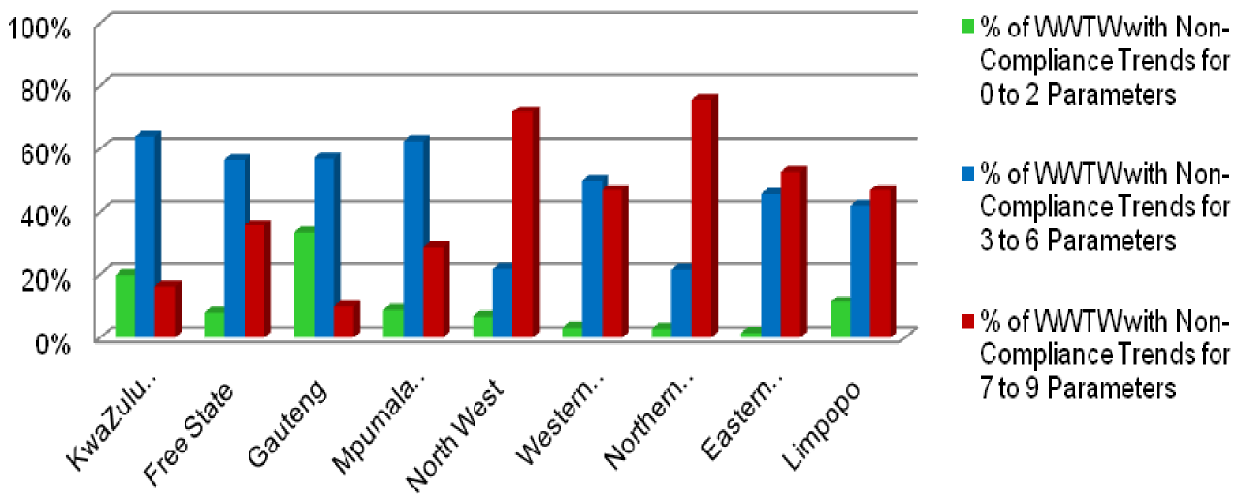


Figure 2.7: Percentage of WWTWs that are considered non-compliant in terms of effluent quality discharged against the specific EQ (DWA) standards. *(South Africa, Department of Water Affairs, 2010*)

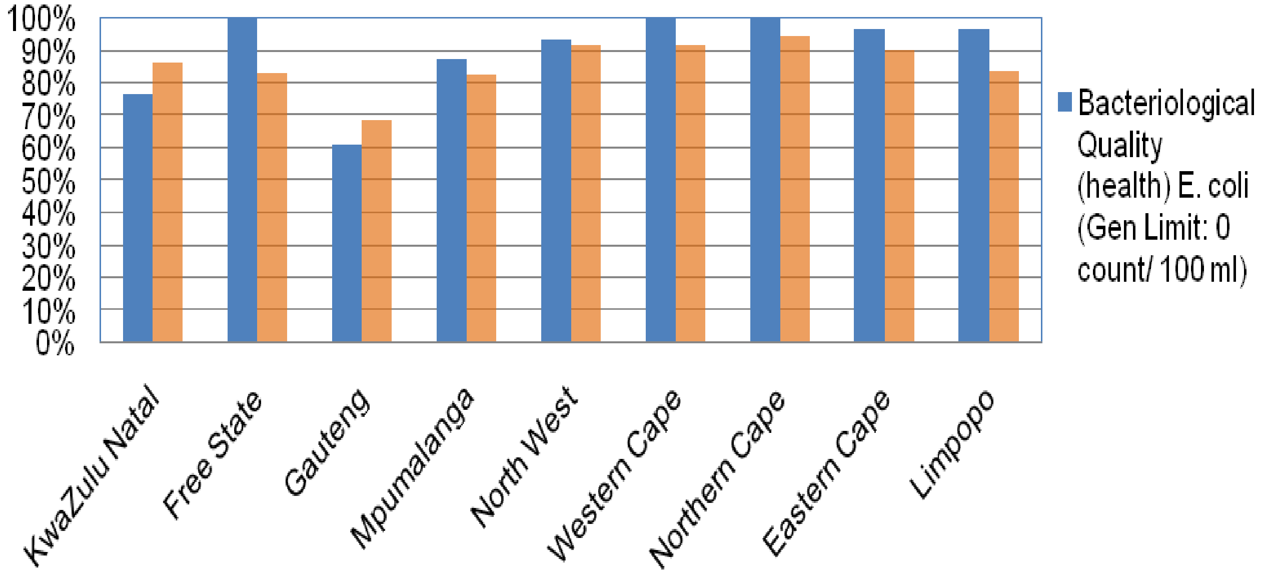


Figure 2.8: Percentage of WWTWs non-compliant for “bacteriological quality” (health-related). *(South Africa, Department of Water Affairs, 2010).*

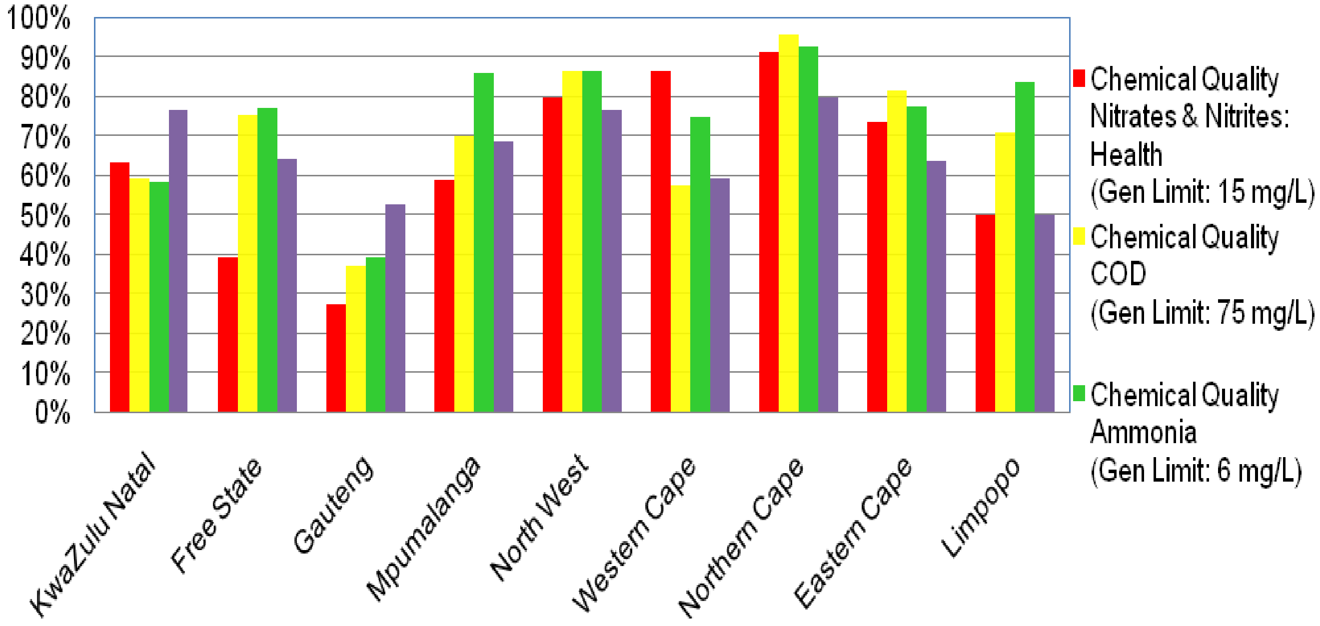


Figure 2.9: Percentage of WWTWs non-compliant for “chemical quality” in terms of COD, nitrates. . *(South Africa, Department of Water Affairs, 2010).*

2.1.4.1 Investigation of wastewater effluent quality currently released into ocean

In this section all figures and specific results will not be shown seen the sensitivity of information provided by several Wastewater Treatment Plant located in the Cape Town area, especially, as I did not record and analyse water samples by myself.

2.1.4.2 Ammonia

Ammonia (NH_3) is a colourless acrid-smelling gas at ambient temperature and pressure. It can be stored and transported as a liquid at a pressure of 10 atm at 25 °C. It dissolves readily in water where it forms, and is in equilibrium with, ammonium ions (NH_4^+). The sum of ammonia and ammonium concentrations is termed "total ammonia" and, because of the slightly different relative molecular masses, may be expressed as "total ammonia-nitrogen (NH_3-N)". In most waters, NH_4^+ predominates, but increases in pH or temperature or decreases in ionic strength may materially increase levels of non-ionized ammonia (Eitzer et *al*., 1995).

Ammonia will adsorb on various solids. At concentrations of between 16 and 27% by volume, it can form explosive mixtures with air. Catalytic oxygenation is an important reaction in the manufacture of nitric acid. Ammonia dissolves in dilute acids to form ionized ammonium salts, which are similar in solubility to alkali metal salts, and can be crystallized. Some of these salts are found in nature. Heating solutions or crystals of the salts yields gaseous ammonia. Ammonia forms chloramines in water containing hypochlorous acid. Ammonia is present in the environment as a result of natural processes and industrial activity, including certain types of intensive farming. Much more significant quantities arise from non-point sources, such as atmospheric deposition, the breakdown of vegetation and animal wastes, applied artificial fertilizers and urban runoff, and these are significant, even in industrial areas (Krupa et *al.*, 2003).

Ammonia in the environment is a part of the nitrogen cycle. It volatilizes into the atmosphere where it may undergo a variety of reactions. Photolytic reactions destroy some of the ammonia and reactions with sulfur dioxide or ozone produce aerosols, most importantly of ammonium sulfate or nitrate, which return to the earth's surface as wet or dry deposition. In surface waters, ammonium may undergo microbiological nitrification, which yields hydrogen and utilizes oxygen so that, in certain systems, acidification and oxygen depletion may result. In one study, one-third of the acidifying effect of precipitation was attributed to ammonium deposition. Ammonia may be assimilated by aquatic plants as a nitrogen source or transferred to sediments or volatilized (Pagans et *al*., 2006).

In soil, major sources of ammonia are the aerobic degradation of organic matter and the application and atmospheric deposition of synthetic fertilizers. The ammonium cation is adsorbed on positively charged clay particles and is relatively immobile. Most ammonium undergoes nitrification; the nitrate ion is mobile and is removed by leaching, plant root uptake, or denitrification (Smet et *al*., 2000). Thus, the next section deals with the way ammonia can be removed by both coagulation/flocculation and denitrification.

2.1.4.3 Coagulation and flocculation

Coagulation theory: In water treatment plants, chemical coagulation is usually accomplished by the addition of trivalent metallic salts such as $Al_2 (SO_4)_3$ (aluminium sulphate) or $FeCl_3$ (ferric chloride). The exact method can be conducted through a four-step mechanism as listed below (Maiti, 2011):

1. ionic layer compression;
2. adsorption and charge neutralisation;
3. entrapment in a flocculent mass; and
4. Adsorption and inter-particle bridging.

1. Ionic layer compression

The quantity of ions in water surrounding a colloid has an effect on the decay function of the electrostatic potential. If this layer is sufficiently compressed, then the van der Waals force will be predominant across the entire area of influence, so that the net force will be attractive and no energy barriers will exist. Coagulants such as aluminium and ferric salts used in water treatment ionise; at the concentration commonly used they would not increase enough the ionic concentration to affect ion layer compression (Bayrak et *al*., 2006).

2. Adsorption and charge neutralisation

Adsorption and neutralisation of both types of coagulants are very similar. The ionisation of aluminium sulphate (alum) in water produces sulphate anions (SO_4^{2-}) and aluminium cations (Al^{3+}). The sulphate ions may remain in this form or combine with other cations. However, the Al^{3+} reacts immediately with water to form a variety of aquometallic ions and hydrogen as shown by the below equations:

$Al^{3+} + H_2O \longrightarrow Al\,(OH)_2^{+} + 2H^{+}$ **1.3.1.2 (a)**

$Al^{3+} + 2H_2O \longrightarrow Al\,(OH)_2^{+} + 2H^{+}$ **1.3.1.2 (b)**

$7Al^{3+} + 17H_2O \longrightarrow Al_7\,(OH)_{17}^{4+} + 17H^{+}$ **1.3.1.2 (c)**

Then

$Al^{3+} + 3H_2O \longrightarrow Al\,(OH)_3 + 3H^{+}$ **1.3.1.2 (d)**

(Maiti, 2011).

Those aquometallic ions will later become part of the ionic bloc surrounding the colloid, and as they have a great affinity for surfaces, will be adsorbed on the colloid surface and they will neutralise the surface charge. After neutralisation, the ionic bloc will dissipate and the electrostatic potential will disappear so that contact between particles will occur freely.

3. Entrapment in a flocculent mass

According to the Equation 1.3.1.2(d), the last product formed in the hydrolysis of alum hydroxide is Al $(OH)_3$. That compound forms in amorphous, gelatinous flocs that are heavier than water and settle by gravity. The process by which colloids are swept from suspension is known as "*sweep coagulation*" (Maiti, 2011).

4. Adsorption and inter-particle bridging

Large molecules may be formed when aluminium or ferric salts dissociate in water. This step is fully assured by the presence of some specific synthetic polymers which are highly surface reactive, so that colloid particles into water may be attached to the surface of the adsorbent until the group polymer-colloids become enmeshed by settling mass at the bottom. As for this project, the synthetic polymers are replaced by the nanoparticles such as zero valent Iron nanoparticles (ZVINPs) to assist in the coagulation process with natural clay (Schulz, 1984).

The flocculation process is concerned with the removal of suspended colloidal particles from suspending liquid and involves surface chemistry, knowing that solid-liquid interfaces play an important role in stabilising colloidal impurities found in water. And by definition, a colloidal system is a set in which particles are dispersed in a continuous medium, where the particles are called the '*dispersed phase'* and the medium in which they exist is called the '*dispersing* *phase'.* And it is by the affinity of the dispersed phase for the dispersing medium that colloidal systems are classified. There are hydrophobic colloids (strong Tyndall effect) and hydrophilic colloids (weak Tyndall effect). This means that hydrophilic colloids, which are often stable suspensions at higher concentrations, react spontaneously with water and create gels that can easily be re-dispersed any number of times in the system and be rehydrated to the original material. The hydrophobic colloids, on the other hand, form gels only under specific concentrations and are relatively stable at lower concentrations (Maiti, 2011).

Although some of the suspended matter present in wastewater would settle out through sedimentation, much of the material is colloidal and does not settle at all or only at a negligible velocity. To ensure satisfactory removal of turbidity due to colloidal particles and micro-organisms, it is usually necessary to "persuade" these particles to coagulate into larger, heavier and more readily settable solids. By adding a suitable reagent which forms an insoluble precipitate, it is possible to enmesh the colloidal particles in a floc, which if gently stirred, flocculates into larger particles having a reasonable settling velocity which can thus be removed by sedimentation. As an added benefit of coagulation, a certain amount of dissolved colour is also removed due to adsorption of the organic molecules (Schulz, 1984).

The process of coagulation takes place in two stages: namely 1) addition of coagulation solution with hydraulic or mechanical stirring/agitation to provide rapid mixing; followed by 2) flocculation achieved by gentle agitation.

The rapid mixing stage is the most important component of coagulation-flocculation processes, since it is here that destabilisation reactions occur and where primary floc particles are formed. In many instances, traditional 30 to 60 second retention times during rapid mixing are unnecessary and flocculation efficiency may not improve beyond rapid mix times of approximately five seconds or less (Divakaran &Pillai, 2002).

2.1.5 Types of coagulants

Currently several types of coagulants are used to treat wastewater effluents, especially in South Africa, they commonly use aluminium sulphate and ferric salts as coagulants (South Africa, Department of Water Affairs, 2011), but according to wastewater effluents analyses, the treatment efficiency is seriously questionable, specifically in terms of ammonia remaining in the water body (Figure 2.12). That is why this project will try to attempt solving the research problem by using another type of coagulant and investigate on its efficiency in ammonia reduction from the final effluents.

Below is the list of popular coagulants used in wastewater treatment:

2.1.5.1 Aluminium Sulphate

Alum is the most widely used coagulant. Alum has no exact formula due to the varying water molecules of hydration which may be attached to its molecules.

In water, Aluminium Sulphate can react with hydroxides, carbonates, bicarbonates, and other anions. Aluminium Sulphate is most effective in the ranges of 5.5 to 7.8, but seems also to work well in most water supplies at pH of 6.8 to 7.5 (Denysschen,1990).

2.1.5.2 Ferric Chloride

Ferric Chloride, in its most common form as a liquid, is available commercially. It contains free hydrochloric acid.

Ferric Chloride forms a separate and dense floc that promotes faster sedimentation. The dense flocs have more available cationic charge allowing for higher reactivity with colloidal solids. One of the other characteristics of Ferric Chloride is its ability to form floc over a very wide pH range (Denysschen, 1990).

2.1.5.3 Ferric Sulphate

The floc formed with ferric coagulants is heavier. When Ferric Sulphate in the reaction acts as an acid, it reduces the pH and alkalinity in water (Bratby, 2006:80).

Ferric coagulants may be used in colour removal at the high pH values; they are also important in removal of iron and manganese and in softening of water. Because of the consumption of alkalinity, CO_2 is produced during coagulation; the pH value may also be lowered after the coagulation process, depending on the amount of coagulant applied and the total alkalinity in the raw water (Bratby, 2006:80-86).

2.1.5.4 Clay (bentonite)

In general, clays originate from the hydrothermal alteration of alkaline volcanic ash and rocks of the Cretaceous period (85-125 million years ago). The airborne ash carried by winds formed deposits characterised by high volume bedding of ash deposited in seas and alkaline lakes. Different opinions have been expressed regarding the mechanism of the ash-to-clay transformation. Probably the change began in marine water in reactions involving sufficient amounts of Mg^{2+} and Na^{+}. Several geological processes may have led to the formation of clays during millions of years ago (Giese et *al*., 2003).

Natural clay, namely bentonite which is rich in Montmorillonite, will be used as coagulant as it is an inexpensive reagent and easily accessible as well as an excellent adsorbent-weighing agent. Bentonic clays, fuller's earth and other adsorbent clays are used to assist in coagulation of waters containing high colour or low turbidity as they supply additional suspended matter to the water upon which flocs can form. These floc particles are then able to settle rapidly due to the high specific gravity of the clay. Some clays swell when added to water and can produce a floc when used alone or with a limited dosage of alum (Giese et al., 2003).

The clay used in this research, bentonite, works quite well in coagulation because it joins with the small floc or suspended solids in river water, making the floc heavier and thus allowing it to settle more quickly. And because clay minerals are natural and local sources, the process cost of treatment with clay minerals may be significantly lesser than other coagulants like polyelectrolyte (Leszek & Utracki, 2004).

The results were clear when comparing costs: the cost of the annual waste water treatment of $\mathbf{2.16x10^{6}}$ m^3 using the common coagulant clay or polyelectrolyte was calculated. The results indicated that the cost in the treatment with clay was about $50 000 whereas it was about $1,600,000 for the treatment with polyelectrolyte (Demirci et *al*., 1998).

Below is a picture (Figure 2.13) of the type of bentonitic clay that has been used in this project to treat the wastewater effluents.

Figure 2.13: Non-activated bentonitic clay, - **Chem. Eng Lab. CPUT Bellville, 2011**

In this study, bentonitic clay, characterised by its waxy appearance and the quality of slaking in water, will be employed as a coagulant. It has less valuable adsorbent properties but swells to a heavy gel and in more dilute suspensions, a form that may remain in suspension for an indefinite period (Ayguna & Yilmazb, 2010).

Bentonite is used advantageously as a coagulant in water having relatively high turbidity content. It is especially effective as a coagulant in the presence of magnesium sulphate. In this study, the clay will be activated by sulphuric acid. Each type of clay performs a definite function according to the quality of material used and character of the water treated.

The ability of clays, especially bentonite, to swell in water is due to the expanding of its lattice-like structures by capillary pressure, pushing apart the stable film around each particle (Hascakir & Dolgen, 2008).

Clay minerals are natural substances used in water treatment and have high ion exchange capacity, absorption, and catalysis properties as well as natural and low-cost materials. Clay minerals can be preferable coagulants for removal of toxic compounds (Ayguna & Yilmazb, 2010).

Since the first reported infrared study of clay-water interactions by Buswell et *al*. (1937), water has been used to probe the clay-water interface. The chemical and physical properties of clay minerals are integrally linked to some aspect of how water interacts with the clay surface. Examples include essentially all of the adsorptive, catalytic and cationic exchange reactions. In fact, many of the interesting features of clay–water interactions are observable at the macroscopic level, including such properties as shrink–swell phenomena, water sorption, plasticity and catalysis. Smectites, for example, as in our project, have exceptional water sorption characteristics. Mooney et al. (1952a, 1952b) were among the first researchers to show that smectites were able to absorb up to half their mass in water and that the water sorption behaviour is strongly dependent on the nature of the exchangeable cation.

Characterisation of clay

Some experimental methods are used to characterise minerals:

The TEM (Transmission Electron Microscopy) (see Figure 2.14) are actually microscopy techniques whereby a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen, it's magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera, basically it provides information on the morphology and mineral structure, the SEM (Scanning Electron Microscopy) which is almost the same;

The Brunner-Emmet-Teller analysis (BET) and Fourier transform infrared (FTIR) spectroscopy that provides sufficient details about the clay surface area, about how its adsorptive properties can be justified, about the clay-water interaction, about the exchangeable cation itself (see Figure 2.15,), and

The X-ray diffraction (XRD) that provides details that will help to understand the structures of minerals (and other crystalline matter) on an atomic scale. It thus established relationships between the crystal structure and the physical and chemical properties of the material under investigation (Bentonitic Clay). In other cases, it related the crystal structure to the special thermodynamic conditions under which a mineral (or a rock) has been formed and thus provided important information for petrology and geology, also the quantification of the different phases of a mixture, a rock for instance (Bish & Post, 1989).

Because of their unique expansive nature, smectites are the most important clay minerals related to clay-water interactions. For these clay minerals, the initial sorption of water and related polar solvents, such as methanol, is influenced mainly by the hydration of exchangeable cations. These cations have substantial single-ion enthalpies and serve as strong hydrophilic sites for water and solvent sorption (Bergaya et *al*., 1980a, 1980b; Cancela *et al.,* 1997). Numerous spectroscopic studies have shown that the properties of sorbed water are different from those of bulk water, especially when less than three layers of water are present in the interlayer region. Water sorption on clay surfaces often shows significant hysteresis because of differences in water adsorption and desorption mechanisms (Mooney et *al.,* 1952a).

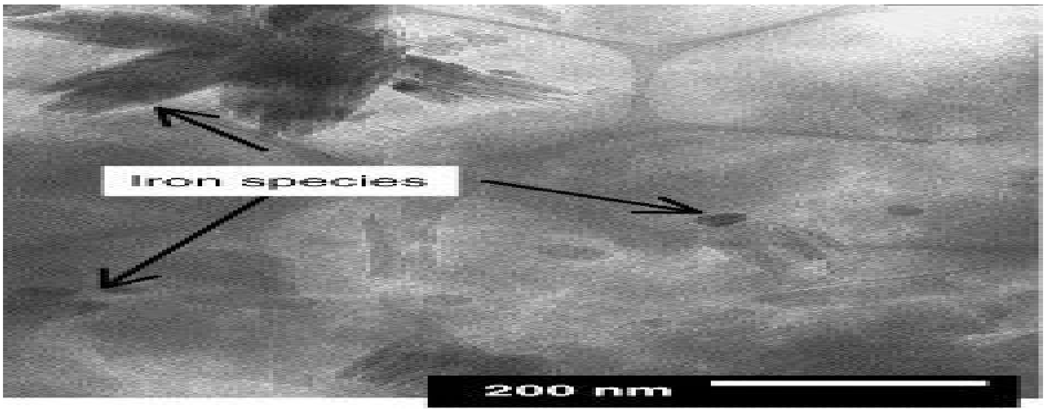


Figure 2.14 Transmission electron microscopy of natural bentonite (geoscienceworld, n.d.)

On the figure above it can be observed the clay structure is compact containing some iron species distributed in a way that they are almost in tendency to agglomerate or aggregate, reasons why the coagulant need to be activated so that the pores will be more open, and in so doing, relative increase in surface area and better adsorptive properties will be achieved.

2.1.5.5 Zero valent iron nanoparticles (ZVINPs)

The understanding of nanostructures has attracted attention of countless research groups, academic institutions and commercial entities. Since the nineties (science.pub, 10 July 2011), Nano-science has been recognised as a distinct field of study with tremendous potential: nanotechnology research has proliferated, scientific journals dedicated to nano-science have been published, nanotechnology research centres have been established, and universities have opened faculty positions related to nano-research. Nano-materials have large specific surface areas and a large fraction of atoms are available for chemical reaction.

Past research has shown that nanoscale metallic iron is very effective in destroying a wide range of contaminates such as chlorinated methanes, brominated methanes and chlorinated ethenes (Nowack, 2008). The basis for the reaction is the corrosion of zerovalent iron in the environment:

$$2Fe^0 + 4H^+ + O_2 \rightarrow 2Fe^{2+} + 2H_2O$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$

Organic compounds can easily accept the electrons from iron oxidation and be reduced to ethene as follows:

$$C_2Cl_4 + 4Fe^0 + 4H^+ \rightarrow C_2H_4 + 4Fe^{2+} + 4Cl^-$$

(Nowack, 2008).

Over the span of little more than a decade, the multi-disciplinary nanotechnology boom has inspired the creation and development of powerful new tools in the ongoing challenge of addressing the industrialised world's legacy of contaminated sites (Masciangioli & Zhang, 2003).

These include improved analytical and remote-sensing methodologies, novel sorbents and pollution-control devices, as well as superior soil-and groundwater-remediation technologies. The nano-scale zerovalent iron (nZVI) technology, being an early stage achievement of the burgeoning environmental nanotechnology movement, has been used in numerous environmental studies in order to restore the ecosystem by removing pollutants that can be eliminated by adsorption due to the very small specific area that reaches the size of 10^{-9}m (Glazier et *al.*, 2003:64-69).

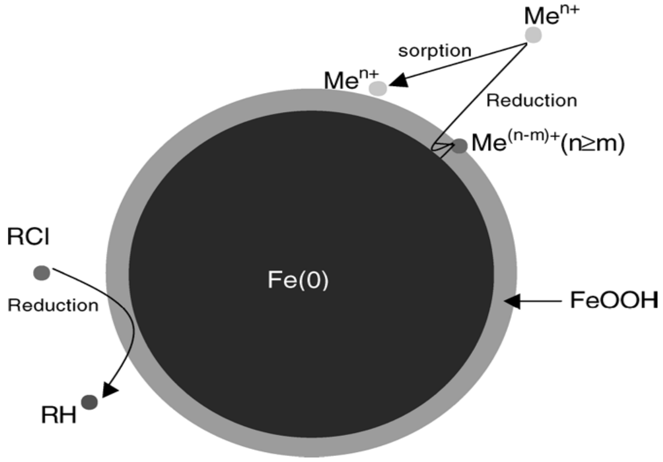


Figure 2.15: The Core-Shell Model of zero valent iron nanoparticles *(*Glazier et *al., 2003)*

The core consists of mainly zerovalent iron and provides the reducing power for reactions with environmental contaminants. The shell is largely iron oxides/hydroxides formed from the oxidation of zerovalent iron. The shell provides sites for chemical complex formation, chemisorption (Li et *al*., 2006).

Synthesised zero-valent iron is unstable in atmospheric conditions and it tends to form oxides/hydroxides in the forms of Fe_2O_3, Fe_3O_4 and FeOOH (Noubactep et *al*., 2005). Nano-scale zerovalent iron is synthesised in open air in the presence of ethanol to prevent massive oxidation. Whatever precautions are taken to avoid oxidation, it is observed that ZVINPs consists of a zerovalent core and an oxide shell (core-shell structure).The thickness of the oxide shell is of about 5 nm and is made only of FeOOH, according to Li and Zhang (2007). In the same way of thinking, Wang declared that the surface of ZVINPs is mostly an iron–boron non-crystalline alloy (2006_a). Some authors suggest that Magnetite/Hematite (Fe_3O_4/γ-Fe_2O_3) is also present in the structure (Zhang et *al*., 2006). Figure 2.15 shows the core-shell structure of ZVINPs suggested by Li and Zhang in 2007.

The application of zerovalent iron for wastewater treatment has been studied increasingly, yet the true mechanism of degradation of contaminants in the presence of iron is not yet completely understood (Junyapoon, 2005:42-49). There are many studies showing that the degradation mechanism is comprised of heterogeneous reactions. The reactions take place when the reactant's molecules arrive at the iron solid outside area. The reactant's molecules unite with the iron surface at site that may be either reactive or non-reactive. The reactive surfaces are those where the breaking of bonds in the reactant solute molecule occur (chemical reaction) while non-reactive surfaces are those where only sorption exchanges occur and the solute molecules stay unchanged (Junyapoon, 2005:49).

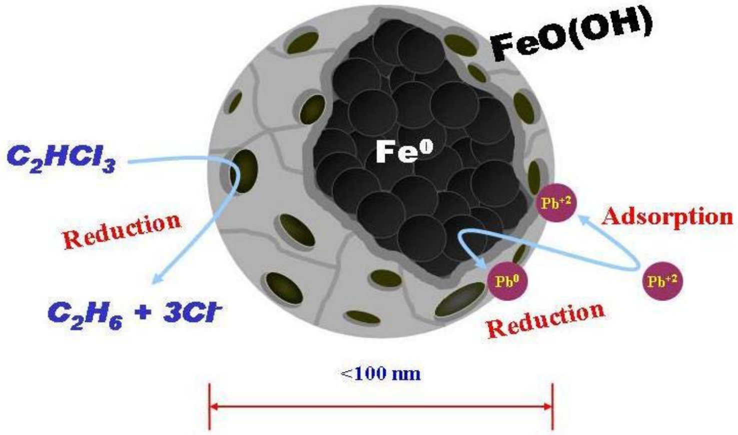


Figure 2.16: A more three-dimensional view of a zero valent iron nanoparticles (Junyapoon, 2005).

This figure also shows the porosity of the nanoparticles, an important factor in physicochemical reactivity. Zerovalent nano iron can also be coupled with trace metals (Pt, Pd, Ag) showing significantly enhanced reaction. Nano iron is potentially benign to the environment and, ultimately, is primarily transformed into Fe_3O_4 and Fe_2O_3, which are abundant in the earth (Junyapoon, 2005:51-59).

Kinetically, zerovalent iron has the ability to remove heavy metals from wastewater, metals such as chromium and arsenic. The degradation mechanisms of heavy metals are done on conversion from toxics to non-toxics or adsorption on the iron surface depending on the kind of heavy metals:

$$Cr^{6+} + Fe^{0} \rightarrow Cr^{3+} + Fe^{3+}$$

Additionally, zerovalent iron is also used to dehalogenate a broad variety of halogenated organic compounds. Zerovalent iron behaves as a reducing agent; during reactions the iron is oxidised (electron donor) while alkyl halide (*RX*) are reduced (electron acceptor) (Junyapoon, 2005).

$$Fe^{0} \rightarrow Fe^{2+} + 2e^{-}$$

$$RX + 2e^{-} + H^{+} \rightarrow RH + X^{-}$$

$$Fe^{0} + RX + H^{+} \rightarrow Fe^{2+} + RH + X^{-}$$

Zerovalent reacts with water to produce hydrogen gas and hydroxide ions which increase the pH of water (Junyapoon, 2005:62).

$$Fe^{0} + 2H_2O \rightarrow Fe^{2+} + 2OH^{-} + H_2$$

$$RCl + H_2 \rightarrow RH + HCl$$

$$NH_3 + H_2O \rightarrow NH_4^{+} + OH^{-}$$

Table 2.5: List of contaminants treated by ZVINPs (Li et *al*., 2006)

Chlorinated Methanes	Trihalomethanes
Carbon tetrachloride (CCl_4)	Bromoform ($CHBr_3$)
Chloroform ($CHCl_3$)	Dibromochloromethane ($CHBr_2Cl$)
Dichloromethane (CH_2Cl_2)	Dichlorobromomethane ($CHBrCl_2$)
Chloromethane (CH_3Cl)	

Chlorinated Benzenes	**Chlorinated Ethenes**
Hexachlorobenzene (C_6Cl_6)	Tetrachloroethene (C_2Cl_4)
Pentachlorobenzene (C_6HCl_5)	Trichloroethene (C_2HCl_3)
Tetrachlorobenzenes ($C_6H_2Cl_4$)	*cis*-Dichloroethene ($C_2H_2Cl_2$)
Trichlorobenzenes ($C_6H_3Cl_3$)	*trans*-Dichloroethene ($C_2H_2Cl_2$)
Dichlorobenzenes ($C_6H_4Cl_2$)	1,1-Dichloroethene ($C_2H_2Cl_2$)
Chlorobenzene (C_6H_5Cl)	Vinyl Chloride (C_2H_3Cl)
Pesticides	**Other Polychlorinated Hydrocarbons**
DDT ($C_{14}H_9Cl_5$)	PCBs
Lindane ($C_6H_6Cl_6$)	Pentachlorophenol
1,1,1-trichloroethane	
Organic Dyes	**Other Organic Contaminants**
Orange II ($C_{16}H_{11}N_2NaO_4S$)	N-nitrosodiumethylamine (NDMA)($C_4H_{10}N_2O$)
Chrysoidin ($C1_2H_{13}ClN_4$)	NT ($C_7H_5N_3O_6$)
Tropaeolin O ($C_{12}H_9N_2NaO_5S$)	
Heavy Metals	**Inorganic Anions**
Mercury (Hg^{2+})	Perchlorate (ClO_4^-)
Nickel (Ni^{2+})	Nitrate (NO_3^-)
Cadmium (Cd^{2+})	
Lead (Pb^{2+})	
Chromium (Cr (VI))	

2.1.6 The effect of pH, concentration, modified coagulant dosage and agitation speed on the removal of pollutants from treated wastewater effluents

It has been reported that solution pH affects the kinetics of both nitrate and nitrite reduction by Fe^0. Slower rates of nitrate and nitrite reduction have generally been observed at higher pH values, around 6.5 to 9.0 (Alowitz & Scherer, 2002; Miehr et *al*., 2003; Westerhoff, 2003). The rate of reduction of nitrite is faster than that of nitrate at pH values less than 8.0, above pH 8.0, identical rates of nitrate and nitrite reduction are obtained; this suggests why differences in pH values emerge with nitrites as an intermediates product. In addition, mass transport controls the kinetics of nitrate and nitrite reduction, while adequate mixing increases the mass transfer of nitrites and nitrites on ZVINPs surface (Rahman *et al*., 1997; Alowitz & Scherer, 2002).

Indeed, adding autotrophic (hydrogenotrophic: denitrifying bacteria) increases nitrate removal rates in Fe^0 and proposes another pathway that extends the end product favouring N_2 over NH_4^+ (Till et *al*., 1998).
Researchers suggest that the mechanisms of nitrate reduction by Fe^0 is favoured at low pH (e.g. 2-4.5), following first-order kinetics with respect to hydrogen ion concentration (Zawaideh & Zhang, 1998; Alowitz &Scherer, 2002; Huang et *al*., 2003).

Higher temperature increases the nitrate and nitrite reduction; the rates of reaction are first order. At the higher temperatures, the solution pH increases above 8.5 and slows down the rate of nitrate/nitrite removal, the considerably slower rates observed at high pH values are trustworthy, with previous work evaluating the effect of pH on nitrate reduction by metal Fe^0 (Alowitz & Scherer, 2002). Most studies reported ammonium as the major product from nitrate/nitrite reduction by Fe^0 (Rahman et *al*., 1997; Kielemoes et *al*., 2000).

A recent study shows that the availability of iron surface is the most important experimental variable that affects the nitrate reduction efficiency. Increasing the amounts of iron elements in the mixture speeds up the first reaction rate; as the content of iron particles is increased, more dynamic sites are available for collision of nitrates ions to reduction. The reaction rate increases in the solution; thus, a high ratio Fe^0 to NO_3^- can cause a high denitrification rate (Kielemoes et *al*., 2000).

2.1.6.1 Evaluation of a modified chitosan biopolymer for coagulation of colloidal particles

In the treatment of water, the removal of colloidal particles was studied by using aluminium sulphate or poly-aluminium chloride (PAC) as coagulants/flocculants (Divakaran & Pillai, 2002).

These two coagulants are primarily used as they are inexpensive and an over dosage of aluminium can be used to ensure coagulation efficiency. However, it has been reported that large amount of aluminium in human body, may lead to the Alzheimer disease (Machlan, 1995:233-275). This article was based on the use of modified chitosan biopolymer as coagulant which was used as a replacement to the aluminium sulphate/PAC for the removal of colloidal particles. To increase the dosage of coagulant for maximum efficiency, chitosan was mixed with the aluminium sulphate and the PAC in two different experiments (Pan et *al*., 1999).

To lower experimental costs, H_2SO_4 can be added to the Montmorillonite KSF, a type of clay with excellent adsorption characteristics, to enhance the adsorptive properties of clay.

This type of clay was selected as Montmorillonite clays have been used as catalysts for a number of organic reactions and offer many advantages over classical acids: strong acidity, non-corrosive properties, cheapness, mild reaction conditions, high yields and selectivity and the ease of setting and working-up (Habibi & Marvi, 2006).

2.1.6.2 Investigations of coagulation–flocculation process by performance optimisation, model prediction and fractal structure of flocs

The treatment of sewage water was investigated by using a modified coagulant of polymeric phosphate-aluminium chloride (PPAC). The operating variables were also investigated to determine the effect of certain parameters on the optimum removal efficiency. The parameters investigated were the P/Al mole ratio, wastewater initial pH, coagulant dosage and agitation speed, which could influence the coagulation behaviour of PPAC. The evaluation of treatment efficiency was determined by measuring both the reduction of chemical oxygen demand (COD) and remaining turbidity. It showed that the optimum removal efficiency was achieved when the P/Al molar ratio was at 1:2, wastewater initial pH was measured to be 9, the coagulant dosage was 0.36g/l and agitation speed was 100rpm. Under optimum conditions, the removal efficiency was 73.5% for COD and 99.5% for turbidity (Zheng et *al*., 2011).

The investigated parameters can be applied when conducting the treatment process. The optimum conditions for the maximum removal of POPs can be found by varying the coagulant dosage, the clay-H_2SO_4 ratio, agitation speed as well as the pH of the solution. The results from each experiment can then be compared for the maximum efficiency of the H_2SO_4-clay coagulant (Zheng et *al*., 2011).

2.1.6.3 Importance of the interlayer exchangeable and effect of the acid treatment on the clay structure

The cation exchange capacity and the exchangeable cation are the most significant properties of clay minerals, because they consist of great influence on the industrial uses of smectites clay minerals; furthermore, they are basic control factors of the physical and chemical properties of the smectites clay mineral.

Smectites clay minerals are acidic solids. Bronsted and Lewis acid sites on their surfaces are proton donors and electron pair acceptors, respectively; the quantity of acid sites as moles in one gram solid is defined as specific surface acidity (n_m/gmol), the acid strength of a solid surface as its proton donating and electron pair accepting aptitudes; the acid strength of a surface can be typified by the equilibrium constant of its neutralisation reaction with a weak base through methods such as the following (Önal et *al*., 2006):

a) Amine titration in the presence of Hammett methods; and

b) Adsorption of polar molecules used to determine the surface acidity of clay minerals.

Clay minerals have been among the main industrial raw materials with some uses in paint, paper, decolourisation, plastics, liquid barriers, chemical carriers, drilling fluids, sealants, cosmetics and catalysts, the purification and physicochemical modifications of pure smectites have great importance in preparing some high technology materials such as pillared clays, organ clays and polymer/smectites nanocomposite. Clay minerals are considerably modified from acid activation, ion exchange, heating and hydrothermal treatments (Önal et *al*., 2006).

The following parameters affect the activation process: (a) acid concentration; (b) particle size distribution; (c) activation temperature; (d) activation time; (e) chemical mineralogical properties of clay; and (f) type of acid used (Amin & Leila, 2009).

The activation of clay is the chemical or physical treatment in order to develop the adsorption capacity. During the activation reaction, the surface area of bentonite increases due to decomposition of smectites structure. The most significant mechanism in activation of clay minerals is cation exchange by H^+ ions. During activation process, the exchangeable cations (Na^+,K^+,Ca^{2+},Mg^{2+}, Al^{3+}, Fe^{3+}) between crystal layers leave and are substituted by H^+ ions (Amin & Leila, 2009). Furthermore, the acid treatment dissolves impurities such as calcite and replaces the exchangeable cations with hydrogen ions. The acid treatment also opens the border of platelets and as a result the surface area and pore diameters increase

(Francisco et *al*., 2001). Moreover, Dombrowsky and Henderson, from Engelhard, affirm the following changes after the acid activation:

a) The edges of the crystal are released and the Al^{3+} and Mg^{2+} cations of the octahedral sheet (from the 2:1 layers) are exposed to the acid and become soluble;

b) The surface pore diameter enlarges;

c) The level of crystallinity of the clay mineral is decreased; and

d) The specific surface area of the smectites increases to a maximum then is decreased by further treatment.

The study performed by Amin and Leila (2009) shows that during activation process microspores are altered into mesopores; the experiment illustrates how the increase in acid concentration increases the surface area up to a maximum value, then decreases again to attain a constant value. As the sulphuric acid concentration increases from 0 to 3M, the exchangeable cations leave and are substituted by H^+ ions; as the acid concentration rises from 3 to 5M, the , Mg^{2+}, Al^{3+}, Fe^{3+} cations melt from the montmorillonite layers. The structure of the clay mineral is attacked by the acid, so the increase in specific surface area is great. As the concentration of acid increases more than 5M, the specific surface area falls to a constant value indicating the destruction of smectites structure.

This study also shows that the specific surface area increases with the activation temperature attaining 90^0C and then decreases significantly to a constant value, while the activation temperature around $100\text{-}120^0$C has no effect on the clay surface area. This proves that the crystal structure of the clay mineral decomposes after an optimum activation temperature and time. After reaching the maximum temperature, the crystal structure is presumed to be decomposed. Furthermore the absorption capacity increases as a function of clay particle specific surface area and charge. The main factor leading to considerable increase in specific surface area when the particle size decreases, is that the contact region of acid and clay rises (Amin &Leila, 2009:912-984).

Seems the coagulation itself it’s done by adsorption, adsorption model (Langmuir Isotherm) were established in order to determine the efficiency of the coagulant in terms of ammonia and other organic pollutants removal.

2.1.7 Water quality characteristics of wastewater

2.1.7.1 Physical characteristics

The physical characteristics of wastewater include the following:

a. **Solids:**

All contaminants of water, other than gases, contribute to the solids content. Natural water carries many dissolved and undissolved solids. The undissolved solids are non-polar substances and consist of large particles such as silt that will not dissolve. Classified by their size and state, chemical characteristics, and size distribution, solids can be dispersed in water in both suspended and dissolved forms (Nollet, 2007).

In water treatment, the most effective means of removing solids from water is by filtration. It should be pointed out, however, that not all solids, such as colloids and other dissolved solids, can be removed by filtration. In wastewater treatment, suspended solids is an important water-quality parameter and is used to measure the quality of the wastewater influent, monitor performance of several processes, and measure the quality of effluent. The size of solids in water can be classified as suspended solids, settle-able, colloidal, or dissolved. Total solids are those suspended and dissolved solids that remain at the bottom when the water is removed by evaporation. Solids particles are also characterised as being volatile or non-volatile (Gray, 2005).

Nowadays most wastewater treatment plants are using special types of membranes (DWA, 2010), because of their effectiveness but due to their very high cost on the market and maintenance in case of fouling (Li et *al*., 2006), in this project only filter paper and sand filtration system were used to evaluate the efficiency of the coagulant in terms of ammonia removal.

b. **Turbidity:**

The turbidity refers to how clear the water is. Water’s clarity is one of the first characteristics people notices, as it is a measure of the extent to which light is either absorbed or scattered by suspended material in water. As absorption and scattering are influenced by both size and surface characteristics of the suspended particles, turbidity is not a direct quantitative measurement of suspended solids (Tebutt, 1973).

Turbidity is measured photometrically by determining the percentage of light of a given intensity that is either absorbed or scattered. Turbidity-meter readings are expressed as FTUs (formazin turbidity units) where formazin is a chemical compound that provides more reproducible standards SiO_2 (that was used for the JTU or Jackson turbidity unit, old apparatus) and has replaced it as a reference, meaning 1mg of formazin dissolved in 1L of distilled water. The term “nephelometry turbidity unit” (NTU) is often used to indicate that the test was run according to the scattering principle (Ayguna & Yilmazb, 2010).

Turbidity in water is caused by the presence of suspended matter, resulting in the scattering and absorption of light rays. The greater the amount of total suspended solids in the water, the murkier it appears and the higher the measured turbidity. Thus, in plain English, turbidity is a measure of the light-transmitting properties of water. Natural water that is very clear (low turbidity) allows you to see images at considerable depths, while high turbidity water appears cloudy. Keep in mind that water of low turbidity is not necessarily without dissolved solids. Dissolved solids do not cause light to be scattered or absorbed, making the water look clear. High turbidity causes problems for the waterworks operator (Wiley, 2005).

c. Colour:

After contact with organic debris such as leaves, conifer needles, weeds, or wood, water picks up tannins, humic acids, and humates and takes on yellowish-brown hues. Iron oxides cause reddish water, and manganese oxides cause brown or blackish water. Industrial wastes from textile and dyeing operations, pulp and paper production, food processing, chemical production, and mining, refining, and slaughterhouse operations may cause substantial coloration to water in receiving streams (Standard Methods for the Examination of Water and Wastewater, 1999).

d. Temperature:

Generally, water temperature does not completely show how efficiently several water treatment processes operate, but the temperature does have an effect on the rate at which chemicals dissolve and react. When water is cold, more chemicals are required for efficient coagulation and flocculation to occur. In wastewater treatment, the temperature of wastewater varies greatly, depending upon the type of operations being conducted at a particular installation. Temperature also has a pronounced effect on the solubility of gases in water. Wastewater is, in most situations, warmer than that of the water supply because of the addition of warm water from industrial activities and households (Spellman, 1998).

e. Electrical conductivity:

Electrical conductivity is defined as the ability of a substance, water in this case, to allow electricity to go through it, and also gives an indication of the concentration of ions or total dissolved solids in the water. It is measured by milli Siemen per metre (mS/m).Water containing high concentrations of inorganic acids, base and salts gives a higher conductivity (Denysschen, 1990).

In this study, conductivity will be used to measure the amount of dissolved suspended solids of wastewater effluents to verify whether or not the activated clay is effective enough to remove suspended solids through the coagulation process.

The value of electrical conductivity can also assist in providing a rough idea of one of the chemical parameters, the total dissolved solids (TDS), by the ability of water to conduct electricity, known as ‘specific conductance’, which is a function of its ionic strength. Unfortunately, the concentrations of TDS and the specific conductance are not directly related on a one-to-one basis; only ionised substances contribute to specific conductance. For instance organic substances and compounds that dissolve without ionising are not measured (Standard Methods for the Examination of Water and Wastewater, 1999).

2.1.7.2 Chemical characteristics

a. The pH:

pH is a measure of the hydrogen ion (H^+) concentration. Solutions range from very acidic (having a high concentration of H^+ ions) to very basic (having a high concentration of OH^- ions). The pH scale ranges from 0 to 14, with 7 being the neutral value (see Figure 2.17). The pH of water is important to the chemical reactions that take place within water, and pH values that are too high or too low can inhibit the growth of microorganisms.

With high and low pH values, high pH values are considered basic and low pH values are considered acidic. Stated another way, low pH values indicate a high level of H^+ concentration, while high pH values indicate a low H^+ concentration (Denysschen,1990).

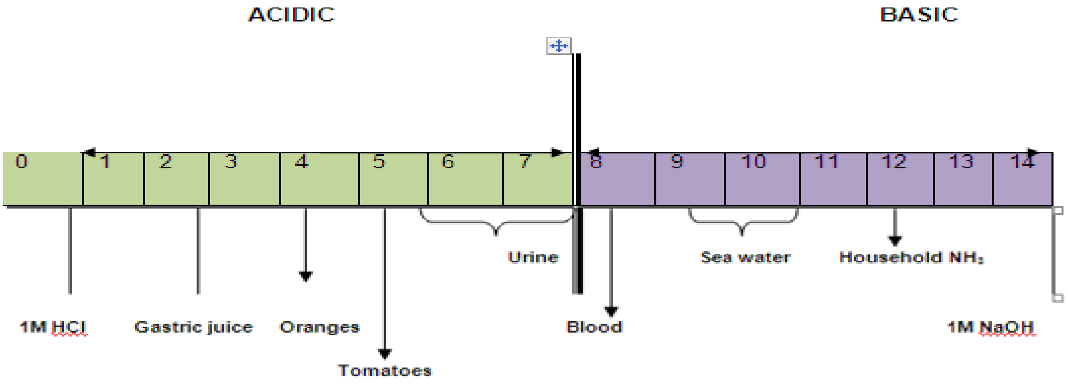


Figure 2.17: pH of selected liquids (Denysschen, 1990).

b. Organic substances:

Proteins are nitrogenous organic substances of high molecular weight found in the animal kingdom and to a lesser extent in the plant kingdom. The amount present varies from a small percentage found in tomatoes and other watery fruits and in the fatty tissues of meat, to a high percentage in lean meats and beans (Katsoyiannis & Samara, 2004).

Proteins and urea are the chief sources of nitrogen in wastewater. When proteins are present in large quantities, microorganisms decompose and produce end products that have objectionable foul odours. During this decomposition process, proteins are hydrolysed to amino acids and then further degraded to ammonia, hydrogen sulphide, and simple organic compounds.

Carbohydrates which are widely distributed in nature and found in wastewater are organic substances that include starch, cellulose, sugars, and wood fibres; they contain carbon, hydrogen, and oxygen. Sugars are soluble while starches are insoluble in water (Chaîneau et *al*., 1995).

The primary function of carbohydrates in higher animals is to serve as a source of energy. In lower organisms (e.g., bacteria), carbohydrates are utilised to synthesize fats and proteins as well as energy. In the absence of oxygen, the end products of decomposition of carbohydrates are organic acids, alcohols, and gases such as carbon dioxide and hydrogen sulphide (Katsoyiannis & Samara, 2004).

Detergents (surfactants) are large organic molecules that are slightly soluble in water and cause foaming in wastewater treatment plants and in the surface waters into which the effluent is discharged. Probably the most serious effect detergents can have on wastewater treatment processes is in their tendency to reduce the oxygen uptake in biological processes. According to Rowe and Abdel-Magid (1995), detergents affect wastewater treatment processes in the following ways:

- lowering the surface, or interfacial, tension of water and increase its ability to wet surfaces with which they come in contact;
- emulsifying grease and oil, deflocculate colloids;
- inducing flotation of solids and give rise to foams; and
- Killing useful bacteria and other living organisms.

c. Inorganic substances:

It has been observed that inorganic compounds are common to both wastewater and natural waters and are important in establishing and controlling water quality. Inorganic load in water is the result of discharges of treated and untreated wastewater, various geologic formations, and inorganic substances left in the water after evaporation. Natural waters dissolve rocks and minerals with which they come in contact. As mentioned, many of the inorganic constituents found in natural waters are also found in wastewater. Many of these constituents are added via human use. These inorganic constituents include chlorides, alkalinity, nitrogen, phosphorus, sulphur, toxic inorganic compounds, and heavy metals (Maiti, 2011).

Table 2.6: Basic requirement of wastewater to be discharged into the environment (South Africa, Department of Water Affairs, 2011)

Constituents	General limit
Chemical Oxygen Demand (COD)	75 mg/L
Ammonia nitrogen (NH_3-N)	6 mg/L
Nitrate nitrogen (NO_3-N)	15 mg/L
Orthophosphates (PO_4-P)	10 mg/L
pH	5.5 - 9.5

Suspended solids (SS)	25 mg/L
Electrical conductivity	150 mS/m

CHAPTER THREE

PROCESS METHODOLOGY

There are two approaches used in this project for the removal of persistent organic pollutants from wastewater effluent:

1. Pre-treatment Process (PP)
2. Nano Pre-treatment Process (NPP)

3.1 Pre-treatment process (PP)

Step 1: Pre-treatment of water with clay-catalysts (coagulants)

Step 2: Filtration of pre-treated water through a passive membrane (0.22µm filter paper)

3.1.1 Apparatus description

For over 50 years, the jar test has been the standard technique used to optimise the addition of coagulants and flocculants used in the wastewater and drinking water treatment industry.

The Standard Practice for Coagulation–Flocculation Jar Test of Water, was first approved in 1980 and reapproved in 1999 (American Society of Testing Materials, 1995:D 2035-80). The scope of this practice ‘‘covers a general procedure for the evaluation of a treatment to reduce dissolved, suspended, colloidal, and non settleable matter from water by chemical coagulation/flocculation, followed by gravity settling’’ (ASTM,1995:D 2035-80).

This standard was utilised to provide a technique to systematically evaluate the variables normally encountered in the coagulation-flocculation process:

- First, the coagulant is added to the effluent water and a rapid and high intensity mixing is initiated. The objective is to obtain a complete mixing of the coagulant with the wastewater to maximise the effectiveness of destabilisation of colloidal particles and initiate coagulation. Critical parameters for this step are the duration and the paddle speed or mixing intensity (velocity gradient, G).

- Second, the suspension is slowly stirred to increase contact between coagulating particles and to facilitate the development of large flocs. Again, the flocculation duration and intensity are critical parameters (e.g., too high an intensity can break up the aggregate floc).
- Third, mixing is terminated and the floc is allowed to settle. The velocity gradient is a measure of the mixing energy and allows an engineer to scale the test results to proportionally larger system sizes (Metcalf & Eddy, 1991).

Figure 3.1: Phipps and Bird six-paddle stirrer with illuminated base

A standard jar test apparatus, the Phipps and Bird six-paddle stirrer with illuminated base (see Figure 3.1) was employed for the tests, with six 2L square (Basis of 15cm side) B-Ker Plexiglas jars, sometimes called ‘gator jars’. The jars are provided with a sampling port, 15 cm below the water line, allowing for repetitive sampling with minimal impact on the test.

This type of jar has several advantages over the more traditional 1L circular jars, including a larger volume for reduced errors in mixing and a larger volume of supernatant for analysis. In addition, the square walls reduce water rotation, making baffles or stators unnecessary. Finally, the thick Plexiglas walls offer sufficient thermal insulation to minimise temperature changes during the testing (Lee & Lin, 2000).

3.1.2 Activation of clay

The bentonitic clay was first ground to a size of 1-2 µm, to considerably increase the surface area for the activation process and for the subsequent coagulation to be very efficient due to an increase in adsorptive properties of the coagulant. Concentrations of H_2SO_4 selected were in a range of 0.1M to 18.4M. The mixture, in the form of suspension, has been activated by sulphuric acid and by keeping the mixture in a tumbling water bath at 97ºC during 6 hours (Sankaya et *al*., 1982). Every activated sample has been filtered under vacuum and the filtrate has been washed with distilled water until it did not contain any SO_4^{2-} ion. The samples dried over the course of 24 hours at 105ºC in an oven (Sankaya et *al*., 1989). They were labelled, keeping the same amount of bentonite but varying the concentration of sulphuric acid to discover how the concentration of sulphuric acid plays a certain role in the increase of adsorptive properties in order to remove ammonia and related organic pollutants.

Samples were labelled and stored in appropriate containers to prevent the reaction between the moisture in the air and the clay.

3.1.3 Coagulant testing conditions

The coagulant was loaded in different dosages and mixed with water at an operating pressure of 1 atm under the following conditions:

- rapid or flash mixing: the suitable chemicals (coagulants, flocculants, and, if required, pH adjusters) are added to the wastewater in the jars, which is stirred and intensively mixed at high speed, 150 rpm for 1 min;
- slow mixing (coagulation and flocculation): the wastewater is only moderately stirred in order to form large flocs, which are easily settled out at a speed of 20 rpm for 20 min; and
- Sedimentation: the floc formed during flocculation is allowed to settle out and is separated from the effluent stream after 30 min; the solution was then filtrated through a 0.22 µm filter paper using a Buchner funnel with a vacuum system.

3.1.4 Nano Pre-treatment Process (NPP)

Preparation of the zero valent iron nanoparticles (ZVINPs) was done as follows:

a. **Type I synthesis of ZVINPs by the chloride method:**

The chloride method synthesis represents the original means of producing nano-scale ZVINPs at Lehigh University (Zhang *et al*., 1998). Consequently “the chloride-method”, also referred to as Type I ZVINPs, was the earliest generation of nano-scale iron used in experimental and in field scale work.

In this synthesis, 0.25molar (M) sodium borohydride was slowly added to 0.045M ferric chloride hexahydrate in aqueous solution under vigorously mixed conditions such that the volumes of both the borohydride and ferric salt solutions were approximately equal (i.e. a 1:1 volumetric ratio). The mixing time was approximately one hour. This reaction is shown below:

$$4Fe^{3+}_{(aq)}+3BH_4^-{}_{(aq)+}9H_2O_{(l)} \rightarrow 4Fe^0_{(s)}+3H_2BO_3^-{}_{(aq)}+12H^+_{(aq)}+6H_{2(g)}$$

(Zhang et *al*., 1998)

b. **Type II synthesis of ZVINPs by the sulphate method:**

The development of the sulphate method for producing ZVINPs arose from two fundamental concerns associated with the chloride method:

1) Potential health-and-safety concerns associated with handling the highly acidic and very hygroscopic ferric chloride salt; and

2) Potential deleterious effects of excessive chloride levels from the ZVINPs matrix in batch degradation tests where chlorinated hydrocarbons are the contaminant of concern. In addition, the reduction of the iron feedstock from Fe(II) requires less borohydride than the chloride method; Fe(III) is the starting material which may favourably enhance overall process economics. Because this method represented the second generation of iron nanoparticles developed at Lehigh University, the iron is referred to as Type II ZVINPs Sulphate-method. ZVINPs were prepared by metering equal volumes of 0.50M sodium borohydride at 0.15 L/min into 0.28M ferrous sulphate according to the following stoichiometry:

$$2Fe^{2+}{}_{(aq)} + BH_4^-{}_{(aq)} + 3H_2O_{(l)} \rightarrow 2Fe^0{}_{(s)} + H_2BO_3^-{}_{(aq)} + 4H^+{}_{(aq)} + 2H_{2\,(g)}$$

(Zhang et *al*., 1998)

3.1.5 Research equipment and their utilities

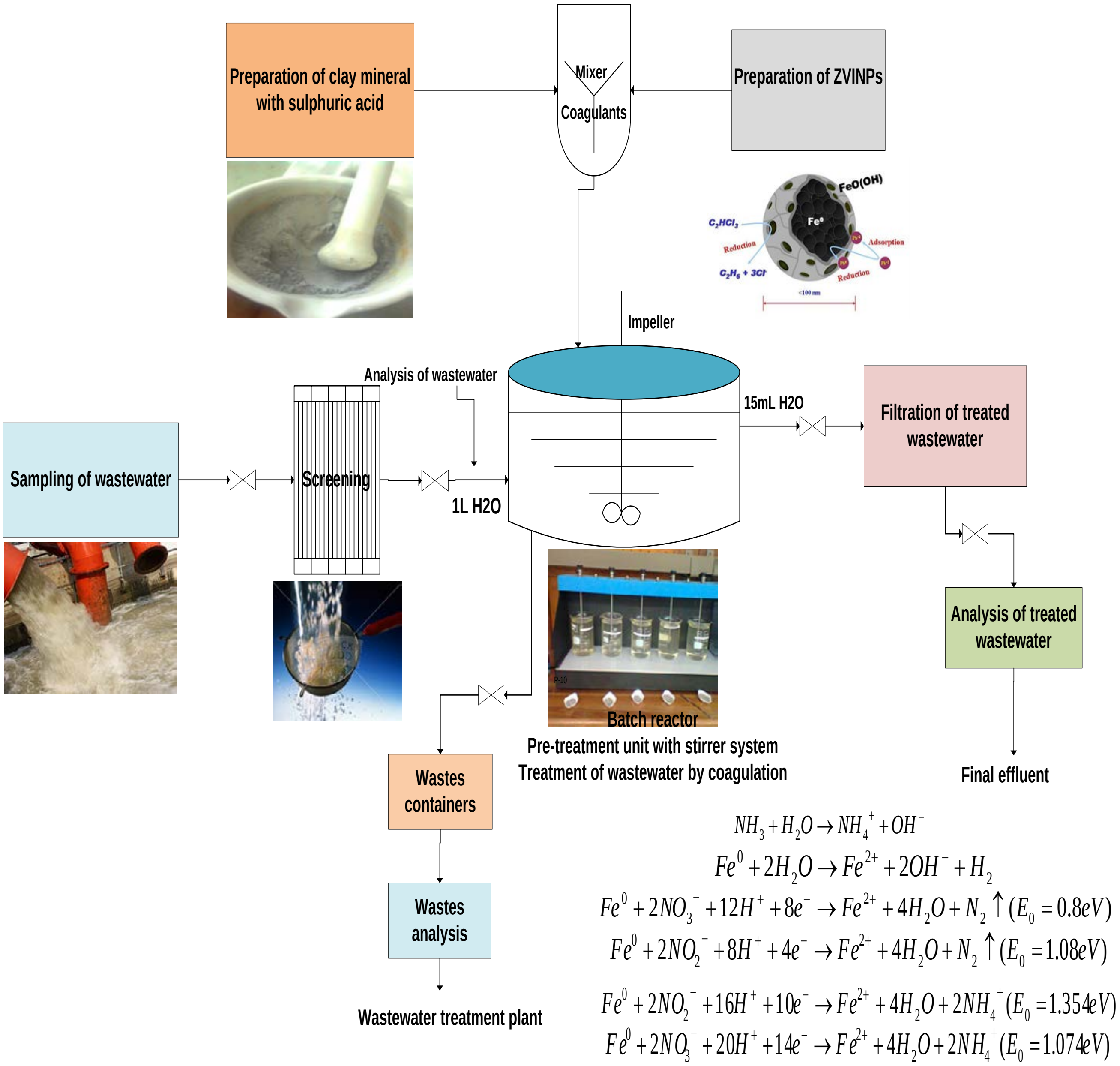
- Jar test: for mixing, coagulation, flocculation and sedimentation;
- Beaker with stirrer: to mix sulphuric acid with bentonite when activating the clay;
- Filter papers: to separate suspended solids from the treated water;
- 20 litres of plastic container: to collect the wastewater effluents;
- 10mL bottles: used in the analysis when testing;
- Turbidity-meter: to perform the turbidity test pH meter and to measure the acidity or alkalinity of wastewater effluents before and after coagulation process;
- Conductivity-meter: to measure total dissolved solids which determine the overall ionic effect in a water source;
- Oven: to dry the bentonitic clay and the nanoparticles;
- Erlen Meyer flask: to collect water when filtering to measure suspended solids;
- Weighing boat: to weigh the filter paper for Suspended Solids analysis and mass of bentonite.

3.1.6 Schematic set-up

The treatment of wastewater effluents was performed in the Chemical engineering laboratory on Bellville campus. The samples of wastewater effluents were collected from the Bellville wastewater plants, screened and analysed before being treated, on the other side, the coagulant was prepared but unfortunately due to a shortage of facilities the process methodology was performed in two ways:

Firstly the treatment was done only using activated clay as coagulant and the ammonia analyses after treatment could not be done due to a shortage of facilities, secondly wastewater samples from the same sources were treated with another type of coagulant that was made of activated clay and ZVINPs, and on top of that ammonia analyses before and after treatment were done to confirm the reduction of ammonia in the final product.

Below is the block flow diagram of the entire process methodology performed in the laboratory:



$$NH_3 + H_2O \rightarrow NH_4^{+} + OH^{-}$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^{-} + H_2$$

$$Fe^0 + 2NO_3^{-} + 12H^{+} + 8e^{-} \rightarrow Fe^{2+} + 4H_2O + N_2\uparrow (E_0 = 0.8eV)$$

$$Fe^0 + 2NO_2^{-} + 8H^{+} + 4e^{-} \rightarrow Fe^{2+} + 4H_2O + N_2\uparrow (E_0 = 1.08eV)$$

$$Fe^0 + 2NO_2^{-} + 16H^{+} + 10e^{-} \rightarrow Fe^{2+} + 4H_2O + 2NH_4^{+} (E_0 = 1.354eV)$$

$$Fe^0 + 2NO_3^{-} + 20H^{+} + 14e^{-} \rightarrow Fe^{2+} + 4H_2O + 2NH_4^{+} (E_0 = 1.074eV)$$

(Li et *al*., 2006)

Figure 3.2: Treatment methodology

The figure below describes the way bentonic clay was activated to enhance its adsorptive properties to treat effectively wastewater effluents, sulfuric acid was used to increase the surface are of the coagulant, a range of different concentrations was made until the concentration that gives optimum results was reached. Afterwards, this coagulant was divided into different amount in order to determine the dosage that will give optimum results in terms of ammonia depletion.

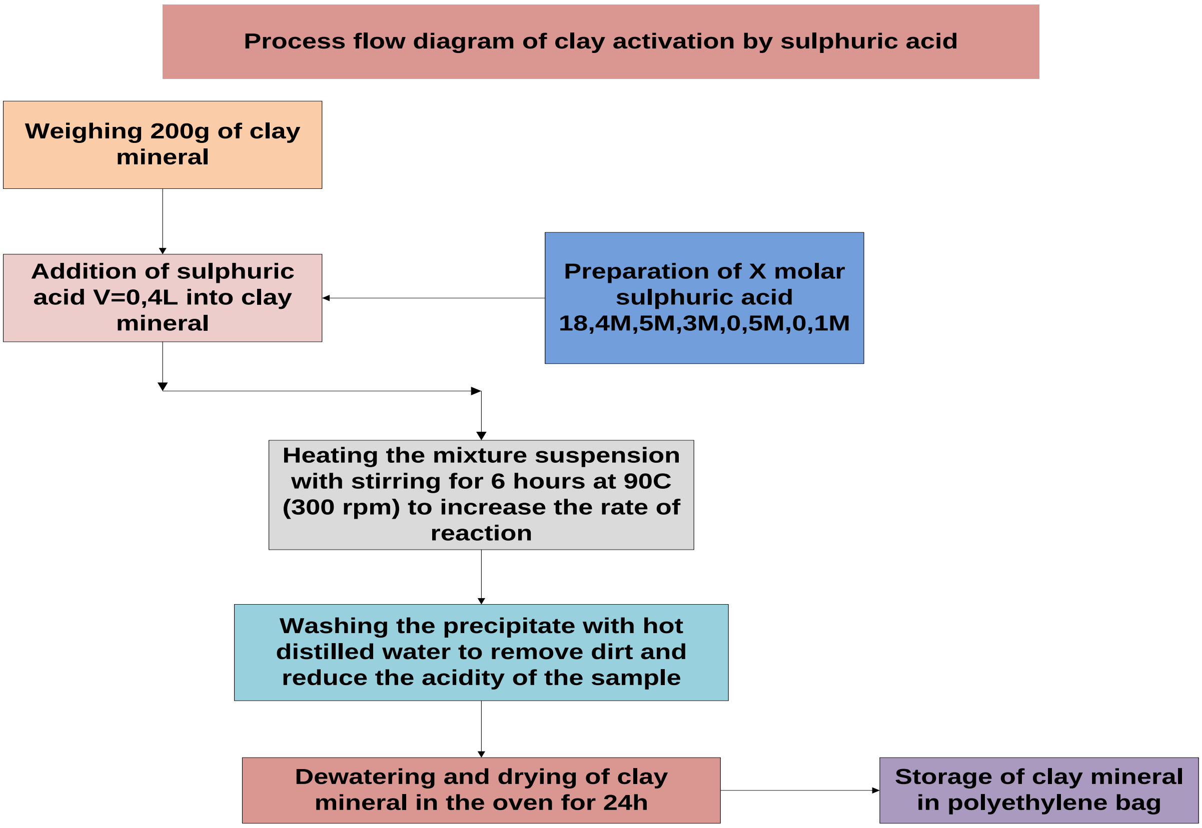


Figure 3.3: Bloc flow diagram of acid treatment of clay mineral

- **Reaction mechanism:**

$$Fe^{2+} + BH_4^- \rightarrow Fe^0 + H_2BO_3^-$$

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 \downarrow + 3H_2BO_3^- + 12H^+ + 6H_2$$

$$3Fe^{2+} + 3H_2O + BH_4^- \rightarrow 3Fe^0 + H_2BO_3^- + H_2 \uparrow + 6H^+$$

$$3FeCl_2 + NaBH_4 + 3H_2O \rightarrow 3Fe^0 + NaH_2BO_3 + H_2 + 6HCl$$

(Li et *al*., 2006)

The activated clay was then mixed with the dried ZVINPs. The samples were crushed in a mortar to obtain a homogenous mixture which was later used in treatment of wastewater.

Here is the following mechanism showing a list of possible reactions that can occurs during the treatment (depending on specific conditions), ammonia conversion and nitrite/nitrates reduction:

$$Fe^0 + 2NO_2^- + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O + N_2 \uparrow (E_0 = 1.85eV)$$

$$Fe^0 + 2NO_3{}^- + 12H^+ + 7e^- \rightarrow Fe^{3+} + 4H_2O + N_2 \uparrow (E_0 = 1.57eV)$$
$$Fe^0 + 2NO_3{}^- + 12H^+ + 8e^- \rightarrow Fe^{2+} + 4H_2O + N_2 \uparrow (E_0 = 0.8eV)$$

$$Fe^0 + 2NO_2{}^- + 16H^+ + 9e^- \rightarrow Fe^{3+} + 4H_2O + 2NH_4{}^+ (E_0 = 2.124eV)$$

$$Fe^0 + 2NO_2{}^- + 16H^+ + 10e^- \rightarrow Fe^{2+} + 4H_2O + 2NH_4{}^+ (E_0 = 1.354eV)$$

$$Fe^0 + 2NO_3{}^- + 20H^+ + 13e^- \rightarrow Fe^{3+} + 4H_2O + 2NH_4{}^+ (E_0 = 1.844eV)$$
$$Fe^0 + 2NO_3{}^- + 20H^+ + 14e^- \rightarrow Fe^{2+} + 4H_2O + 2NH_4{}^+ (E_0 = 1.074eV)$$

(Li et *al*., 2006)

The reactions show that during chemical reduction of nitrites/nitrates using ZVINPs both nitrogen gas and ammonium can be produced.

The water treated must be analyzed meticulously so that the reduction of ammonia can be confirmed. In so doing, the standards of wastewater effluents targeted, according the South African Environmental regulations can be reached (DWA, 2010).

Furthermore, ammonia analysis was performed by using the Lambert Beer method to determine the unknown concentration of ammonia in the treated wastewater effluent by measuring the absorbance by a quantitative method using a spectrophotometer, by doing a quantitative analysis of water.

The physical state of Ammonia depends on temperature but mostly the pH (Palmer et *al*., 2002). At high pH, ammonia is expressed as NH_3 (free ammonia), toxic and partially soluble in water. There is conversion of ammonium to ammonia. Conversely, at low pH, ammonia dissolves completely in water and is converted into NH_4^+ ionised ammonia. Under acidic environment, the high concentration of hydrogen ions, H_3O^+, alters ammonia to ammonium.

$$\boldsymbol{NH_3–N + H_2O \rightarrow NH4^+–N + OH^-}$$

The samples were prepared at Chemical Engineering Laboratory (CPUT). A solution of Zinc sulphate V=30mL was added to 30mL of treated wastewater, while the pH of the solution was maintained at10.5 by the addition of NaOH (V=7mL). To allow sedimentation of flocs to occur, the mixture was allowed to rest and the supernatant was taken for nesslerisation. The EDTA (disodium salt: $C_{10}H_{14}N_2O_8.2H_2O$) reagent V=50mL was added to the mixture, and finally, Nessler reagent V=2mL was poured into the mixture.

A blank was prepared by using distilled ammonia-free water with Nessler reagent. The sample of treated wastewater was placed in 1cm standard tubes of the apparatus and the absorbance noted at 400-500nm wavelengths. A calibration curve was prepared as follows: 0; 0.2; 0.4; 0.7; 1.0; 1.4; 1.7; 2.0; 2.5; 3; 4mL; 5mL of standard ammonium chloride solution in 50mL of distilled water. The samples were then nesslerised and the absorbance was noted. The graph was plotted mg NH_4Cl along x-axis and absorbance along the y-axis and a straight line was drawn. Ammonia concentration was determined from the calibration curve.

Figure 3.4: Spectrophotometer used for ammonia analysis (CPUT, Food Technology, 2012).

$$\%\textbf{\textit{Ammonia Removal Efficiency}} = \frac{\textbf{\textit{Mass}}\ (\textbf{\textit{Untreated}}) - \textbf{\textit{Mass}}\ (\textbf{\textit{Treated}})}{\textbf{\textit{Mass}}\ (\textbf{\textit{Untreated}})}$$

CHAPTER FOUR

RESULTS AND DISCUSSION

After treating the wastewater effluents with a special coagulant prepared in the Chemical engineering laboratory at the CPUT Bellville campus, coagulant which was on the first attempt mainly the activated clay and secondly supported with the Zero Valent Iron Nanoparticles to form a coagulant hybrid, it is important to recapitulate once more on the specific wastewater parameters governmental standards:

Chemical Oxygen Demand	**75 mg/L**
Total Suspended Solids	**25 mg/L**
Electrical Conductivity	**150mS/m**
Ammonia	**10 mg/L**
pH	**5.5 – 9.5**

4.1 Wastewater effluent treatment with H_2SO_4 activated bentonic clay (Attempt One)

4.1.1 Effect of clay activation procedure and dosage on treated wastewater – Turbidity

The concentrations used to activate bentonitic clay were 6M, 8M and 11M respectively. Its dosage ranged from 0.5g in Jar 1, 1g in Jar 2, 1.5g in Jar 3, 3g in Jar 4, 5g in Jar 5 and 10g in Jar 6. Timing: rapid mixing for one minute at 150rpm, slow mixing for 20minutes at 20rpm and settling time of 30minutes. Before the wastewater effluents collected from the plant, be treated, it went through a certain number of analysis and here are the results obtained: **Conductivity: 837*µ*S /cm; pH: 8.75; Turbidity: 1.27 NTU**

Now after treatment for the first run and analysis, in comparison with South African standards of wastewater effluent for discharge in the environment, here are the results:

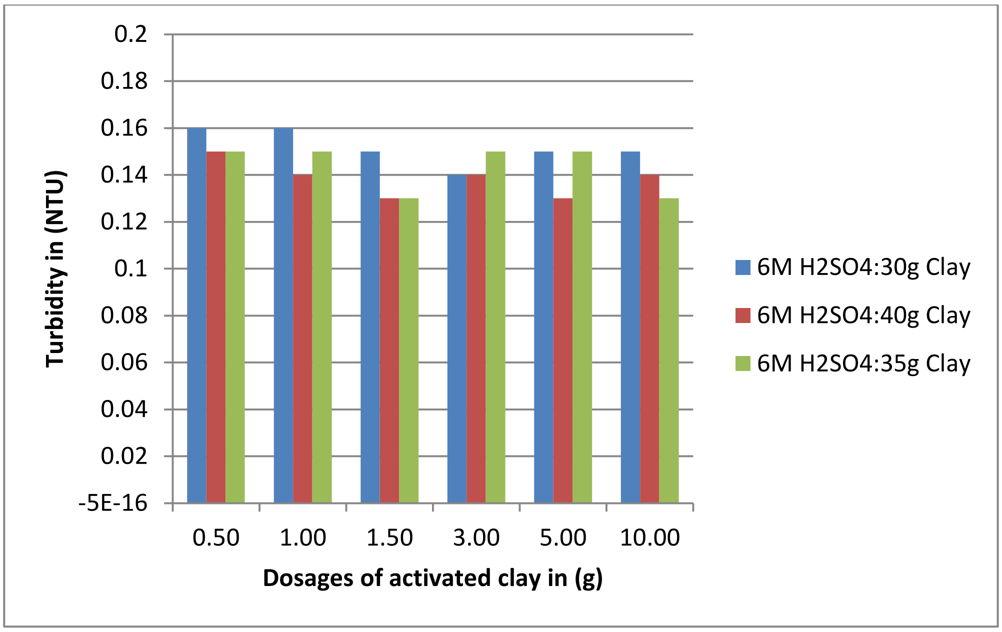


Figure 4.1a: Turbidity graph with 6M H_2SO_4

The graph above shows that all samples tended to have turbidity between 0.13-0.16. The good result in turbidity was obtained for a coagulant of 35g Clay-6M H_2SO_4 and 40g Clay-6M H_2SO_4 for a coagulant dosage from 1.5g to 10g clay. This indicates that better coagulant dosage was reached at 1.5g and the rest is redundant. During the experiment, it was observed that with a dosage of 1.5g of activated clay, the clay expanded with the absorption of the impurities. With a higher dosage, only a portion of bentonite expanded, indicating over-dosage. After the treatment, the water appeared clear, which may indicate the removal of humic acid (one the POPs components), which is responsible of the yellowish colour of the water. The water also had a fresh smell compared to the influent; therefore it can also be assumed that significant amount of organic pollutants have been removed. The following figure presents samples for untreated and treated water.

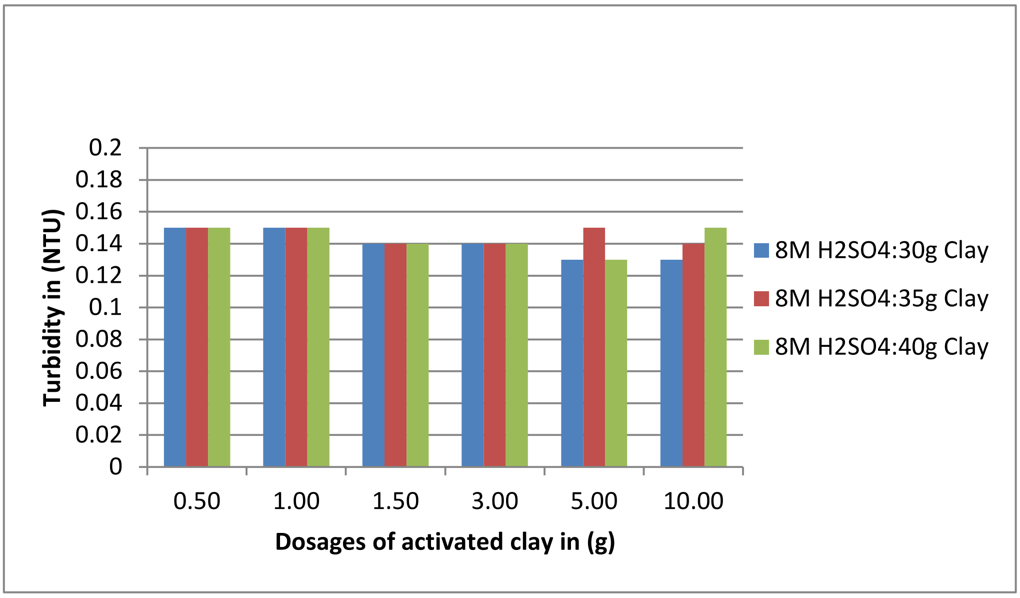


Figure 4.1b: Turbidity graph at 8M H_2SO_4

According to Figure 4.1b, the optimum treatment for the lowest turbidity was for a coagulant of 30g Clay: 8M H_2SO_4 and 40g Clay: 8M H_2SO_4 for a coagulant dosage of 5g and 10g. This follows the same trend as for a concentration of 6M H_2SO_4.

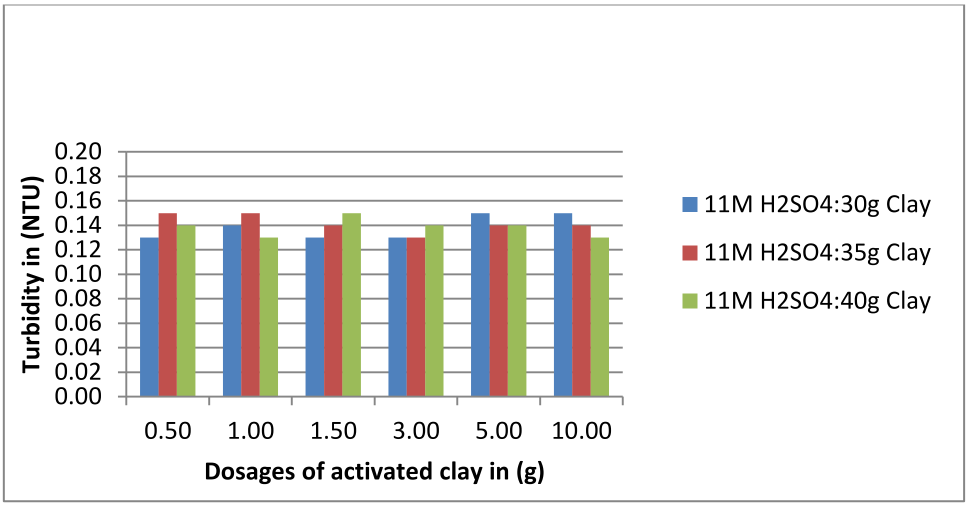


Figure 4.1c: Turbidity graph at 11M H_2SO_4

The optimum treatment for the lowest turbidity was for a coagulant of 30g Clay:11M H_2SO_4, 35g Clay:11M H_2SO_4 and 40g Clay:11M H_2SO_4 for a coagulant dosage of 0.5g,1.5g,3g and 10g. This follows the same trend as for a concentration of 6M H_2SO_4.

The turbidity results (Figure 4.1d) obtained with activated bentonitic clay were then compared to what was previously obtained with the non-activated clay, to examine how the coagulant has improved its adsorptive properties after activation with sulphuric acid.

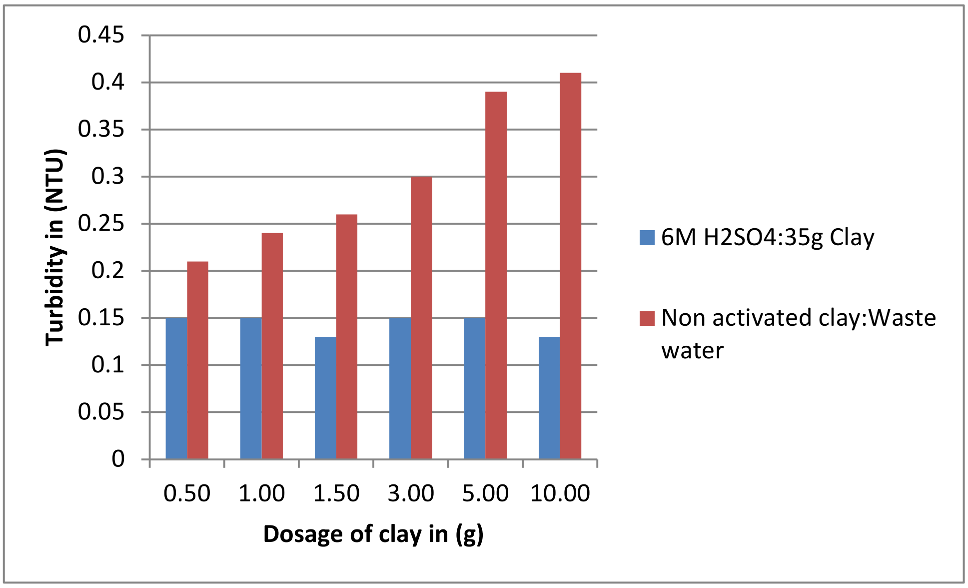


Figure 4.1d: Turbidity comparison between activated and non-activated clay performance

Figure 4.1d shows that the activation of clay plays a major role in removing impurities in wastewater, which is expressed in significant reduction of solution turbidity.

4.1.2 Effect of Clay activation procedure and dosage on treated wastewater - pH

For the wastewater to be released back into the environment, it requires a pH ranging between 6.5 and 9.0. Figure 4.2a reveals that the pH decreases with an increase in the activated clay, due to the H_2SO_4 in the coagulant. With an increase in acid, there is an increase in acidity and therefore the pH is low.

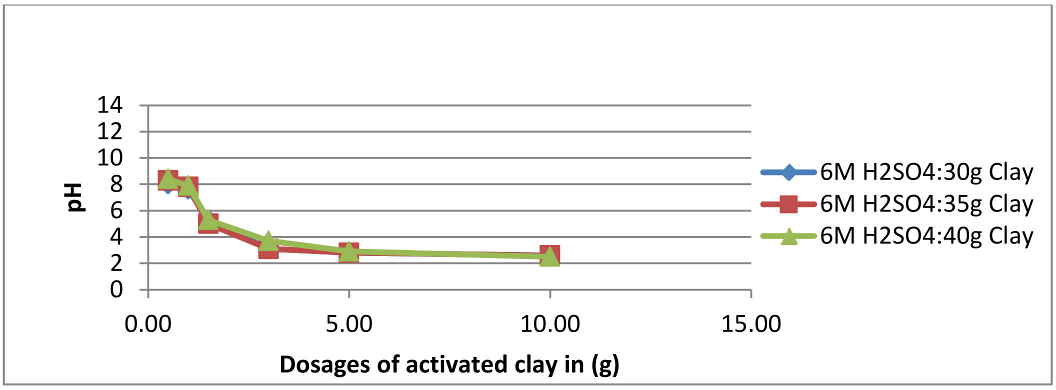


Figure 4.2a: pH graph at 6M H_2SO_4

From the graph above it can be noticed that the trend was almost the same in all cases, while the pH is decreasing depending on an increase in dosages of coagulants. Figure 4.2a reveals that the pH first decreases with addition of activated clay (6M) and then stabilises with coagulant loading. This could be due to the dilution effect although the coagulants have been treated with the acid of same concentration.

To increase the pH to an acceptable range, sodium hydroxide was added to buffer the water.

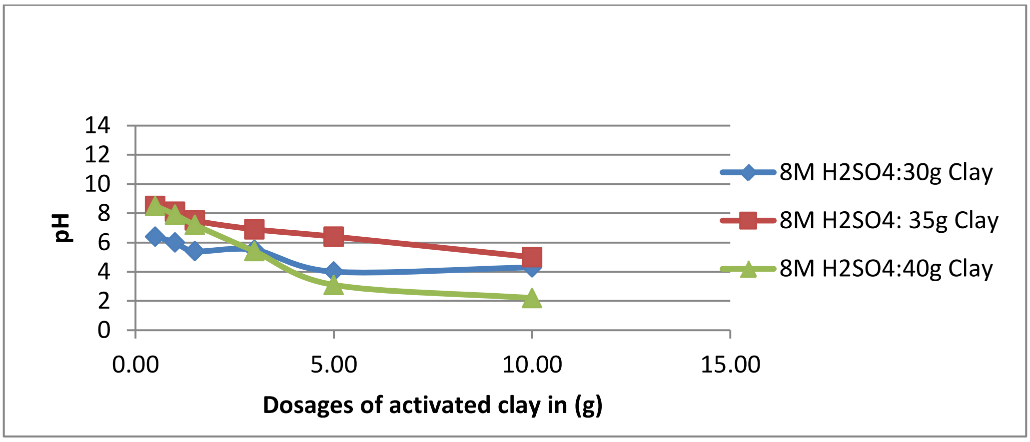


Figure 4.2b: pH graph at 8M H_2SO_4

It can be observed that as much that the concentration of H_2SO_4 that was used to activate the coagulant increase, it automatically tends to stabilize the value of the pH on although the variation of the coagulant dosages, this observation can also be confirmed on the following graph (Figure 4.2b):

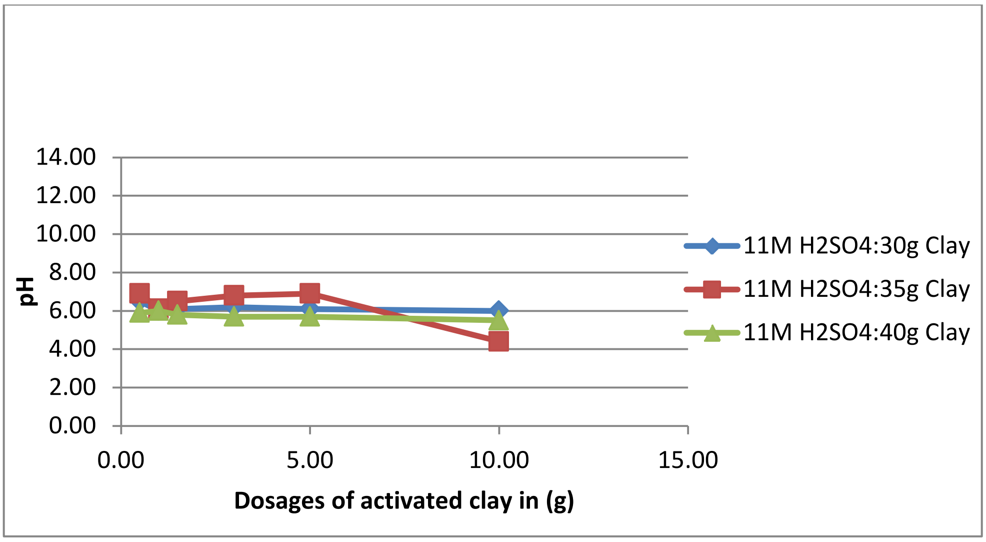


Figure 4.2c: pH graph at 11M H_2SO_4

The pH for 8M H_2SO_4 (see Figure 4.2b) follows the same trend as that for 6M H_2SO_4. The pH can be increased by adding a base for example NaOH to buffer the water.

4.1.3 Effect of Clay activation procedure and dosage on treated wastewater – Conductivity

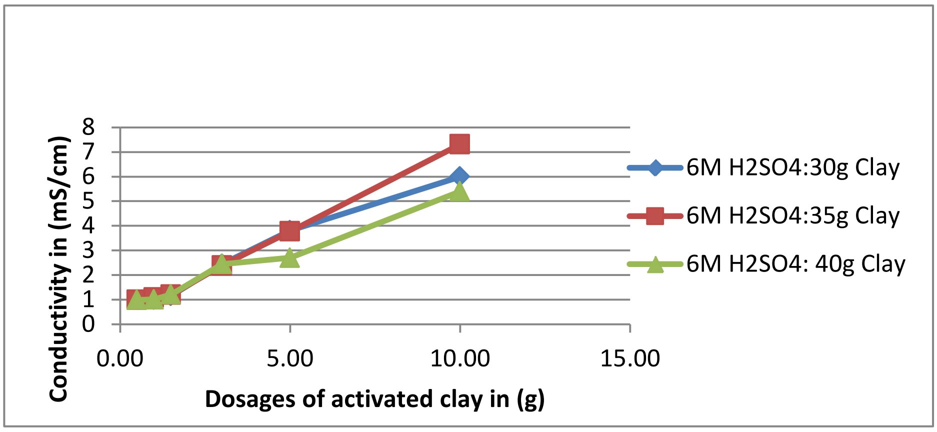


Figure 4.3a: Conductivity graph for 8M H_2SO_4

The conductivity on Figure 4.3a of the treated water samples with 6M H_2SO_4 show that there is significant increase; this could be due the presence of remained activated clay particles after filtrations in the water.

An increase in conductivity is due to the presence of ions in the solution. Ions are attained from the SO_4^{2-} and H^+ ions as well as the other ionic matters found in the clay. A mineralogy study needs to be conducted on the bentonite clay in order to establish contents of water after treatment. The bentonite mainly consists of Ca^{2+-}, Mg^{2+-} or Na^{+-}ions and Al, Fe, Mg and other metals. Therefore, with a higher dosage of coagulant, there is an increase in the conductivity of the treated water due to the presence of ions H^+ in the medium.

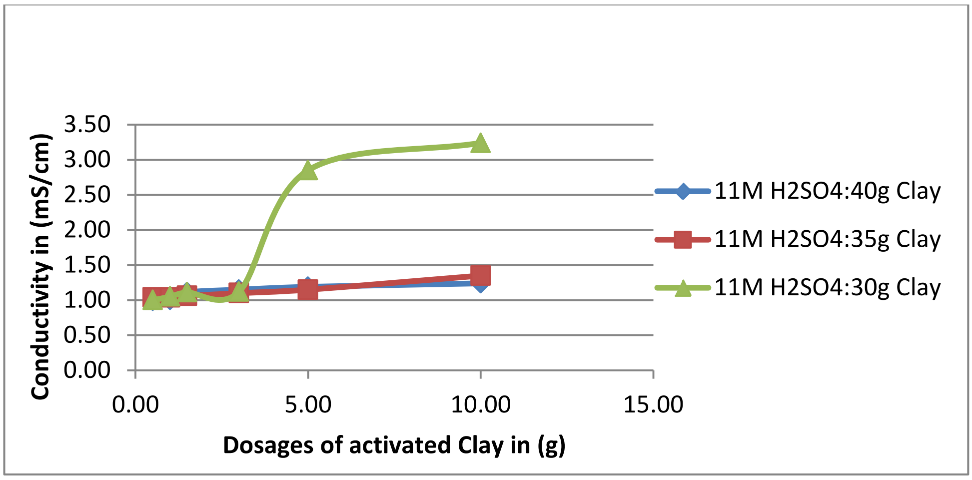


Figure 4.3b: Conductivity graph at 11M H_2SO_4

Afterwards, it has been observed that the wastewater effluent treated could not comply with the South Africa requirements of wastewater to be released back into the blue ocean. In particular, the electrical conductivity was not adhering to the standards and no analyses were done to confirm the ammonia reduction. This is the reason why it was decided to perform a second attempt where the ratio between clay and sulphuric acid was constant but only the concentration used to activate the clay and the coagulant dosage were different. Though the bentonic clay activated with 6M H_2SO_4 gave relatively good results, ammonia analysis could not be done due to a lack of facilities, the picture below (Figure 4.4) show the disappearance of colour, meaning that at least a certain amount of humic acid was removed.

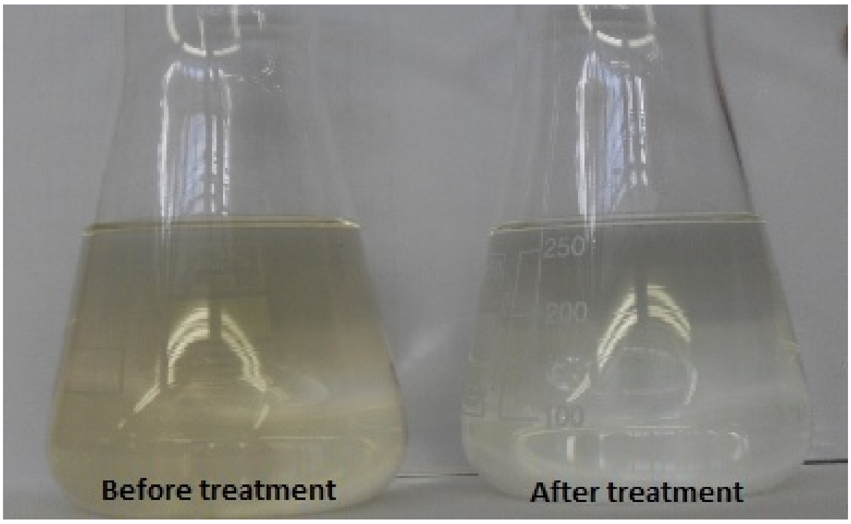


Figure 4.4: Treated and treated water (Without ZVINPs) – **ATTEMPT ONE.**

4.2 Wastewater effluent treatment with H_2SO_4 – Activated bentonic clay mixed with ZVINPs (Attempt Two)

4.2.1 Attempt two – pH results

All the operating parameters were constant except the H_2SO_4concentrations (0.5M; 1M; 3M; 5M; 6M; 9M; and 18.4M).

Those samples had a constant volume of 400cm^3 to activate 200g of bentonitic clay. All calculations concerning the way samples were calibrated are shown with much details into the appendix (Table B.3 and Figure B.3). Below is a summary of the results:

Table 4.1: pH results

	Jar 1	**Jar 2**	**Jar 3**	**Jar 4**	**Jar 5**	**Jar 6**
0.1M montmorillonite	7.42	7.91	8.09	7.78	7.91	7.90
0.1M montmorillonite+ZVINPs	7.6	7.84	8.02	7.72	7.3	7.86
0.5M montmorillonite	8.5	8	8.02	8.28	8.10	7.82
0.5M montmorillonite+ZVINPs	7.54	7.52	7.69	7.57	7.56	7.43
3M montmorillonite	7.46	7.63	7.83	7.69	7.65	7.67

3M montmorillonite+ZVINPs	7.74	7.78	7.75	7.58	7.48	5.91
5M bentonite	7.69	7.39	7.84	7.51	7.49	7.99
5M bentonite+ZVINPs	7.5	7.46	7.46	7.46	7.43	8.18
18.4M bentonite	7.66	4.18	2.81	2.49	2.31	2.33
18.4M bentonite+ZVINPs	7.83	4.24	3.08	2.65	2.47	2.36

Above are the corresponding values of the pH with the w/w ratio between the ZVINPs and the activated clay, secondly a comparison of the pH values obtained with the South African standards (figure 4.5):

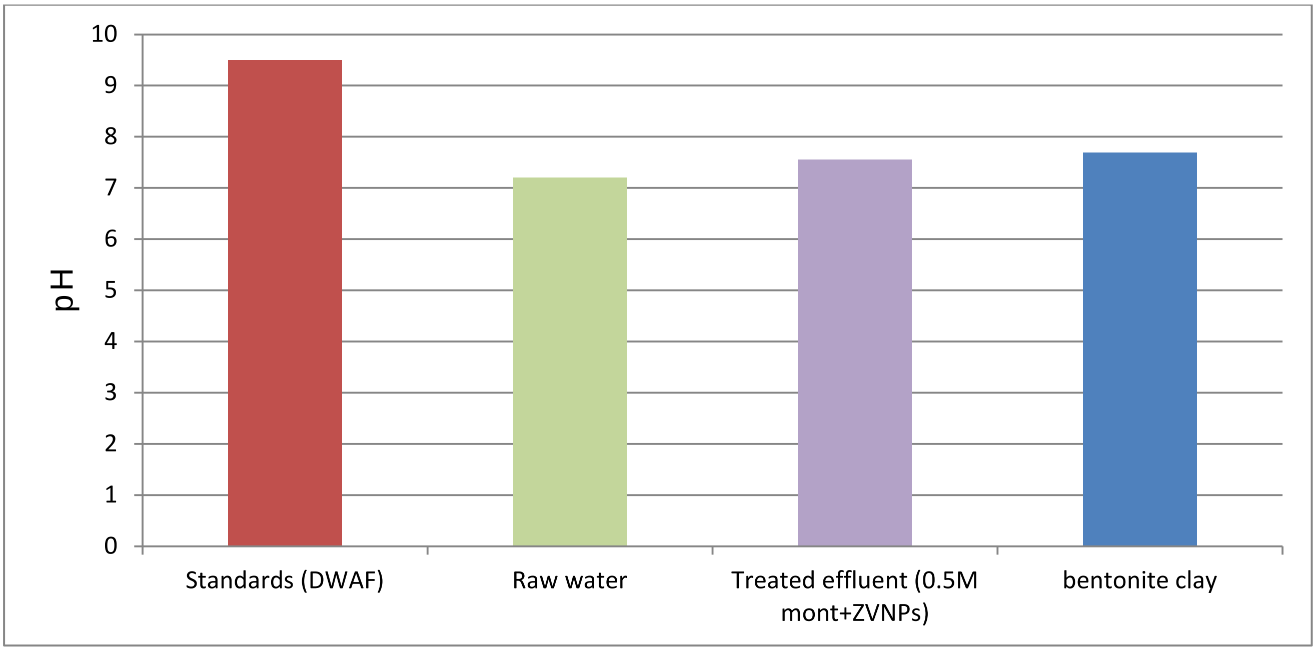


Figure 4.5: pH comparison

4.2.2 Attempt two – Conductivity results

The conductivity, being the ability of a substance to conduct or transfer heat, electricity, is one of the important parameter beside the pH that also need to be measured and checked as well, if it does correspond to the standards of wastewater to be discharged into the environment:

Table 4.2: Conductivity results

	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
0.1M montmorillonite	947	962	986	1024	1015	1032
0.1M montmorillonite+ZVINPs	289	264	279	273	296	295
0.5M montmorillonite	300	260	296	281	285	284
0.5M montmorillonite+ZVINPs	284	284	286	274	277	261
3M montmorillonite	287	289	302	293	280	266
3M montmorillonite+ZVINPs	302	288	292	289	283	304
5M bentonite	300	302	306	306	302	303
5M bentonite+ZVINPs	259	286	265	269	277	269
18.4M bentonite	295	404	822	1325	1781	207
18.4M bentonite+ZVINPs	278	359	593	994	1390	1672

The effect of conductivity on the coagulant dosage was also investigated to see what can be the required coagulant dosage for a less conductivity value; the conductivity obtained for each water samples was generally compared to the standards:

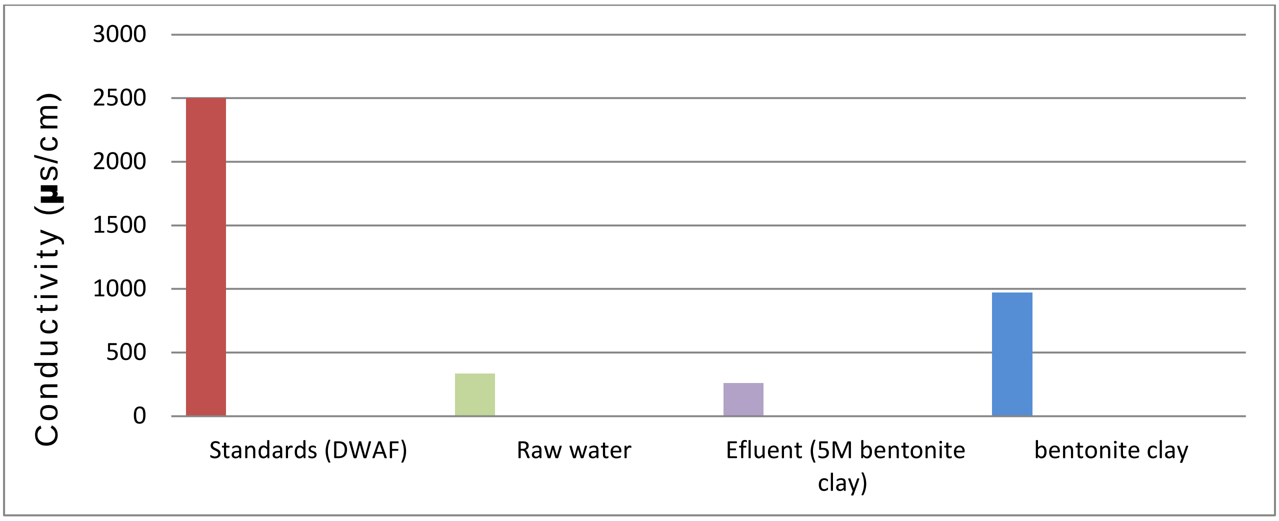


Figure 4.6: Comparison of conductivity

4.2.3 Attempt two – Ammonia results

The section comprises ammonia results obtained after treating wastewater effluents with a coagulant made of activated clay and ZVINPs, ammonia level were compared with the one set by the department of water affairs and the efficiency removal were determined.

Table 4.3: Results of ammonia concentrations for different samples

Sample	Jar	Absorbance	C(g/L)	C(mg/L)	Ammonia removal efficiency (%)
Untreated	-	0.1298	0.277	277	0
0.1M+ZVINPs	6	0.0089	0.0182	18.80	93.21
3M	1	0.0741	0.1582	158.4	42.81
	2	0.0320	0.0685	68.50	75.27
	3	0.0121	0.0260	26.01	90.61
	4	0.0280	0.0599	59.96	78.35
	5	0.0215	0.0461	46.08	83.36
3M+ZVINPs	6	0.0284	0.0608	60.82	78.04
5M+ZVINPs	1	0.0040	0.0087	8.710	96.85
	3	0.0839	0.1800	180.0	35.02
	5	0.0413	0.0883	88.36	68.10
18.4M	1	0.0076	0.0164	16.40	94.10
	4	0.0729	0.1558	155.8	43.75
	5	0.0323	0.0691	69.14	75.04
	6	0.0305	0.0653	65.30	76.42
18.4M+ZVINPs	2	0.0652	0.1394	139.4	49.67
	3	0.0740	0.1582	158.2	42.88
	5	0.0150	0.0322	32.20	88.37
	6	0.0183	0.0392	39.20	85

Simple calculations can be made, after getting the ammonia level in terms of the calibration curve that was previously plotted on figure B.3 (Appendix B). To determine the ammonia removal efficiency:

% Ammonia Removal Efficiency= $\frac{277-8,71}{277}\times 100\% = 96,85\%$

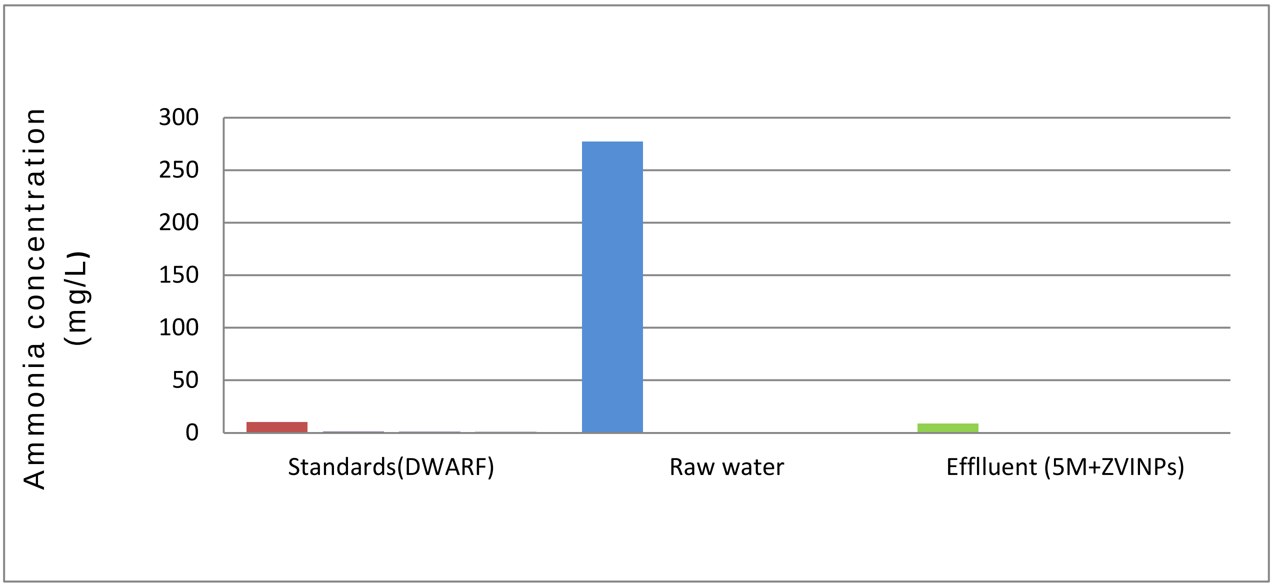


Figure 4.7: Comparison of ammonia concentration

4.3 Discussion of results

Generally adding a supplemental source of alkalinity, such as lime or soda ash, may be necessary for proper floc formation. However, adding lime (or other alkali supplements) and iron- or aluminium-based coagulants at the same point can degrade turbidity removal performance, the same as it does with naturally occurring turbidity or alkalinity (Bratby, 2006).

Therefore, the addition of lime typically creates the demand for more ferric- or alum based coagulant and the operator will probably add more coagulant in response to this demand. More coagulant can cause the pH to decrease, and more lime is typically added to compensate, but with clay there is no need to add an alkaline substance because the pH actually do not decrease comparatively to other coagulants; According to the department of water affairs here in South Africa (Green Drop Index, 2011), the pH should be in between **5.5 and 9**. Thus the pH results obtained for 0.1M, 0.5M, 3M, and 5M fell under acceptable criteria. The lowest pH was 2.2 for 18.4M without ZVINPs and the highest pH obtained was **8.28** for 0.5M without ZVINPs.

Conductivity is the measure of the ability of a solution to carry electric current. The values obtained after analysis are below the standard 2500µs/cm (South Africa, Department of Water Affairs, 2011). The highest and lowest values were obtained at 18.4M without ZVINPs

[**207-1781µs/cm**]. The conductivity obtained for the sample **5M+ZVINPs** at a dosage of 0,0616g was **259µs/cm.** On the other hand, the turbidity results obtained for inactivated clay and 0.1M montmorillonite clay were below the standard (lesser than 9.67NTU).

The untreated wastewater had an amount of ammonia of **277mg/L**, which was more than the standards, **<10mg/L** (South Africa, Department of Water Affairs, 2011). However, the results obtained from this research showed that ammonia content was reduced for most of the sample. The best ammonia reduction was obtained at 5M+ZVINPs for a dosage of **61.6mg** coagulant. The ammonia was reduced from 277mg/L to **8.71mg/L** yielding a removal efficiency of **96.85%.**

The conductivities results obtained range between 207-1781µs/cm and below 2500µs/cm. The most accurate conductivity was 5M bentonite clay with a lowest standard deviation of 2.19. It was noticed that the increase in coagulant dosage increased the conductivity, illustrating the presence of more ions in the solution as the coagulants were added. The 18.4M sample had the highest conductivity at maximum dosage because of the acid concentration (98%) which dissociated completely in solution providing more ions and higher conductivity, contrary to diluted solution (0.1M; 3M; 5M). These results were consistent to previous studies finding that higher concentrated acid solution conduct electricity better as compared to weak or diluted acid.

The sample 0.5M montmorillonite with ZVINPs demonstrated the most accurate pH with a standard deviation of 0.078.The pH obtained for 18.4M samples were acidic. This may be explained by the higher acid concentration.
The results obtained with the coagulant activated with 18.4M sulfuric acid leads to two conclusions: either the structure of clay was destroyed, because it was unable to adsorb correctly or otherwise the effect of acid on the clay adsorptive surfaces modified the optimum conditions and the mechanism of ammonia molecules to migrate to the coagulant surface was disturbed.

The increase in concentration increases the surface areas and pores to such an extent value and drops significantly with increase acid concentration (Önal, 2006). This proves that at 18.4M, the clay structure dissolves and was completely destroyed due to the acid high concentration and in so doing, reducing the adsorption capacity of the coagulant.

The treatment of wastewater was performed in a neutral environment with no control of pH solution; pH was just analysing before and after treatment. Previous researches have shown that neutral pH slows down ammonia reduction; thus the obtained results are consistent with previous observations. No pH control was performed during treatment (Thomsen et *al*., 1994). Precedent work demonstrated that nitrate, nitrite as well as ammonia have a similar sensitivity to pH with an almost 100-fold decrease in rate constant over a pH range of 5.5 to 9.0 (Alowitz & Sherer, 2002). As pH increases beyond 8.5, nitrate/nitrite reduction generally slows down to a greater extent (Thomsen et *al*., 1994; Glass & Silverstein, 1998).

The maximum reduction obtained at 5M+ZVINPs with a neutral pH is defined by the maximum surface area obtained at 5M during acid treatment.

Researchers have proposed that reduction of nitrate/nitrite and ammonia by granular iron is favoured at low pH (2-4.5) (Zawaideh & Zhang 1998; Alowitz & Scherer, 2002; Huang et *al*., 2003). Therefore, the 18.4M+ZVINPs did not reduce ammonia even though the environment was acidic because of the smectites structure destruction; these results are consistent with previous studies.

From the results generated, the augmentation in coagulant dosage had no effect on the contaminants removal efficiency for most samples. It had been reported that increase in catalysts' dosage increases the reduction efficiency; this means that maximum dosage obtains the highest contact surface between catalysts and contaminants. Previous research showed that nitrite was rapidly removed in the presence of 7 g /L of Fe^0 over a temperature range of 5 to 50°C (Rahman et *al*., 1997).Thus, the highest amount of catalysts dosage was 5g for clay and 0.0505g for iron metal. The iron metal amount is low compared to findings in previous research (Alowitz & Scherer, 2002; Huang et al., 2003).

The mixing intensity was kept constant at 20rpm during treatment processes; the impellers provided proper mixing and enhanced the transport of mass on granular iron surface (Miehr et *al*., 2003).

The 5M bentonite+ZVINPs gave the most ammonia removal efficiency and it can be predicted that the best adsorption capacity of acid treatment was obtained at 5M, yielding best results of conductivity at dosages **Jar1** (0.0616g), **Jar2** (1.0586g), **Jar3** (2.0566g), **Jar4** (3.0545g), **Jar5** (4.0525g), and **Jar6** (5.0505g). The significantly slower removal observed at higher pH values was consistent with previous research findings.

CHAPTER FIVE

GENERAL CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

It can be summarised that reduction of contaminants from wastewater is slower near neutral environments and the removal efficiency is highly affected by the following: the type of coagulants used; the dosage of coagulants; the pH and temperature of the solution; the mixing speed; and the reaction time.

The activated clay was appropriately activated and the structural change obtained by analysis indicates that the destruction of the octahedral sheet is a function of acid concentration, on the other hand ZVINPs were decorously synthesized and at the end of the process, the obtained results with the hybrid coagulant show that the maximum concentration for sulfuric acid to be used as clay activator was 5M, and the optimum w/w ratio of activated clay with ZVINPs to treat 1L of wastewater effluents, which constitutes the coagulant dosage was 60.6mg (60mg of clay + 0.6mg of ZVINPs), enhancing the rate of ammonia removal in wastewater. Bentonitic clay mixed with ZVINPs was effective to reduce the level of ammonia in wastewater effluent from 277mg/L (Untreated from the plant) to 8.71mg/L (Treated in the Lab.).

The results of this work have demonstrated that clay with ZVINPs is a valued source of adsorbent for treating wastewater effluents before its discharge into the environment in order for it to comply with set standards (Table 5.1).

Table 5: The resulting effluent's parameters by the 5 M (optimum) clay-modified coagulant

Parameter	Basic standard	Final effluent (from WWTP)	Treated effluent
Conductivity (mS /m)	250	334	239
pH	5.5 – 9.5	7.21	7.5
Ammonia (mg/L)	10	277	8.71

And finally here is a picture (Figure 4.5) of the final treated effluent (on the right hand side) processed with the hybrid coagulant at the left hand side and the raw water which is the final wastewater effluents from Bellville Wastewater Treatment Plants (BWWTPs).

Figure 5: Untreated and treated water (With ZVINPs).

5.2 Recommendations

1. Further analyses such as SEM, BET and XRD (especially on the ZVINPs) should be considered for characterization of the coagulant to confirm and explain appropriately the improvement of the coagulant’s adsorptive properties;
2. Economic studies need to be done in order to evaluate the cost effectiveness of the technology and its possibility to be implemented.

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APPENDICES

Appendix A: TREATMENT WITH NATURAL AND ACTIVATED BENTONITIC CLAY (First Attempt)

A.1 Wastewater influent (from Bellville wastewater treatment plant) analysis results

Table A.1: Analysis results from Bellville waste water treatment plant

Bellville Settling Tank Effluent (S)					
Total Suspended Solids	mg/l	6	7	10	7
COD	mg/l	39	46	39	58
Ammonia	mg N/l	17.2	7.7	19.4	19
Nitrate/Nitrite	mg N/l	0.2	<0.1	0.2	0.4
Ortho-Phosphate	mg P/l	1	0.8	1	0.4
pH		7.3	7.3	7.3	7.4
Conductivity	mS/m	97	87	93	91
Chloride	mg/l	111	92	97	96
Alkalinity	mg CaCO$_3$/l	256	236	272	269

▨ Analysis made on the first attempt

🟥 Analysis made on the second attempt

Table A.2: Analysis results conducted in laboratory

Waste water influent	
Turbidity (NTU)	0.19
pH	8.30
Conductivity (mS/cm)	1.03
Conductivity (µS /cm)	837.00

A.2 Water treatment results after coagulation with non-activated clay

Table A.3: Analysis results for a coagulation of wastewater with non-activated clay

Non activated Clay: WW						
Dosage	**0.50**	**1.00**	**1.50**	**3.00**	**5.00**	**10.00**
Turbidity (NTU) before filtration	0.24	0.27	0.29	0.37	0.42	0.94
Turbidity (NTU) after filtration	**0.21**	**0.24**	**0.26**	**0.3**	**0.39**	**0.41**
pH before filtration	8.90	8.70	8.60	8.60	8.60	8.70
pH after filtration	**6.7**	**6.9**	**6.7**	**6.8**	**6.8**	**6.6**
Conductivity (mS/cm) before filtration	0.90	0.97	0.98	0.98	1.01	1.03
Conductivity (µS /cm) before filtration	765.00	778.00	776.00	755.00	817.00	838.00
Conductivity (mS/cm) after filtration	**0.82**	**0.87**	**0.88**	**0.94**	**0.99**	**0.8**
Conductivity (µS /cm) before filtration	**563**	**741**	**732**	**745**	**786**	**771**

A.3 Water treatment results after coagulation with a concentration of 6M H_2SO4

Table A.4: Analysis results for a coagulation mixture of 30g Clay: 6M H_2SO_4

6M H_2SO_4: 30g Clay						
Dosage	**0.50**	**1.00**	**1.50**	**3.00**	**5.00**	**10.00**
Turbidity (NTU) before filtration	0.19	0.19	0.19	0.15	0.14	0.14
Turbidity (NTU) after filtration	**0.16**	**0.16**	**0.15**	**0.14**	**0.15**	**0.15**
pH before filtration	6.30	5.90	4.90	3.10	2.70	2.50
pH after filtration	**8.00**	**7.60**	**5.30**	**3.10**	**2.80**	**2.60**
Conductivity (mS/cm) before filtration	1.14	1.10	1.23	2.07	3.44	6.13
Conductivity (µS /cm) before filtration	945.00	964.00	1048.00	1830.00	*	*
Conductivity (mS/cm) after filtration	**0.99**	**1.00**	**1.15**	**2.45**	**3.81**	**6.00**
Conductivity (µS /cm) before filtration	**801**	**815**	**951**	**1670**	*****	*****

* - over the limit of the machines capabilities

Table A.5: Analysis results for a coagulation mixture of 35g Clay: 6M H_2SO_4

6M H_2SO_4: 35g Clay						
Dosage	**0.50**	**1.00**	**1.50**	**3.00**	**5.00**	**10.00**
Turbidity (NTU) before filtration	0.17	0.20	0.16	0.41	0.43	0.41
Turbidity (NTU) after filtration	**0.15**	**0.15**	**0.13**	**0.15**	**0.15**	**0.13**
pH before filtration	6.90	6.80	5.10	3.20	2.80	2.50
pH after filtration	**8.3**	**7.8**	**5**	**3.1**	**2.8**	**2.6**
Conductivity (mS/cm) before filtration	1.11	1.14	1.27	2.51	4.03	7.27
Conductivity (μS /cm) before filtration	841.00	873.00	928.00	1951.00	*	*
Conductivity (mS/cm) after filtration	**0.99**	**1.08**	**1.2**	**2.39**	**3.77**	**7.31**
Conductivity (μS /cm) before filtration	**798**	**870**	**960**	**1927**	*****	*****

Table A.6: Analysis results for a coagulation mixture of 40g Clay: 6M H_2SO_4

6M H_2SO_4: 40g Clay						
Dosage	**0.50**	**1.00**	**1.50**	**3.00**	**5.00**	**10.00**
Turbidity (NTU) before filtration	0.21	0.21	0.32	0.34	0.39	0.35
Turbidity (NTU) after filtration	**0.15**	**0.14**	**0.13**	**0.14**	**0.13**	**0.14**
pH before filtration	6.60	6.60	6.10	3.40	2.80	2.60
pH after filtration	**8.4**	**7.9**	**5.3**	**3.7**	**2.9**	**2.5**
Conductivity (mS/cm) before filtration	1.16	1.22	1.25	1.97	3.22	5.68
Conductivity (μS /cm) before filtration	944.00	1001.00	1040.00	1063.00	*	*
Conductivity (mS/cm) after filtration	**0.99**	**1.01**	**1.21**	**3.45**	**2.7**	**2.4**
Conductivity (μS /cm) before filtration	**839**	**899**	**938**	**988**	*****	*****

* - over the limit of the machines capabilities

A.4 Water treatment results after coagulation with a concentration of 8M H_2SO4

Table A.7: Analysis results for a coagulation mixture of 30g Clay: 8M H_2SO_4

8M H_2SO_4: 30g Clay						
Dosage	**0.50**	**1.00**	**1.50**	**3.00**	**5.00**	**10.00**
Turbidity (NTU) before filtration	0.29	0.24	0.17	0.23	0.18	0.38
Turbidity (NTU) after filtration	**0.15**	**0.15**	**0.14**	**0.14**	**0.13**	**0.13**
pH before filtration	6.00	5.90	5.90	5.20	4.60	4.20
pH after filtration	**6.4**	**6**	**5.4**	**5.5**	**4**	**4.3**

Conductivity (mS/cm) before filtration	1.01	1.07	1.11	1.18	1.32	1.76
Conductivity (µS /cm) before filtration	846.00	862.00	890.00	942.00	1059.00	1405.00
Conductivity (mS/cm) after filtration	**0.97**	**0.99**	**1.1**	**1.11**	**1.33**	**1.62**
Conductivity (µS /cm) before filtration	**772**	**820**	**901**	**913**	**1240**	**1320**

Table A.8: Analysis results for a coagulation mixture of 35g Clay: 8M H_2SO_4

H_2SO_4: 35g Clay						
Dosage	**0.50**	**1.00**	**1.50**	**3.00**	**5.00**	**10.00**
Turbidity (NTU) before filtration	0.21	0.26	0.29	0.35	0.36	0.34
Turbidity (NTU) after filtration	**0.15**	**0.15**	**0.14**	**0.14**	**0.15**	**0.14**
pH before filtration	7.10	7.10	7.10	6.90	6.80	6.60
pH after filtration	**8.5**	**8.1**	**7.5**	**6.9**	**6.4**	**5**
Conductivity (mS/cm) before filtration	1.13	1.12	1.13	1.20	1.18	1.24
Conductivity (µS /cm) before filtration	909.00	906.00	921.00	968.00	965.00	1002.00
Conductivity (mS/cm) after filtration	**0.98**	**1**	**1.12**	**1.25**	**1.23**	**1.26**
Conductivity (µS /cm) before filtration	**891**	**899**	**911**	**955**	**966**	**1004**

Table A.9: Analysis results for a coagulation mixture of 40g Clay: 8M H2SO4

8M H_2SO_4: 40g Clay						
	0.50	**1.00**	**1.50**	**3.00**	**5.00**	**10.00**
Turbidity (NTU) before filtration	0.22	0.16	0.19	0.15	0.15	0.15
Turbidity (NTU) after filtration	**0.15**	**0.15**	**0.14**	**0.14**	**0.13**	**0.15**
pH before filtration	6.50	6.10	5.60	3.40	2.80	2.50
pH after filtration	**8.5**	**7.9**	**7.2**	**5.4**	**3.1**	**2.2**
Conductivity (mS/cm) before filtration	1.16	1.22	1.26	1.88	3.17	6.08
Conductivity (µS /cm) before filtration	965	1016	1049	1561	*	*
Conductivity (mS/cm) after filtration	**1.01**	**1.12**	**1.13**	**1.27**	**2.88**	**5.02**
Conductivity (µS /cm) before filtration	**812**	**905**	**952**	**1021**	*****	*****

* - over the limit of the machines capabilities

A.5 Water treatment results after coagulation with a concentration of 11M H_2SO4

Table A.10: Analysis results for a coagulation mixture of 30g Clay: 11M H_2SO_4

11M H_2SO_4: 30g Clay						
Dosage	**0.50**	**1.00**	**1.50**	**3.00**	**5.00**	**10.00**
Turbidity (NTU) before filtration	0.15	0.14	0.15	0.15	0.17	0.21
Turbidity (NTU) after	**0.13**	**0.14**	**0.13**	**0.13**	**0.15**	**0.15**

filtration						
pH before filtration	5.00	5.80	4.90	4.80	3.50	2.70
pH after filtration	**6.50**	**6.00**	**6.10**	**6.20**	**6.1**	**6**
Conductivity (mS/cm) before filtration	1.33	1.27	1.39	1.48	3.54	4.57
Conductivity (µS /cm) before filtration	1081.00	1032.00	1125.00	1200.00	1358.00	1452.00
Conductivity (mS/cm) after filtration	**1.00**	**1.05**	**1.11**	**1.12**	**2.85**	**3.54**
Conductivity (µS /cm) before filtration	**905.00**	**925.00**	**998.00**	**1004.00**	**1115**	**1254**

Table A.11: Analysis results for a coagulation mixture of 35g Clay: 11M H_2SO_4

11M H_2SO_4: 35g Clay						
Dosage	**0.50**	**1.00**	**1.50**	**3.00**	**5.00**	**10.00**
Turbidity (NTU) before filtration	0.24	0.19	0.19	0.23	0.26	0.24
Turbidity (NTU) after filtration	**0.15**	**0.15**	**0.14**	**0.13**	**0.14**	**0.14**
pH before filtration	6.50	6.70	6.80	6.70	6.50	4.80
pH after filtration	**6.90**	**6.10**	**6.50**	**6.80**	**6.90**	**4.40**
Conductivity (mS/cm) before filtration	1.03	1.07	1.09	1.12	1.16	1.33
Conductivity (µS /cm) before filtration	784.00	805.00	823.00	846.00	873.00	1004.00
Conductivity (mS/cm) after filtration	**1.04**	**1.04**	**1.06**	**1.10**	**1.15**	**1.35**
Conductivity (µS /cm) before filtration	**840.00**	**853.00**	**855.00**	**888.00**	**917.00**	**1075.00**

Table A.12: Analysis results for a coagulation mixture of 40g Clay: 11M H_2SO_4

11M H_2SO_4: 40g Clay						
Dosage	**0.50**	**1.00**	**1.50**	**3.00**	**5.00**	**10.00**
Turbidity (NTU) before filtration	0.25	0.25	0.29	0.23	0.21	0.29
Turbidity (NTU) after filtration	**0.14**	**0.13**	**0.15**	**0.14**	**0.14**	**0.13**
pH before filtration	6.90	6.90	6.80	6.70	6.60	6.50
pH after filtration	**5.90**	**6.00**	**5.80**	**5.70**	**5.70**	**5.50**
Conductivity (mS/cm) before filtration	1.12	1.13	1.15	1.19	1.21	1.25
Conductivity (µS /cm) before filtration	910.00	928.00	934.00	964.00	984.00	1018.00
Conductivity (mS/cm) after filtration	**0.99**	**1.00**	**1.11**	**1.15**	**1.19**	**1.24**
Conductivity (µS /cm) before filtration	**823.00**	**855.00**	**905.00**	**915.00**	**965.00**	**1005.00**

* - over the limit of the machines capabilities

Appendix B: TREATMENT ACTIVATED BENTONITIC CLAY with ZVINPs (Second Attempt)

For this specific section, graphs and calculations were included into the methodology chapter, therefore, only some apparatus pictures and parts of the operating procedures that have not been mentioned wholly or partially during the previous chapters will be displayed.

Clay Activation

Figure B.1: Filtration of activated clay and washing with hot distilled water

ZVINPs Synthesis

Figure B.2: Formation of ZVINPs just during titration and stabilisation of ZVINPs under fume cupboard

Preparation of ZVINPs:

A volume of 584mL water was used in order to prepare 0,5M solution of sodium borohydride.

$m_{NaBH4} = 11{,}1g$ And $M_{NaBH4} = 38g/mol$

$n = \frac{m}{M} = CV$ Thus $\frac{11{,}1g}{38g/mol} = 0{,}5M \times V_{H2O} \Leftrightarrow V_{H2O} = 584mL$

Alternatively, 1L water was used to prepare 0,28M solution of iron chloride tetra-hydrate

$M_{FeCl24H2O} = 199g/mol$ And $V_{H2O} = 1L$

$n = \frac{m}{M} = CV$ Thus $0.28M \times 1L_{H2O} = \frac{m_{FeCl2.4H2O}}{199g/mol} \Leftrightarrow m_{FeCl2.4H2O} = 55.72g$

Mixing ZVINPs to clay:

The ratio is 99% clay to 1% ZVINPs

If 0.0609g clay → 99% clay

Mass of ZVINPs →1% ZVINPs $M_{ZVINPs} = \frac{1\% \times 0{,}0609}{99\%} = 0.0006gZVINPs$

The coagulant dosage weighing between 60mg to 5000mg with a linear addition of dosages in between is obtained using the equation:

$T_n = C_1 \times (h-1)d$

$T_n = a + (n-1)d$ We have n=6 samples

$T_6 = a + (6-1)d$
$5000 = 60 + 5d \Leftrightarrow d = 998mg$

$T_2 = 60 + 998 = 1698mg$
$T_3 = 60 + 2(998) = 2036mg$
$T_3 = 60 + 3(998) = 3024mg$
$T4 = 60 + 4(988) = 4012mg$
$T_5 = 60 + 5(998) = 5000mg$

Table B.1: Volume of sulphuric acid to be used to activate clay

Concentration	VH_2SO_4	VH_2O	**Clay** $mass: 200g$
-	-	1L	200g bentonite
18.4M	400mL	1L	200g bentonite
5M	272mL	1L	200g bentonite
3M	163mL	1L	200g montmorillonite
0.5M	27mL	1L	200g montmorillonite
0.1M	5.4mL	1L	200g montmorillonite

Table B.2: Dosage ratio of catalysts

Jar testers	**Weighed mass of clay(g)**	**Weighed mass of ZVINPs(g)**
1	0.061	0.0061
2	1.048	0.0106
3	2.036	0.0206
4	3.024	0.0305
5	4.012	0.0405
6	5	0.0505

Analysis calculation:

Concentration of ammonium chloride:

$$n = \frac{m_{NH4CL}}{M_{NH4CL}} = CV \Leftrightarrow C = \frac{m}{M} \times 1L$$

$$C_{NH4CL} = \frac{3.811g}{53.5g/mol} \times 1L = 0.0712mol/L$$

$$C_{STANDARD}V_{SATANDARD} = C_1V_1 \Leftrightarrow C_1 = \frac{CV}{V_1} = \frac{0.0712 \times 0.2}{50.2} = 2.8.10^{-4}mol/L$$

To determine the mass concentration:

$$n = \frac{m}{M} = CV \Leftrightarrow m = CVM = (0.00028 mol/L) \times (0{,}0502 L) \times (53{,}5 g/mol) = 7{,}5.10^{-4} g/1L$$

From those calculations a general table can be drawn (Table 4.3) to relate the concentrations obtained with the absorbance value that was displayed from the spectrophotometer:

Baseline is the measurement of I_o as a function of λ using a cuvette with only a solvent. Sample reading is the measurement of I as a function of λ using the cuvette with a sample.

According to Lambert Beer law, light goes through a number of cuvettes.

$I_o = I_o.10^{-kL} k = \varepsilon C$

$I = I_o.10^{-\varepsilon CL}$

$\frac{I}{Io} = 10^{-\varepsilon CL} \Rightarrow \log\frac{I}{Io} = \varepsilon \times C \times L =$ ***absorbance***

And the transmittance **T** will be:

$T = \frac{I}{Io} = 10^{-A}$

Transmittance (***T***) which is the ratio of the radiant energy transmitted to the total radiant energy incident on a given substance:

A: Absorbance (dimensionless)

ε molar absorptivity with units of L mol-1 cm-1

C: Path length of the light that passes through the solution into the cuvette (cm)

L: Concentration of the compound in solution, expressed in mol L^{-1}

Table B.3: Absorbance results

VNH_4Cl mL	***C***NH_4Cl **(mol/L)**	***V***$_T$ mL	***Mw***t (g/mol)	***C***$_{Standard}$**(mol/L)**	***C***(g/L)	**Absorbance**
0.0	0.0712	50.0	**0.0**	0.00000	0	0.0
0.2	0.0712	50.2	**53.3**	0.0002	0.0008	0.0002
0.4	0.0712	50.4	**53.3**	0.0006	0.0015	0.0026
0.7	0.0712	50.7	**53.3**	0.001	0.0027	0.0033
1.0	0.0712	51.0	**53.3**	0.0013	0.004	0.0021
1.4	0.0712	51.4	**53.3**	0.002	0.0053	0.0021
1.7	0.0712	51.7	**53.3**	0.0023	0.007	0.002
2.0	0.0712	52.0	**53.3**	0.003	0.008	0.007
2.5	0.0712	52.5	**53.3**	0.0034	0.0095	0.001
3.0	0.0712	53.0	**53.3**	0.004	0.012	0.004
4.0	0.0712	54.0	**53.3**	0.00525	0.01519	0.0023
5.0	0.0712	55.0	**53.3**	0.00645	0.01899	0.0070

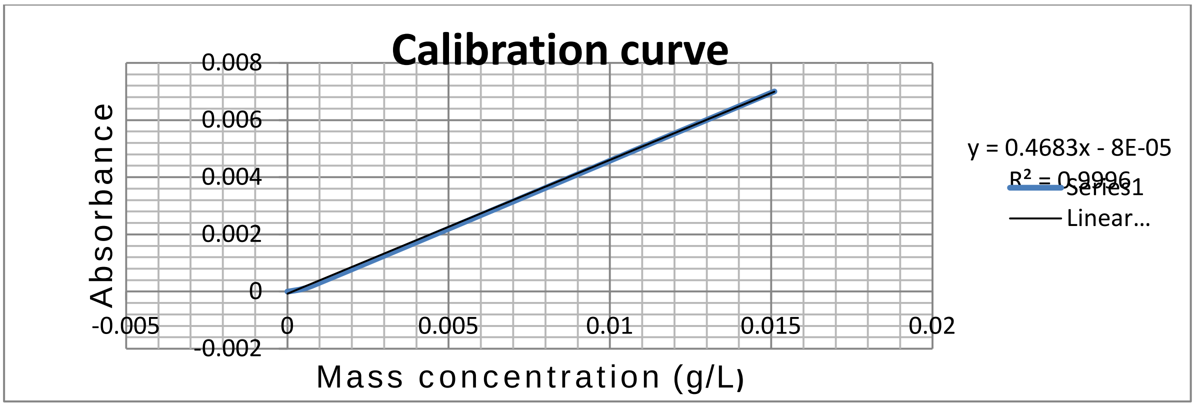

Figure B.3: Calibration curve

Above is the calibration curve trend that was obtained in order to establish the related ammonia concentration contained in the water samples that were collected after coagulation and filtration. Then after the pH (Table 4.4) of each wastewater samples were also measured, in all the jars according to different coagulant dosages that was used, so that the conclusion can be made on how the standard was reached:

Appendix C: Disposal method of waste generated

Proper disposal of wastewater is necessary not only to protect the public's health and prevent contamination of groundwater and surface water resources, but also to preserve fish and wildlife populations and other beneficial uses (e.g., water-based recreation) (Nelson et al., 2009). Failure to assess the environment can result in the development of health hazards and the degradation of living conditions, recreational areas, and natural resources that are essential to the well-being of the general public (Nelson et al.,2009). In addition, dumping of waste may not be allowed or, if it is, it may be prohibitively expensive; some form of treatment, such as dilution, neutralisation, purification or separation may be necessary prior disposal.

The following six criteria were used to design and operate the disposal system of wastewater after treatment by coagulation:

1) Prevention of microbiological, chemical, and physical pollution of water supplies and contamination of fish and shellfish intended for human consumption;
2) Prevention of pollution of bathing and recreational areas;
3) Prevention of nuisance and unpleasant odours;
4) Prevention of wastewater and toxic chemicals from coming into contact with man, grazing animals, wildlife, and food chain crops, or being exposed on the ground surface accessible to children and pets;
5) Prevention of fly and mosquito breeding and exclusion of rodents and other animals; and
6) Adherence to surface and groundwater protection standards as well as compliance with state and local regulations governing wastewater disposal and water pollution.

Taking into account the above criteria, the wastes generated during project research were treated as follow: a) the formed filtrated was washed with hot distilled water to increase its

PH, and b) the settled solids recovered after coagulation were stored in a container. Waste liquid was analysed and the mixture was then returned to the Bellville wastewater treatment plant.

Appendix D: Health and safety considerations

The Department of Chemical Engineering Bellville Campus co-operates with environmental laws set out by the government: a) OSHA (Occupational Safety Health Act 85 of 1995), and b) National Environmental Management Act (NEMA: Act 73 of 1998). These laws are intended to promote and maintain the highest degree of well-being of students. Occupational health is performed at the Chemical Engineering Laboratory by identifying hazards in order to manage risk. Once the hazards are identified, risk analysis follows, through which the level of risk and threat that the hazards pose are analysed and determined:

Table D.1: Hazards characteristics in the Chemical Engineering Laboratory

Physical hazards	Equipment failure, fire, chemical burns or cuts, ingestion of chemicals
Chemical hazards	Poisoning, allergies, chemical spills, unsafe work practice, handling equipment with contaminated gloves
Biological hazards	Diseases caused by micro-organisms in wastewater

Appendix E.1: Safety in the laboratory

- **General**

The safety rules are general and applicable to all in the Chemical Engineering Laboratory:

a) No visitor may work in the laboratory without the written permission of the Head of the Department of Chemical Engineering.

b) No person may work alone in the Chemical Engineering Laboratory outside normal hours without permission letter.

- **Protective Clothing and equipment**

Personal safety equipment: dust coat/overall, safety glasses, gloves, face shields.

Safety glasses: must be worn when working with the following: ammonia, concentrated and strong acids, strong bases, acid chlorides, all irritant substances.

Dust coat/overall: must be worn by all students at all times in the laboratory; coats and overall must be neat and clean; coats must reach down the knee; only cotton coats/overalls are acceptable.

Gloves: leather gloves (worn when handling cylinders or heavy objects), never wear when handling chemicals, cotton gloves (worn when handling hot or cold materials), insulated gloves (thermal gloves) (worn when handling cryogenic materials: solid CO_2, liquid nitrogen), plastic and rubber gloves (worn when handling corrosive chemicals like acids, bases, phenols), latex gloves (surgical gloves) (worn for the general protection of hands against samples and chemicals).

- **Fume hoods**

All dangerous and poisoning gases and materials must be handled in a fume hood to prevent the gases and vapours from entering the laboratory, the handling of CCl_4, CS_2, H_2S, and benzene.

- **Handling of glassware**

Never force glass because it cannot stretch; use holders or insulated gloves to pick up hot glassware; do not use your hands; broken glassware must be thrown in the container immediately; never clamp glassware between metal surfaces; use a suction bulb to draw liquids into pipettes; do not use your month.

- **Handling and storage of chemicals**

No chemicals may be given to anyone for any other purposes; no chemicals may be used for human consumption; read labels on chemicals (corrosive, poisoning, flammable).

Chemicals must be stored in proper locations; only take as much as you need for your test; leaving excess chemicals sitting around the laboratory creates unnecessary hazards.

- **Chemical contamination**

Chemical contamination takes place when a student is exposed to hazardous chemical released into a work space, chemicals spills, equipment failure, unsafe work practices, and contaminated gloves.

- **Eating, drinking, smoking and dressing in Chemical Engineering Laboratory**

Eating: no food is allowed in the laboratory.

Drinking: no coffee, tea or cool drinks are allowed in the laboratory.

Smoking: not allowed in the laboratory.

Dressing: wear your PPE before to enter the laboratory; use bathrooms to change.

- **Ingestion or Inhalation of chemicals**

Call emergency services, drink water or milk, and perform first aid (CPR) to the unconscious victim.

- **Chemicals burns or Cuts**

Call emergency services, flood the affected area with large quantities of water for a minimum of 15 minutes, and do not apply chemicals or ointments unless directed by a physician.

- **Laboratory courtesy**

Remove excessive reagents, but never return excess reagent to the reagent container; solids should be discarded in designated waste containers; ask before disposing of any chemicals (do not dispose organic solvents by pouring them down the sink); always clean up lab bench and make sure the equipment is ready for the next class.

Appendix E.2: Material safety data sheet of chemical used

Table E.2a: Material safety data sheet of all chemicals

Name	**Handling and storage**	**Hazards identification**	**Safety measures and first aid**	**spillage**
H_2SO_4	non-reactive acid bottles keep away from combustible store in a well-ventilated area handle in fume cupboards	reacts violently with water causes skin and eyes burns produces H_2 gas in contact with metals	add H_2SO_4 into water flush contacted area with water	neutralise the spills with lime absorbed by dry sand
$NaBH_4$	Keep away from air/ moisture store in a dry place	extremely hazardous in the case of skin contact may cause blindness	flush eyes and skin with running water do not use ointment unless prescribed by physician remove the contaminated clothes as soon as possible	use the broom to remove the solid material and dispose in waste container
Clay mineral	store in a cool area handle the substance with care	causes damage in lungs when inhaled and irritant on skin	wash hands with water and soap after contact avoid eye contact	spread with water on the contaminated surface after cleaning
ZVINPs	keep container tightly sealed store in a cool dry place, ensure good ventilation store away from oxidizing material, halogens, air,	irritating to eyes and respiratory systems irritant to skin and mucous membranes chronic toxicity: pink urine, vomiting, diarrheal, liver damage, kidneys damage	operate in fume hood PPE (gloves, coat, glasses, mask, face shield) avoid contact with eyes wash hands before breaks and after work	use the broom to remove the solid material and dispose in waste container wash the affected area with soap and water

	water/moisture store under dry inert gas (ethanol)			supply fresh air
wastewater	keep in a safe place labels containers	vomiting, can cause skin infections contain viruses, bacteria	always wash hands before breaks and after work avoids contact with eyes and skin	disinfect the affected area with soap and water
C_2H_5OH	Keep away from heat and oxidizing material store in a well ventilated space	strong oxidizing agent cause eye, skin, lever and heart damage	flammable colourless liquid flush the contacted area with plenty of water	absorb with dry sand remove all sources of ignition

Table E.2b: Hazard identification and risk assessment

Parameter	**Guide words**	**Deviation**	**Cause**	**Consequences**	**Actions**
Pressure	Low	Lower pressure	blocked outlet vacuum failure	inadequate vacuum filtration	call for assistance maintenance services
Temperature	High	High temperature	heater malfunctioning	increase the rate of reaction and helps to dissolve inorganic elements from clay structure the PH will increase as the temperature rises and nitrate/nitrite reduction will slow down	control the solution PH by the addition of acids to keep the PH low as it favours nitrate/nitrite reduction
Concentration	Less of	Less of concentration	Chemicals out of order insufficient chemicals in the	improper acid treatment of clay minerals ineffective treatment of	inform the Head of Department inform the

			laboratory	wastewater goals of research not achieved	supervisors ask for help
Catalysts loading	More of	More of dosage	increase in ratio Dosage	appropriate coagulation because the increase in catalysts content increases the removal efficiency of contaminant	continue with process operation
Mixing intensity	Less of	Less of mixing than calibrated	jar tester failure propeller malfunctioning	insufficient mass transfer of nitrates to the iron surface	call for assistance maintenance should be done fix the equipment

The standard deviation as a statistic tells us how tightly all the various examples are clustered around the mean in a set of data. The standard deviation can be small or a relatively large, depending on how the examples are pretty tightly bunched together and the bell-shaped curve is steep or are spread apart and the bell curve is relatively flat.

In this case the standard deviation determined was based on the HSVM (Horizontal standard deviation method).

Table E.2c: Statistical evaluation confirming the result obtained

	Jar 1	**Jar 2**	**Jar 3**	**Jar 4**	**Jar 5**	**Jar 6**	$\bar{X}$	$\sum\left(x-\bar{x}\right)$	σ	σ^2
0.1M - MMT	7.42	7.91	8.09	7.78	7.91	7.90	7.83	0.256	0.206	0.0420
0.1M MMT+ZVINPs	7.6	7.84	8.02	7.72	7.3	7.86	7.72	0.315	0.229	0.0525
0.5M - MMT	8.5	8	8.02	8.28	8.10	7.82	8.12	0.285	0.217	0.0475
0.5M MMT+ZVINPs	7.54	7.52	7.69	7.57	7.56	7.43	7.55	0.035	0.078	0.0061
3M MMT	7.46	7.63	7.83	7.69	7.65	7.67	7.65	0.103	0.131	0.0171
3M MMT+ZINPs	7.74	7.78	7.75	7.58	7.48	5.91	7.37	2.67	0.667	0.4450

5M bentonite	7.69	7.39	7.84	7.51	7.49	7.99	7.65	0.302	0.224	0.0503
5M bent+ZVINPs	7.5	7.46	7.46	7.46	7.43	8.18	7.58	0.432	0.268	0.0720
18,4M bentonite	7.66	4.18	2.81	2.49	2.31	2.33	3.61	22.21	1.924	3.7010
18.4M bent+ZVINPs	7.83	4.24	3.08	2.65	2.47	2.36	3.77	22.11	1.919	3.6850

Standard deviation $$\sigma = \sqrt{\frac{\sum\left(X-\bar{X}\right)^2}{N}} \Leftrightarrow \sigma = \sqrt{\frac{0.256}{6}} = 0.206$$

A population mean of 7.83 and standard deviation of 0,206 indicates that most of the values are around 7.83, and if they are not they will be +/-0.206 units between (7.83-0.206) and (7.83+0.206) = [7.62-8.03]

Variance $$\sigma^2 = \frac{\sum_{k=1}^{n}\left(X-\bar{X}\right)^2}{N} = \frac{0.256}{6} = 0.0427$$

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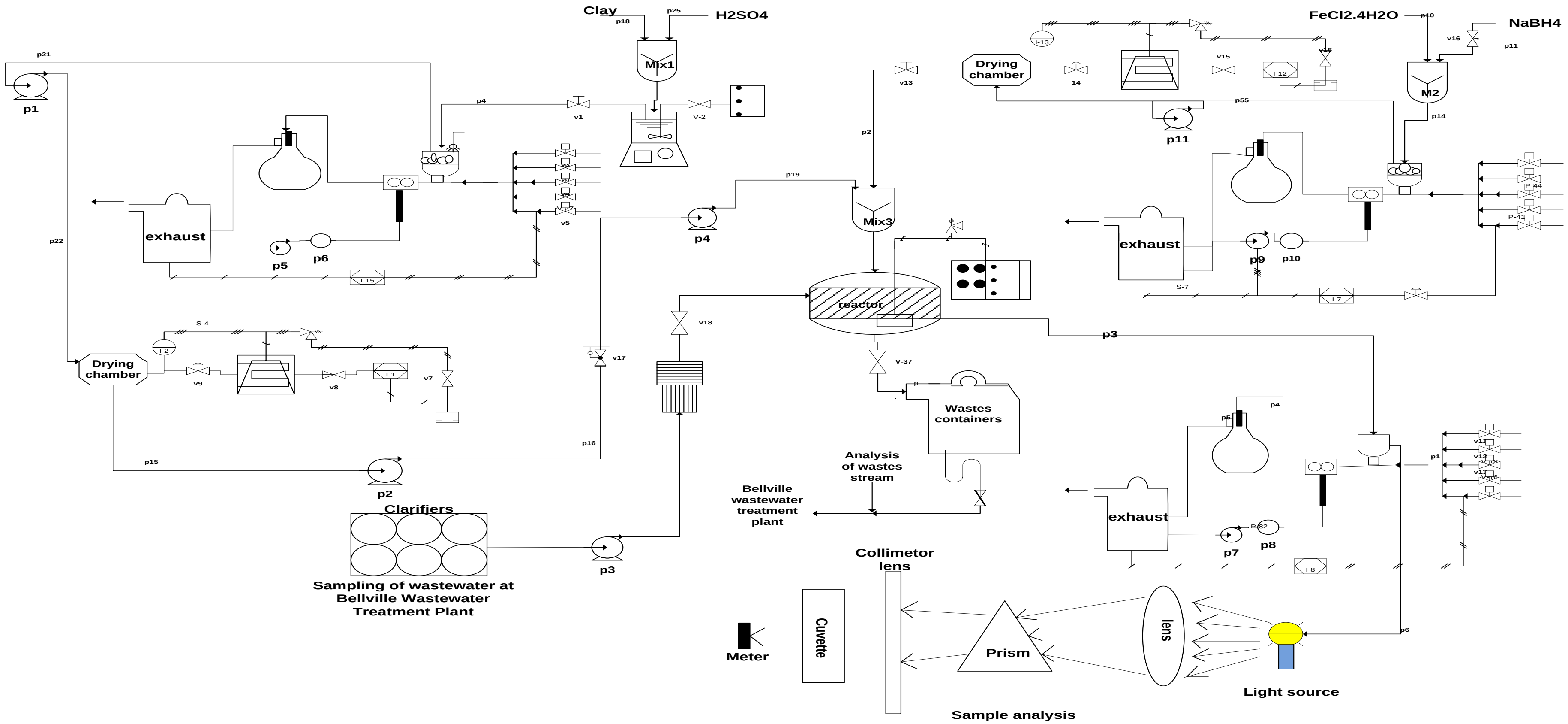

Figure D: Piping and instrumentation of wastewater treatment