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INVESTIGATING THE PHYSICAL-CHEMICAL PROPERTIES AND DETERMINING THE SUITABILITY OF CONVENTIONAL TREATMENT VERSUS ADVANCED COAGULANTS, NANO-IRON AND NANO IRON COMPOSITES IN THE TREATMENT OF COFFEE WASTEWATER FROM NESTLE’ ESTCOURT.

by

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Dissertation in fullfilment of the requirement for the degree

MASTER OF TECHNOLOGY
in
BIOTECHNOLOGY
in the
FACULTY OF SCIENCE
of
UNIVERSITY OF JOHANNESBURG

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DECLARATION
I declare that I am solely responsible for my own actions during the study and I am aware that I may be put into dangerous situations and that the supervisors are not responsible for my safety or any healthcare related costs that may incur.

I hereby declare that the dissertation that I submit under the research qualification of:

**M-TECH BIOTECHNOLOGY**

At the University of Johannesburg under the faculty of Biotechnology is my own work along the support of my supervisors. This work has not been previously submitted to other Universities for any qualification and recognition.

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DEDICATION
This project is devoted to my parents (Bonginkosi and Sibongile Duma). Many thanks for showing me the way to life is through studying, dedication and patience and for giving me the opportunity that you did not have, this work belongs to you both, my pillars.
ACKNOWLEDGEMENTS

- I would love to direct my appreciation to the subsequent people:
- Many thanks and sincere gratitude is first to the Lord Almighty for being with me thus far, giving me an enormous experience of meeting such wonderful people, experience and understanding throughout my studies.
- Specific thanks are due to my pillars of strength: my parents Sibongile Duma and Bonginkosi Duma for giving me the opportunity to be whatever I wish to be and for the support and positivity especially during the challenges I experienced during my studies but they taught me to be humble and believe in my dream.
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- The technicians and to my research group members: Dolla, Dr. Lawal, Matshidiso, Unathi and Veronica, thank you for the support.
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ABSTRACT

In South Africa, the discharging of industrial wastewater into a municipal system needs full compliance with the Department of Water and Sanitation (DWS) water effluent quality standards and failure to meet these standards is often penalised. Semiconductor photocatalysis is emerging as an advantageous technique for the treatment of many industrial wastewaters. Titanium dioxide (TiO$_2$) has been seen as one of the pre-eminent semiconductor that is capable to degrade organic pollutants in water using a light source, however difficulties arises during the recovery of the titanium dioxide also known as titania in the treated wastewater. Magnetic particles have therefore been effectively used as recyclable supports. Titania-mediated photocatalytic oxidation and reduction offers potentially a facile and cheap method for removing inorganic and organic pollutants from wastewater. This photocatalysis method has been used frequently in numerous industries to remove inorganic and organic pollutants in wastewater.

In this study, coagulation and nanotechnology studies were conducted to assess their effectiveness in reducing the number of organic, inorganic and microbiological content in coffee wastewater from Nestle Estcourt. The outcomes of this study are summarised as follows:

- The wastewater from Nestle’ coffee processing factory was studied for the physical, chemical and microbiological characteristics. This coffee wastewater's characterisation showed results that were rich in a range of inorganic compounds such as TOC, COD, phenols that arises from the ingredients (coffee bean), metals (Lead, zinc, copper, chromium, mercury, arsenic), and coliforms.
- The pH was adjusted to 6.5 using 0.1 mol L$^{-1}$ NaOH or 0.1 mol L$^{-1}$ HNO$_3$ before coagulation/flocculation experiments because the lower the pH the less effective the destabilisation process was found to be. The most effective coagulant was found to be the flocculant BUFLOC5170 when compared with the other coagulants chemicals used.
- Iron oxide (Fe$_3$O$_4$) was synthesised using the co-precipitation method and this iron oxide nanoparticle was used to prepare the hybrid composite material Fe$_3$O$_4$TiO$_2$ using Tetrabutyl Titanate as a Titania source. These two materials
were characterised using XRD, XRF, FTIR, TEM and BET. The crystal structure of the nanoparticles was anatase, spheres and rods were observed for Fe₃O₄. The specific surface area of iron increased from 79.13 m²/g to 121.49 m²/g, the agglomeration of ferrite particles reduced the pore radius by reducing the pores that could suitable in the solid.

- Iron oxide and titania composite were used to degrade pollutants in coffee wastewater; the effect of pH at (4, 6 & 8), retention time (60-480 minutes) was studied for each material.
- The homemade photoreactor was used for the titania composite photodegradation process and LED as a light source.
- The resulting water from each treatment process was studied for coliforms, TOC, colour, metals, TDS and COD because these parameters were present at high concentration in the coffee wastewater before treatment.
- The following parameters TOC, TDS, COD, and coliforms were found to be minimal in the final effluent after treatment, COD being the most removed pollutant with the average of 67% for all the chemicals used, the following formulae was used:

\[
\text{Original COD-final COD/original COD X100}
\]

\[
14454\text{mg/L-4800mg/L/14454mg/LX100}
\]

67%
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<tr>
<td>AAS</td>
<td>Atomic absorption Spectroscopy</td>
</tr>
<tr>
<td>AOPs</td>
<td>Advanced oxidation processes</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer -Emmett -teller</td>
</tr>
<tr>
<td>BOD</td>
<td>Biological oxygen demand</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>Iron oxide</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transmission infrared radiation</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma- optical emission spectroscopy</td>
</tr>
<tr>
<td>ISO</td>
<td>International organisation of standardisation</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural organic matter</td>
</tr>
<tr>
<td>NPs</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>TDS</td>
<td>Total dissolved solids</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Titanium dioxide (titania)</td>
</tr>
<tr>
<td>TN</td>
<td>Total nitrogen</td>
</tr>
<tr>
<td>TNB</td>
<td>Titanium butoxide</td>
</tr>
<tr>
<td>TP</td>
<td>Total phosphates</td>
</tr>
<tr>
<td>TSS</td>
<td>Total suspended solids</td>
</tr>
<tr>
<td>WHO</td>
<td>World health organisation</td>
</tr>
<tr>
<td>WWTPs</td>
<td>Wastewater treatment plants</td>
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<td>XRF</td>
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CHAPTER ONE

General introduction

1.1 Background

The Coffee processing industry uses enormous quantities of water that are mainly used during wet processing of coffee. In this procedure, the fruit covering the seeds/beans is removed before they are dried. The wet method requires specific equipment and substantial volumes of water. The process is more sophisticated than the dry process but leads to better quality coffee bean (Clifford & Wilson, 1985). Coffee processed by the wet method is called wet processed or washed coffee bean. It is better than the coffee coming from dry process; although the wastewater and solid waste produced can pollute the environment. Through the wet processing, more than 80% of harvest volume is left as organic waste (Novita, 2016). It is estimated that 40-45L of wastewater is produced per kilogram of coffee produced. Most of this water is used during the extraction of coffee solids in the cells.

In summary, many industrial wastewater effluents from food and beverages in South Africa do not meet minimum requirements of environmental standards of wastewater effluent that can be disposed off on land or water bodies. This is a result of the presence of solvable, persistent carbon-based contaminants and other related pollutants (Ammonia, humic acid, peptones and tannic acid) (Ilunga, 2013). The current wastewater guidelines, for example, state that the pH levels should not outstrip 6.5-9.0 (South Africa Department of Water Affairs, 2013).

Global water crises’ were ranked as the highest risk in 2016 by the World Economic Forum (WEF) and they were among the biggest threats facing the planet over the next decade (WEF, 2016). Within this context, South Africa is ranked as the 30th driest country in the world and is a high water-stressed country, with the ratio of withdrawals to supply of >80% (Figure1.1).
The idea of recycling processing water in food plants in an innovative initiative. United States through the support of Australia, Netherlands, India, Germany, France and the International Dairy Federation arranged and anticipated a revised Draft Guidelines at the 31st sitting of the Codex Alimentarius Commission (Codex Alimentarius, 1999).

1.2 **Coffee processing to coffee wastewater**

Green coffee beans are the most source of the coffee prepare and the world’s green coffee generation. Fig 1 shows the production of Robusta (*Coffea Canephora*), washed Arabica (*Coffea Arabica*) and unwashed Arabica by country. The graphic shows that Brazil is the most coffee producing country.
Figure 1.2: The world’s green coffee production for Robusta, unwashed Arabica and washed Arabica.

At Nestle’ Estcourt, the quality of Robusta, washed Arabica and unwashed Arabica are used in the manufacturing of different coffee products that are of superior quality. Wet processing in used where water is removed during roasting, then the water and solids are added during extraction and water is removed during the evaporation and drying process.

In addition, the current method results in variable COD levels and very low pH values (3.5-4.5), which can be problematic (and may have future legal implications) when discharging the treated effluent on the municipality. There are also intervals where the effluent is contaminated with caustic soda that would have been used in the cleaning process and this poses another difficulty in the pre-treatment process. Aerobic and anaerobic processes have been used on similar effluent streams; however, they were effective to a lesser extent because of the presence of toxic compounds in the coffee wastewater, which inhibited fermentative processes (Aguilera, Consuegra, 1998).
1.3. Problem statement

Coffee is the most popular beverage that is consumed by 40% of the world’s population. There are 52 coffee producing countries around the world. Coffee wastewater is an environmental problem as it acidifies the soil and is a threat to aquifers which subsequently causes an economic problem. Additionally, the untreated wastewater generates a great amount of greenhouse gases, carbon dioxide and methane (Arnott, 2014). This wastewater possesses a high polluting power due to high organics and colour coming from the various stages of coffee processing such as extraction of coffee solids. During the coffee and dairy product’s manufacturing process, numerous and very complex mixture of organic materials find their way into the waste water stream. The wastewater generated by different departments within the Coffee and Dairy products factory, is partially treated by the on-site waste water treatment plant (Four-effect falling film evaporator) before being disposed off into the community sump for further secondary handling (Majozi, 2015).

Four-effect falling film evaporator is a pre-treatment method which was installed in 2011 with the aim of primary treatment of this wastewater under study. The effluent is pumped to its first top chamber and steam is added as effluent flows down the tubes and it is evaporated @85°C until it reaches to the fourth chamber. Sludge is then removed to the Calandra and pumped to the boiler where it is used as fuel. The clean condensate is sent to the municipality for further treatment. This current method, shown in figure 2 (Four-effect falling film evaporator) is energy intensive since it uses a large amount of steam.
It is increasingly becoming necessary to recycle and reuse water as an option for the food and beverage industries as they are amongst some of the highest consumers of water. Moreover, recycling efforts have emanated from environmental concerns; constantly changing and much more stringent discharge standards set by the government for improving environmental security and friendliness in South Africa. The National Water Act No. 108 of 1998 together with the National Environmental Management Act No. 107 of 1998 (NEMA) state that everybody has the right to an environment that is harmless, this is done through sustaining, controlling and caring for our water resources (NEMA, 1998).

The European Union “The Directive 91/271/ EEC” has set clear and binding objectives aimed at preventing and protecting the quality of water. The directive requires each member to report on the state of its wastewater and the measures that have been taken (Falkenberg, 2010).

The World Water Development Report (WWDR 2017) that was launched this year in South Africa, under 2017 edition theme: “Wastewater” focuses mainly on improving water excellence by decreasing a fraction of raw effluent, increasing recycling and worldwide safe reprocess. (World water day, 2017). Therefore, this study falls within this globally and nationally relevant thematic area.
1.3.1 Aim and objectives of the study

The aim of this study is to find an efficient and economically competitive wastewater treatment technology for the by-product wastewater from the production of Coffee (Ricoffy, Ricoffy mild and Nescafe’ classic) and Dairy products (Milo, Hot Chocolate, Nesquik Chocolate and Nesquik Strawberry) from Nestle’ SA in Estcourt factory.

The goals of this project are to:

i. Explore physical-chemical possessions and microbial features of the wastewater.

ii. Perform coagulation/flocculation experiments for examination of the suitability of conventional coagulants in the handling of water discharged from Nestle’ Estcourt.

iii. Synthesise Nano-iron and Iron based nanocomposites.

iv. To conduct a cost benefit analysis on the current and proposed methods

1.3.2 Research questions

This project is proposing a way of treating wastewater from Nestle’ SA factory, located in Estcourt. This study will attempt to answer the following questions:

- Can coagulants, flocculants and Nano-iron based composites be able to remove metals, organics and microbiological contaminants that are present in the Nestle’ wastewater to meet South African wastewater discharge standards?.
- Will the process under study be more effective than the current method used at the Nestle’ factory?.

1.4 General treatment of food and beverages wastewater

There are three different wastewater treatment approaches namely chemical, physical and biological methods. In food and beverages wastewater treatment, it has been established that the principle method to remove pollutants from wastewater is by combining different treatment techniques in one treatment system. In some food industries, wastewater treatment plants do not exist and the wastewater effluent generated during the manufacturing process is directly sent to the municipal sewer, whereas others usually have some type of pre-treatment system and then further discharges to the local municipality. This type of system unfortunately can have high
connection fees which include the maintenance of the system as well as the surcharges for going over on biological oxygen demand, chemical oxygen demand and total suspended solids (Lu, Pei & Bai, 2015).

1.4.1 Coagulation
Coagulation is a process that is employed in wastewater treatment to separate suspended solids. Coagulation-flocculation has received substantial consideration for acquiescent of great pollutant removal, especially colour removal. Colour in wastewater is connected with aromatic compounds produced from the deterioration of natural materials. Water with high amount of colour is not suitable for beverages, food and dairy production as well as dyeing, paper and plastic industries. Coagulation was found to be effective in colour removal compared to other techniques based on cost efficiency (Madhavi, et.al., 2014). The chemically enhanced wastewater treatment methods have produced significant results amongst the presently employed unit processes in wastewater treatments. For example coagulation/flocculation processes have been extensively employed in the treatment of many effluent types; dyes, paints, cosmetics and food.

1.4.2 Advanced oxidation processes
Advanced oxidation processes (AOPs) involve the creation of oxidants in a reaction mixture with high oxidation potentials. The commonly used light-assisted remediation procedures are direct photolysis, deprivation with UV/H₂O₂, photolysis with ozone, and photocatalysis. Photocatalysis is a variation in the rate of chemical reactions beneath the light in the existence of a photocatalyst. These photocatalysts are sequences of complexes that yields electron-hole pairs upon the captivation of light quanta and they prompt chemical conversions in reaction to substrates that interact with them, for example: TiO₂. The application of advanced oxidation using TiO₂ nanoparticles has appeared to be the leading catalyst for water due to its good photocatalytic movement, high organic, biological immovability along with low toxicity (Lim, et.al., 2016).

1.4.3 Nanotechnology
Nanotechnology has been considered as an effective solution for wastewater problems. There are numerous phases of nanotechnology and nanoscale development research that have made it possible to come up with economically
feasible and environmentally stable treatment technologies that are able to meet the constantly changing water quality standards (Amin, et al., 2014).

Nano-iron is an environmental material that can be applied openly on a polluted area without secondary contamination. This means that this material does not create any harmful reactions with the reactants. Nano-iron has also been shown to be biocompatible and has some remarkable magnetic properties (Ali, et al., 2016).

Titanium dioxide nanoparticles represent a promising alternative regarding contaminated wastewater treatment. They have been found to be suitable for general environmental remediation, inexpensive, stable in biological and chemical environments as well as stable to photo-corrosion. TiO₂ nanoparticle is used widely for its photocatalytic commotion in oxidation/reduction reactions. The present applications for iron oxide nanomaterials in polluted water treatment can be grouped into two categories. These include the usage of iron oxide nanomaterials as a Nano sorbent or control carrier for the improvement of removal efficacy, this is the first group. The second group uses Fe₃O₄ nanomaterials as photocatalysts to separate or to transform pollutants into a a lesser poisonous form. Many technologies, conversely may apply both processes (Xu, et al., 2012).

1.5 The dissertation outline

The dissertation titled: “Investigating the physical-chemical properties and determining the suitability of conventional treatment versus advanced coagulants, nano-iron and nano iron composites in the treatment of coffee wastewater from nestle’ Estcourt” consists of 5 chapters.

Chapter one gives brief introduction to the field of wastewater treatment, its importance and history. This is followed by brief summary of the methods that were applied as well as the major objectives of the current study.

Chapter two focuses on the literature of the general treatment of wastewater to food and beverages as well as coffee processing industries. It reviews the coagulation/flocculation, advanced oxidation process and nanomaterials.

The experimental approach is outlined in chapter three where resources and procedures are clearly detailed.
The results of this study are discussed in chapter four and chapter five contains the discussion and conclusion.
1.6 References


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CHAPTER TWO

Literature review

2 Introduction

Wastewater treatment is generally a common process and is applied all over the world. The handling and disposal of effluent produced from industrial water is a challenging risk and requires careful attention. This is because if wastewater is directly sent to the river or a treatment plant, bacteria and algae will grow in it and these microorganisms consume oxygen that could eventually lead to deterioration of aquatic life and anaerobic conditions in the treatment plant. The available literature on wastewater treatment shows many well-known conventional decolourisation approaches connecting to physicochemical, organic and microbiological processes, as along with approximately the evolving techniques such as advanced oxidation methods. There are however, limited economical and technically sustainable methods to resolve this delinquent. There are typically two or three approaches that have to be joint in one treatment system in order to achieve acceptable colour, toxic heavy metals, organics and micro-organism’s removal (Saritha, et.al., 2017). Evolving a proficient and operative water contamination renovation solution, which can eliminate contaminants in an cautiously viable way, is precarious to support business, civic amenities and local government to comply with environmental regulatory necessities (Chen, et.al., 2011). In this chapter, the researcher discuss selected wastewater, the general treatment methods and review the examination of several expertise made for removing colour in coffee wastewater as well as well as the treatment of wastewater from food and beverages industries.

2.1 South African wastewater status

The source of water and sanitation means in South Africa is categorised by both accomplishments and challenges. The numerous problems that are facing the water sector in South Africa have been accentuated. The first of these is the insufficient infrastructure to the current facilities, secondly, the networks that are frequently outdated, thirdly, the inadequate or under-maintained facilities, resulting in poor quality of water and the last one is the high level of water seepage that reaches up to 45 % in some regions.
The deteriorating water superiority and increasing costs are forcing South African industries to reuse water. This is consecutively giving momentum to the industrial water and waste effluent handling chemicals market in the country. In despite of the market undergoing contests due to an uncertain economic and climate factors, the combination of stricter legislation and better environmental sentence amongst end users has improved the and recycle of waste effluent according to novel examination.

In South Africa, most of the municipalities have wastewater treatment plants originally designed for the treatment of domestic wastewater. The discharge of industrial wastewater in these treatment plants introduces difficulties within the treatment process, because of the intricate and varying nature of industrial wastewater (Bakare, et.al., 2017). The discharging of wastewater into a municipal system needs full compliance with the set standards and failing to meet these standards is often penalised by the WSA with fines. Environmental discharge can often be stricter, with operations disturbed and financial and criminal penalties imposed. Once an industrial user has treated its effluent to an acceptable disposal standard, it might realise it meets its water quality criteria process stages and decide to reuse it on-site. There are many costs associated with the water violations. Figure 2.1 shows some of the examples from a risk assessment conducted, for example, if the impact is high and the likelihood is also high, this might lead to a plant shutting down.
2.2 General wastewater treatment process

Wastewater can be classified as domestic, storm, infiltration and industrial according to its origin. The general treatment methods for treating wastewater comprises of three groups, these are:

- Biological methods,
- Physical methods and
- Chemical methods

In general, the choice of the “best” wastewater treatment system is based first on economic and technical constraints. Wastewater treatment processes moderately remove solids in wastewater and to some extent change its decomposition from highly complex organic solids to relatively stable organic solids. Primary treatment and secondary treatment usually removes Biological Oxygen Demand (BOD), Chemical oxygen demand (COD) and suspended solids (SS). However, in many effluent treatment plants, additional treatment steps have been introduced to deliver additional
organic and hard exclusions as well as for elimination of nutrients and poisonous constituents. The possibility for reprocessing of water by food manufacturers is happening at various countries such as the Netherlands (Sonune & Ghate, 2004).

2.3 Industrial and commercial wastewater treatment
The characteristics of industrial wastewater can differ extensively both within and among industries. The exact structure and capacity of industrialised wastewater differs due to the industry's production or the manufacturing plant (Bonton, et.al., 2012). Industrial wastewater can be categorised into two sections:

- Inorganic industrial wastewater: This type of effluent comes from coal, steel, blast-furnace gas and metal industries. It contains a large proportion of suspended matter.

- Organic industrial wastewater: This form of effluent contains waste materials from chemical industries, chemical works where they use organic substances for chemical reactions, pharmaceutical, glue, dye, breweries, oil refineries and paper manufacturing factories (de Sena, et.al., 2009).

This section presents the challenges and outcomes from the treatment of wastewater from industrial and commercial treatment plants.

2.4 Wastewater from metallic and non-metallic processing

2.4.1. Indium Tin Oxide
Indium-Tin-Oxide (ITO) is widely used as a transparent conductive oxide for its tremendous physical possessions and chemical possessions in numerous industrial uses for example electroluminescent displays, touch panels and windshields. It uses the etching process where the etching wastewater immersion needs to be predisposed of the minute an amount of throughputs have passed and extraneous components that contaminate the progression after numerous sequences. This wastewater is rich in metals that are of importance to the secondary source, for example copper. It also can be a probable wellbeing danger to individuals and an environmental concern if it is discarded to rivers and lakes. Chonan (2008) and Nogami (2007) stated that respiratory illnesses are related with Indium-Tin-Oxide waste. A research test site viable green development for the handling of ITO etching wastewater over retrieval of In, Mo, and Sn by liquid–liquid abstraction and retrieval of Cu Nano powder using wet
chemical procedure was industrialised. The established procedure instantaneously recovered treasured industrial (high pure) metals like Indium (In) and Copper (Cu). After the wastewater was treated with Nano powder in a liquid extraction system, it was found to be free of metals and was discharged of and recycled in the similar ITO at different etching procedural stages. (Swain, et.al., 2015).

2.4.2 Selenium
Selenium is a naturally occurring non-metal, released by different industries for example coal and mineral mining. The selenium contaminated wastewater is mainly produced from global industrial activities like coal, mineral mining, metal smelting, oil extraction and refineries. Selenium is an extremely problematic pollutant to eliminate from effluent because of its range of solubility, poisonousness, and the state of substance above diverse oxidation conditions. At low levels, it is a trace dietary element, however at high concentrations, it can bio accumulate in aquatic organisms and is a source of toxicity for many organisms, including humans (Holmesa & Gu, 2016).

2.5 Wastewater from textile industries
Textile finishing industry is a high water exhaustive industry (about 80-100 m³/ton of water per complete textile). This process results in wastewater with different pollutants; acids, bases, salts, metals and pesticides. 12 dye-baths were arranged following the company instruction and 11 wastewater samples were treated using membranes, coagulation and advanced oxidation treatment. The colour removal was found to be at 40% and COD removal at 60%, however further pilot studies would need to be investigated as studies are often carried at laboratory scale (Jerič, et.al., 2016).

2.6 Wastewater from petroleum and refineries
Petroleum industries and refineries are leading to the financial growth of countries, with wastewater containing an excessive amount of mainly oil and organic matter. Petroleum refinery discharges comprises of enormous amount of lethal and refractory aromatic compounds such as Benzene, Toluene, Ethyl benzene, and Xylene that are identified as the most dangerous composites brought out into the environment (Aranda et al., 2010).
Effluent costs, water scarcity, stern protective environmental laws and pressure for eco-friendly and sustainable practices have encouraged the petroleum refinery to
implement wastewater reuse systems (Mosera, Riccia, Reisa, Netab, Cerqueirac, Amaral, 2018).

A study on the handling of effluent coming from petroleum industries using sequencing batch reactor was conducted. The results showed a removal percentage of around 57% in COD by sonication (Kulkarni & Goswami, 2015).

The performance of direct (UV) and hydrogen peroxide-assisted (UV/H₂O₂) photolysis, applied to membrane bioreactor technology (MBR) permeate, as a pre-treatment for Nano filtration systems was conducted for the treatment of petroleum refinery wastewater. For the MBR process, a MBR pilot plant with a 90L-biological tank was connected in series to a 30L-membrane tank and operated under hydraulic retention time of 8 hours. Sludge was retained after 45 days. For oxidation tests, a Pure Pro Ultraviolet water sterilizer cylindrical reactor was used, with mercury vapour as light source. Lastly, Nano filtration experiments were performed with a Dow Film Tec NF90 membrane, consisting of three layers in a batch scale unit. The use of H₂O₂/UV pre-treatment showed that the advanced oxidation process as a pre-treatment step, not only reduced the effluent fouling potential, but also led to a higher permeate flow which changed the chemical characteristics of fouling. MBR showed a good removal in ammonia and organic compounds (> 85%) concentration. Furthermore, nitrite and nitrate concentration increases were observed due to the nitrification process. Regarding the conductivity and TDS, a low removal was observed, meaning a polishing step would be advantageous within this treatment process to comply with regulations for reusing of wastewater (Mosera, et.al., 2018).

2.7 Wastewater from pulp and paper

Pulp and paper production are among the world’s third water-consumption industries. The composition of wastewater from pulp and paper differs, but mostly being highly concentrated. The application of microbial fuel cells (MFCs) in the handling of wastewater from pulp and paper is an evolving field of research. MFCs are found to have short start-up times, generate a stable power output within a few days and they allow for a decrease in energy usage as well as clean energy production during the treatment process (Toczyłowska-Mamińska, 2017).

A study to review the limits of conventional treatment systems and the production of electricity from electrogenic microorganisms using microbial fuel cells in pulp and
paper wastewater was conducted by Wu, et.al. (2012). Of the methods studied was coagulation/flocculation with limitations resulting from environmental impacts from the production of metal hydroxide toxic sludge and the creation of greenhouse gas emissions (Wu, et.al., 2012).

A single-chamber 300-ml MFC with a graphite brush anode and air-cathode was used for the treatment of paper recycling wastewater with simultaneous electricity production in a batch mode. The substrate for the MFC was paper-recycling wastewater collected from the primary clarifier that was used both as the sole inoculum and as fuel. The paper wastewater was used as a substrate for the MFC microorganisms while anaerobic digester sludge from a domestic wastewater treatment plant was used as the inoculum for biofilm production. A COD removal in the paper wastewater-fed MFCs was 78% with a maximum current production of 125 mA/m2, which was found to be the highest when compared to the other researched wastewaters from the brewery, bakery and dairy. The overall characteristic of MFC technology seemed promising and beneficial although the pulp and papermaking effluents contained complex substrates. More research on this effluent treatment would be advantageous (Budzianowski & Budzianowska, 2015).

2.8 The treatment of wastewater from food and beverages

This section presents the challenges and outcomes from the treatment of wastewater from food and commercial treatment plants.

It has been a mandatory requirement in the food industry to implement various technologies that have minor influence on the surroundings. In the food manufacturing industry, the key ingredients which are needed in making the product that are healthy and safe for consumers consists of water, resources, and energy. One of the biggest challenge is to purify effluent and reduction of pollutants from effluent while using a technology that is sustainable and inexpensive. The food-manufacturing sector, the capacity of effluent disposed off and wastewater characteristics varies according to the product type and process used (Chellapa, et.al., 2015).

The capacity of requisite water in food processing industries is high; this water is used for washing, cleaning of equipment, conveyor of raw materials and sanitizing plant machinery. This discharge contains suspended solids, organic matter, nitrogen, fats, oils, and additional inert constituents (Hegde, et.al., 2018). High feature of (portable)
water is required for production. The foremost difficult in these divisions is the handling of the effluent to make it suitable for discharging into water bodies or be recycled back to the process. This effluent from food industries is nutrient-rich and its disposal to water bodies or surface water is a serious ecological problem (Bharati, et.al., 2017).

### 2.8.1 Dairy processing

Dairy industries release wastewater from water used for washing equipment, machineries leakage and washing processes. Water is also released from cooling, air conditioning, boilers, sanitation, and chemical cleaning of equipment before and after the cleaning. These effluents have organic nitrogen in elevated form and some ions; NH$_4$+, NO$_2$−, and NO$_3$− (Meneses, et.al., 2017). The most communal liquid discharges comprise that comes from dairy product’s manufacturing, whey from tofu manufacturing, bakery wastewater coming from washing of tools, brewery discharge, oil discharge and juice production discharged water. (Hegde, et.al., 2018).

The handling of waste effluent from dairy production in Turkey was assessed using chemical coagulation with (Ca (OH)$_2$, Al$_2$ (SO$_4$)$_3$·18H$_2$O, FeCl$_3$·6H$_2$O, and FeSO$_4$) as coagulants, Fenton’s experiments, Ozonation and activated sludge inhibition tests. The dairy industry is the largest source of food processing which involves milk production and milk processing. In Turkey, the amount of milk produced is expected to be around 17 million lots yearly. Wastewater samples were collected from the homogenization tanks of the dairy plant. Iron sulphate (FeSO$_4$) was found to exhibit higher performance, according to the COD parameter in the dairy wastewater treatment. The inhibition test showed that raw dairy wastewater had poisonous and inhibitory effects on the activated sludge mixture. Ozonation was found to be efficient but was not a practical solution for the pre-treatment alternate before discharge whereas the best results were from Fenton’s experiments with efficiency of COD removal >69 % (Sivrioglu & Yonar, 2015).

### 2.8.2 Brewery processing

Wastewater from breweries contains high levels of organic contaminants with Chemical Oxygen Demand ranging from 2000 to 6000 mg/L and Biological Oxygen Demand ranging from 1200 to 3600 mg/L. These need to be treated in order to avoid landfilling or incorrect handling that can result in higher greenhouse gas emissions and other forms of pollution such as soil pore clogging. The treatment of this
wastewater by municipal treatment plants represents a very significant cost to brewery operators (de Diego-Díaza, Fernández-Rodríguez, Vitas, Peñasa. 2018).

In the beer manufacturing, the main sources of effluent are water consumed within the practices, water used for cleaning. The amount of wastewater produced per volume of beer produced is high. Advanced oxidation treatment processes (AOP) are widely used in wastewater treatment especially in alcohol distilleries, which generate almost the same type of effluent as the brewing industry, with high levels of organic compounds. The production process in distilleries is almost the same as in breweries because they both involve fermentation. Ozone, hydrogen peroxide and ultraviolet irradiation are used to produce hydroxyl radicals (•OH) during the first stage of the oxidation. In the second stage, hydroxyl radicals (•OH) react with organic contaminants to produce precipitates (Jaiyeola & Bwapwa, 2015). The composition of wastewater produced from the brewery fluctuates as a result of the various processes that take place within the brewery.

A study to assess the performance of two laboratory-scale aerobic sequencing batch reactors (SBRs) under two schemes (continuous low aeration and cyclic aeration) was conducted. The aim was to find their feasibility in the treatment of wastewater generated from a local brewery in Durban, South Africa. Wastewater pollutant strength was determined by characterisation of the wastewater samples collected from the brewery before any further treatment and then the performance of the two reactors was investigated. The samples collected for the operation of the two sequencing batch reactors were carried out once a week, fed into the SBRs and treatment proceeded immediately. Samples were collected daily and the adaptation of the activated sludge in brewery wastewater after inoculation was 21 days. The two sequencing batch reactors were seeded with equal volumes of activated sludge and were fed with brewery wastewater without aeration and mechanical mixing during the filling period. The performance of the sequencing batch reactor which operated under continuous low aeration scheme was found to be higher than that of the sequencing batch reactor which operated under cyclic aeration scheme in terms of the chemical oxygen demand and biological oxygen demand reduction (Bakare, et.al., 2017).
2.8.3 Meat and poultry

In the manufacturing of meat, poultry, and seafood, the resulting effluent contains protein and nitrogen. This emanates from the slaughtering and translation processes that produce plasma as derivatives and effluents, that are high in Biological Oxygen Demand (BOD) coupled with pathogenic organisms that can spread and high Chemical Oxygen Demand (COD). Poultry by-products and waste contains several different species of microorganisms including potential pathogens such as Salmonella sp., Staphylococcus sp., and Clostridium (Bakare, et.al, 2017).

A research study on the handling of poultry slaughterhouse effluent in Eskisehir, Turkey by means of electrocoagulation was conducted. The rationale for the study was the reduction in the accessibility of freshwater resources and environmental concerns when this kind of effluent was discharged into the rivers. Wastewater collected samples were subjected to screening followed by electrocoagulation experiments in a constant flow reactor. The poultry slaughterhouse effluent treatment was found to be effective with the use of peroxo electrocoagulation. The COD elimination efficacy was 95.48% and an improved pollutant removal was observed (Eryuruk, et.al., 2018).

2.8.4 Acid and preservatives

Citric acid is extensively found from food and beverages production. The wastewater produced from citric acids has low pH values (4-4.8) and high COD values (15000-20000mg/l) per ton of citric acid. The most common method for this wastewater treatment is anaerobic digestion and further treatment by the municipality. The main problem with this method is that a large portion of sludge is produced and treatment costs are high. This makes the handling of the wastewater from citric acid production difficult to manage (Wang, et.al., 2014).

A combined citric acid methane-fermentation method was established using an industrial strain (A. Niger-H519), shake flask citric acid fermentations, and an up flow anaerobic sludge blanket (UASB) reactor followed by ultrafiltration and Nano filtration. Within this treatment combination, water produced was similar to water from the tap in colour and in terms of quality characteristics (Zhang, et.al., 2017).
2.9 Wastewater from coffee processing

This section presents the challenges and outcomes from the treatment of wastewater from coffee.

Coffee is one of the most popular beverages in the world and the second merchandised product after petroleum (Dadi, Mengistie, Terefe, Getahun, Haddis, Birke, Beyene, Luis & Van der Bruggen, 2018). It is produced using the wet processing method. This method is well known for producing coffee of superior quality. This is called wet process and also referred to as (washed coffee) since water is the principal resource for moving coffee through the process and for creation of the extracts and permitting for the elimination of deficiencies that drift over the surface (Garde, et.al., 2017).

Coffee processing wastewater contains wastewater that is an environmental concern. This wastewater is acidic and has high concentrations of organic pollutants like pectin, proteins, caffeine, soluble salts, and sugars, Biological Oxygen Demand (BOD) values between 8000-20000mg/l and higher in Chemical Oxygen Demand (COD). The great sourness of this effluent lessens the lifespan of oxygen in the water bodies; rivers and sewers it is joining and the mixture of high acidity and high BOD that surpasses self-cleansing volume of rivers (Kulandaivelu, et.al., 2012).

Haddis & Devi (2008), conducted a study in Jimma Zone, Ethiopia which was on the effects of effluent coming from a coffee manufacturers, on human health and the environment.

Garde et. al (2017) used Moringa Oleifera germ extract in the handling of coffee fermentation effluent and concluded that the use of Moringa Oleifera seed extract in coffee fermentation effluent was a promising technology but it could not be a stand-alone process. This is because the scaling up of this process is time intensive and the process is a pre-treatment process where Total Suspended Solids (TSS), insoluble Chemical Oxygen Demand levels and microbial bacteria were reduced to a certain level. The process was able to remove nitrate and nitrite in wastewater. However, a disadvantage to this is that M. Oleifera needs to be easy to process into Moringa Oleifera seed extract and needs to be available in tolerable ranges to handle volumes of coffee wastewater. An additional disadvantage is that, with coagulation the wastewater needs to be neutralized before adding Moringa Oleifera seed extract or
the coagulant used, the optimum pH for pollutant removal is found to be at 5 and 6 (Garde, et.al, 2017).

Despite pH adjustment, microorganisms may possibly acclimatise in acidic conditions excluding at COD high concentrations. The aerobic and anaerobic processes have been used for coffee wastewater treatment. Results showed a low effectiveness and this is owing to the existence of toxic compounds hindering fermentative processes in the coffee wastewater. In addition, anaerobic process can only achieve stability after 28 days (Aguilera & Consuegra, 1998).

Anaerobic digestion is commonly used for the recovery of bioenergy from wastewater while treating suspended solids (SS). This bio-waste has received much attention as a co-substrate to enhance biogas production. Carvalho, Fragoso & Duarte (2017) studied the improvement in efficiency of SS bio-methanization by the addition of the drained coffee bio-waste liquid fraction in anaerobic digestion trials. The addition of the co-substrate led to 3 times higher specific methane production as well as improvements on the biogas production rate. It was clearly demonstrated that the feeding mixture composition had a significant influence on methane yields, suggesting that the co-substrate, balances the low SS bioconversion, contributing to wastewater treatment plant's energy self-sufficiency (Carvalho, et.al., 2017).

Anaerobic fixed bed reactors have been successfully applied for the treatment of different types of residual water due to their ability to retain microorganisms (Novita, 2016).

Another study used three anaerobic reactors filled with blast furnace cinders, polyurethane foam and crushed stone for the treatment of wastewater from coffee bean processing and when foam was used, adequate performance was achieved.

A study explaining the effects of coffee processing residues, has on the anaerobic microbes and digestion performance was conducted by Rojas-Sossa, et.al. (2017). Nine reactors were used in this study with 17 mL feed being nourished and purged with Nitrogen on a daily basis. Biogas production was measured and the digested samples were analysed for total solids and volatile solids. The digestion performance and metagenomics concluded that microbial communities were related to feeding
conditions. The more microbes were fed on the system the higher the digestion performance (Rojas-Sossa, et al, 2017).

When coffee wastewater was treated by coagulation-flocculation in combination with UV/H$_2$O$_2$, a COD reduction of 86% was achieved. However, when the same wastewater was treated by chemical coagulation–flocculation alone, a reduction in COD (67%) was achieved. The raw coffee wastewater showed that at pH 4.6, the system with Ecofloc 6260 as the flocculent in combination with the coagulant T-1 gave the greatest reduction in COD (55%–60%). The use of various coagulants and flocculants in the chemical coagulation-flocculation treatment of this coffee wastewater was assessed by measuring the separation of suspended solids from the wastewater as the coagulant and flocculants were added. In addition, the combination of lime (1.0 g) and coagulant T-1 (8 mL) at pH 4.6 gave even a better reduction in COD (about 67%). The results showed that the use of chemical coagulation-flocculation treatment in conjunction with UV/H$_2$O$_2$ photo oxidation, a COD reduction percentage of 86 was achieved, but required a long irradiation time of 120 min (Zayas, et al., 2007).

2.10 Treatment methods

The treatment of wastewater is key to sustainable and acceptable industrial growth. In addition, the treatment methods may vary with the wastewater characteristics (Kulkarni, et al., 2015). As per global environmental protection concerns, manufacturing sites are discovering innovative resolutions for evolving expertise that can ease eco-friendly damages (Verma, et al., 2012). Chemical, biological and physical methods are the general treatments that are being used by researchers. The most efficient way to remove pollutants in wastewater is by combining different treatment processes in one treatment system as stated by Saritha et al. (2017).

Physical methods are where physical forces are applied to remove dirt form wastewater for example screening and sedimentation. Chemical methods are designed to bring some form of chemical reaction in a wastewater treatment system, for instance adsorption and disinfection. The biological process uses microorganisms, particularly bacteria to change the colloidal and organic substances for example activated sludge and anaerobic digestion process (Metcalf & Eddy, 2003).
2.10.1 Theory of coagulation/flocculation process

In industrial wastewater, chemical coagulation-flocculation is widely employed for the removal of waste materials in a suspended or colloidal form and for reducing its COD content. This process has received substantial courtesy for acquiescent high contaminant elimination, especially colour elimination (Zayas, et.al., 2007).

A research study on the handling of fish canning wastewater was conducted using coagulation-flocculation process, with different coagulants, such as Aluminium sulphate and lime. This proposed system was found to be promising for re-using the fish canning wastewater in the process plant water and it was concluded that conducting a large-scale experiment would be advantageous for both environmental and economic benefits (Cristóvão, Botelho, Martins, Loureiro & Boaventura, 2015).

Cardboard plant wastewater (CPW) was purified using electrocoagulation (EC) using aluminium conductors and the thickness (CD), operational time (t), and initial pH (pHi) on the wastewater was studied. The outcomes indicated an optimal handling circumstances between these parameters ;CD: 7.5 mA/cm², pHi: 7.0 and t: 60 min partly removed total organic carbon (TOC; 17.1%) and chemical oxygen demand (COD, 14.2%), but for turbidity, the removal efficiency was at its highest (98.7%). A secondary treatment was therefore introduced based on the results obtained on the primary treatment process. The primary wastewater was exposed to electro oxidation by using a boron nobbled diamond conductor. The results showed a greater TOC (83.7%) and COD (82.9%) elimination efficacies under the optimal handling settings (CD: 100 mA/cm², pHi: 7.2, Ce: 5.0 g/L Na₂SO₄ and t: 180 min). Gengec (2017)'s study revealed that the grouping of electrocoagulation with electro oxidation had an adequate possible for tangible manufacturing effluent with an elevated organic content, suspended solids and poisonousness. This referred to handling of exceedingly poisonous cardboard plant effluent by the mixture of electrocoagulation and electro oxidation practices (Gengec, 2017.)

The efficiency of dissolved air flotation (DAF) and advanced oxidation processes (AOP) through photo-peroxidation (H₂O₂/UV) and Photo-Fenton reactions were assessed in a laboratory scale system for the handling of the meat wastewater in Brazil. This meat processing plant generated about 350m³ of wastewater per hour from slaughtering, processing of swine and poultry activities. Plasma is the most
challenging constituent, since it has a capability to prevent floc creation. The presence of blood from the meat processing wastewater inhibited coagulation/flotation. The chemicals were sited onto the flotation cell to stimulate the coagulation development and organic matter removal was high with DAF. The effluent was found to be rich in organic contents and turbidity due to the presence of blood (de Sena, et al., 2009).

2.10.2 Theory of advanced oxidation processes

The term advanced oxidation processes (AOPs) denotes precisely on procedures in which oxidation of organic pollutants arises mostly over responses with hydroxyl radicals. In the handling of water, AOPs typically denote to a precise subsection of processes that include O₃, H₂O₂, UV light and TiO₂ catalysis. The handling of radical effluent may be distributed into three groups:

• Tertiary handling: any treatment process in which unit operations are added to the flow scheme following conventional secondary treatment.
• Physicochemical treatment: a treatment process in which biological and physical-chemical processes are intermixed to achieve the desired effluent.
• Combined biological-physical treatment: a process where biological and physicochemical treatments are combined (Sonune & Ghate, 2004).

The advanced oxidation technology is used for removing low levels of persistent organic pollutants and sterilizing microorganisms in water. It has been widely tested with traditional ultraviolet light and later using solar light, in an environmental remediation process called photocatalysis. Semiconductor photocatalysis is emerging as an advantageous technique for the treatment of many effluents. This is an advanced oxidation process that couples ultraviolet light with semiconductor technology as a photocatalyst and has been widely studied for the removal of pollutants from air and water (Zhuang, et al., 2016).

Photocatalysts have been proven to be effective reaction inducers involved in reducing environmental pollution. Photocatalytic degradation under visible-light irradiation has gained widespread attention because it is rapid, highly efficient, and economical and causes no secondary pollution.

Jo & Tayade (2014)’s study focused on recent progress of the degradation of dyes in water under Light Emitting Diodes (LEDs) light irradiation. LEDs are small, do not comprise of mercury, have an extensive lifecycle compared to conventional light
sources, functions on a straight current and are ecologically friendly. These possessions of LEDs suggests new alternates to old-fashioned ultraviolet lights and opportunities for photocatalytic deprivation using compact power consumption. In the case of using mercury lamps, they contain hazardous mercury, difficult to operate, have shorter lifespan. The solar light requires a very large area for the effective application and high source installations as well as limitation to daylight hours. Additionally, future predictions and difficulties for the application of LEDs for photocatalytic ecological contaminant deprivation have been emphasized (Jo & Tayade, 2014).

The success of solar-driven photocatalytic processes in water de-contamination depends on the semiconductor’s ability of absorbing visible and infrared light, along with its ability to overturn a fast mixture of photo-generated electrons and holes. Titanium dioxide (TiO₂) is widely used as a photocatalyst because it is inexpensive, stable in biological and chemical environments. It has also been found to be most suitable for environmental remediation.

The biofabrication of Fe nanoparticles using *Hibiscus sabdariif*a (HS) red flower extract under photocatalytic conditions was studied by Zazoulia, Ghanbarib, Yousefid & Madihi-Bidgolie (2012). *Hibiscus sabdariif*a is an effective stabilizing agent without the addition of a stabilizer or capping agent. The aqueous extraction solution of *Hibiscus sabdariif*a and FeCl₃ was used for the preparation of Fe nanoparticles.

The handling of waste effluent from food dye manufacturing was done using Fe₃O₄ and TiO₂ nanoparticles under UV light irradiation. Fe₃O₄–TiO₂ nanoparticles (FTNs) were prepared by a simple method (precipitation titration using ammonia). All photocatalysis experiments were conducted in a cylindrical reactor made of quartz with a height of 15 cm and diameter of 7. For comparison of the different UV sources, two low pressure UVC lamps (6 W-Philips), 12 UVA-LEDs (1 W, 365–370 nm) and 12 UVC-LEDs (1 W, 254–258 nm) were used for light irradiation under similar conditions with photocatalysis experiments with low pressure UVA lamps. Comparing with UVA irradiation, UVA-LED provided a higher degradation rate since complete decolourization was achieved in 40 min reaction time while 60 min irradiation time was required for UVA system to complete decolourization. UVC irradiation performance
was better when compared to UVA irradiation (Zazoulia, Ghanbarib, Yousefid & Madihi-Bidgolie, 2012).

In the beverage industry, water is used as an ingredient, an initial and intermediate cleaning source, an efficient conveyor of raw materials, and a principal agent for sanitizing plant machinery and work areas. These effluents contain high concentrations of organics due to the use of raw materials, such as oranges, grapes or sugar (Al-Mutairi, et.al., 2004). The mineralization of actual beverage wastewater effluent was studied using a continuous ferrioxalate-induced solar Photo-Fenton process as an alternative to conventional anaerobic digestion or as a rapid pre-treatment step (to reduce the total treatment time). Physio-chemical pre-treatment of the raw wastewater was performed using precipitation and sedimentation to improve the photocatalytic treatment efficiency. Under optimal conditions, 70.6% and 96.6% of total organic carbon (TOC) was removed from industrial effluent with 1386.8 mg/L of initial TOC after 55 and 125 min. The treatment process completely removed the toxicity and COD and removed 99.8% of the BOD (Duran, et.al., 2015).

2.10.3 Theory of Nanoparticles

Nanotechnology has been considered as an effective solution for wastewater problems. Nanoparticles can be made from organic and inorganic materials (Sadeghi, et.al., 2017). Conducting a risk assessment of nanoparticles, displays results that some nanomaterials disturb severely on social health and on the atmosphere. There are four stages need used on the study of the risk level of nanoparticles; this is shown in (Figure 2.2).
There is a limited number of research that is done concerning the practise of Nanotechnology in the food production. The utmost research was conducted in the United States, Japan, and China from 2013. In wastewater treatment and water purification, Nanotechnology offers an efficient method for the removal of pollutants and microorganisms. The ecological chance and poisonousness of these materials are precarious concerns in terms of choosing the material and project for water refinement. Nanotechnology was observed to be better than other methods at laboratory scale but currently the information about their eco-friendly destiny, carrying and poisonousness is at initial stages (Tiwari, et.al., 2008).

A study validating enhancing solar absorption by introducing disorder in the surface layers of Nano phase Titanium dioxide (TiO$_2$) through hydrogenation was conducted by Chen, et.al. (2011). The Nano phase TiO$_2$ was used because of the large surface area and its ability to facilitate a fast rate of surface reactions. TiO$_2$ was prepared with a precursor solution consisting of titanium tetraisopropoxide (TTIP). The dried Titanium dioxide samples (white coloured powder) were kept in a vacuum and hydrogenation was then carried out in a 20.0 bar H$_2$ atmosphere. The titanium crystals structures were investigated before and after hydrogenation using these characterisation techniques: TEM, SEM, XRD and RAMAN (Chen, et.al., 2011). Hydrogenation of the TiO$_2$ material made a disorderly coat on the nanocrystal surface,
followed by a dramatic colour change. The solar driven photocatalytic activity was assessed by observing the modification in visual immersion of a contaminant from the dying process. The complete photo degradation was complete after 8 minutes and for the black crystals, it took an hour.

Vu, et.al (2017) developed the hydrothermal method through a mixture of mesoporous products imparted with metallic oxide nanoparticles and titanium nanoparticles for the use in water treatment. The produced samples were verified for their ability to remove carbon-based dye and smidgeon metals. The infused nanoparticles (black powder) had a change in the absorbent arrangement of the mixture. The size of their pores was much smaller and there was a higher adsorption rate for the blue dye when compared to pure TiO$_2$ nanoparticles (Vu, et.al., 2017).

A study for the removal of caffeine from water was conducted using a irresistible cobalt with carbon nanocomposite (CCN) arranged from carbonization of a cobalt based Zeolitic Imidazole Framework crystals (ZIF-67). ZIFs represent a superior class of Metal Organic Frameworks (MOFs) due to their zeolitic arrangements and excellent steadiness. Caffeine is one of the most common pharmaceutical that is used in food, beverages and medicine. Wastewater resulting from the caffeine is difficult to treat and there are various methods that have been used. The advanced oxidation processes being the most preferred method as they can destroy recalcitrant and non-decomposable biological contaminants in a small period using extremely sensitive oxygenic classes for instance ozone, hydroxyl and sulphate radicals. Batch-type experiments were conducted for the elimination of caffeine using ozone. Model aliquots were taken out of the solution and the remaining attentiveness at definite intervals was studied by means of UV-Vis. TOC analyser was used to study the organic concentration of caffeine. The UV-Vis spectral variation of the caffeine constituent revealed that caffeine was slowly removed from water. (Lin & Chen, 2016).

(Guo, et.al., 2015) made use of cobalt sulphate to initiate ozone for the deprivation of caffeine and they concluded that the straight tallying of cobalt ions might be a hazard as it turned out that cobalt ions cannot be recuperated thereby and this will result into secondary contamination.
The removal of lead ions from aqueous solution using copper Nano composite catalysts was studied. These Nano composites were prepared in a laboratory and their efficacy was tested using the adsorption process. These tests were conceded out in a collection arrangement, using 50 mL solution containing 10 ppm of lead solution and 0.1 g of adsorbent at room temperature at pH adjusted to 8. The prepared Nano composites appeared to be effective for the removal of heavy metal ions at pH ranging from 5 to 10, which is also a promising method for wastewater treatment (Said, et.al., 2017).
2.11 References


3. Introduction

The purpose of this study is to evaluate the use of coagulants, advanced oxidation process and nanocomposites in the treatment of wastewater from Nestle’ Estcourt. The Nestle Estcourt factory, located in KwaZulu-Natal is an “Instant Beverages Manufacturing Company”. This chapter describes the materials used, preparation of samples, analyses techniques, and methods used for characterisation.

3.1 Materials and chemicals

The substances that were part of this project were bought from Sigma-Aldrich

**Table 3.1**: Chemicals used in this research project

<table>
<thead>
<tr>
<th>NAME</th>
<th>FORMULA</th>
<th>HAZARDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (III) chloride tetrahydrate</td>
<td>FeCl$_2$.4H$_2$O</td>
<td>Harmful if swallowed &amp; May be corrosive to metals</td>
</tr>
<tr>
<td>Iron(III) chloride hexahydrate</td>
<td>FeCl$_2$.6H$_2$O</td>
<td>Corrosive &amp; Acute toxicity</td>
</tr>
<tr>
<td>Tetrabutyl Titanate(titanium butoxide)</td>
<td>Ti(OBU)$_4$</td>
<td>Flammable &amp; Corrosive</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>NH$_2$.NH$_2$</td>
<td>Flammable, Corrosive, Acute toxicity</td>
</tr>
<tr>
<td>Anhydrous ethanol</td>
<td>C$_2$H$_2$O</td>
<td>Skin irritant</td>
</tr>
<tr>
<td>Ammonia solution</td>
<td>NH$_4$OH</td>
<td>Corrosive</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>Corrosive</td>
</tr>
<tr>
<td>Sodium hypochlorite</td>
<td>NaClO</td>
<td>Corrosive</td>
</tr>
</tbody>
</table>
3.2 Experimental methods

3.2.1 Chemical characterisation of the waste water

Sampling of the wastewater was done according to the South African National Standards for sampling and analyses. It was carried out in a SANS 17025:2005 accredited lab. Samples were analysed as soon as possible after collection.

i. Determination of trace elements using ICP-MS

The samples were introduced into a radiofrequency plasma. The ions were extracted into the plasma. The calibration curve was determined using the blank and calibration solutions and after the calibration curve was checked for validity with a reference sample. Total Organic Carbon, Chlorine, Chemical Oxygen Demand, Total suspended solids was prepared using the pH meter, Spectro quants colorimeter move 100 and TOC analyser.

ii. Determination of turbidity, colour and pH in water

The instrument (optical turbidimeter for turbidity and pH meter for pH) was well calibrated and measurements were conducted on well-mixed sample. Turbidity values were recorded from the instrument.

3.2.2 Microbiological characterisation of the waste water

A computation of viable heterotrophic bacteria were studied as biological parameters. Faecal coliforms, total plate counts and pathogenic *Escherichia coli* (*E. coli*) were analysed using membrane filtration. Before examination, the flasks were cleaned with alcohol and glassware was sterilised by autoclaving at 121°C for 30 minutes. The samples were poured (100 mL or 250 mL) in a sterile, transparent, non-fluorescing flask with screw cap.(e.g. Idexx WV120SB 200 or WV290SB 100). The content of one pack of pre-measured reagent (WP for 100 mL or WP250 for 250 mL was added. These were incubated at 36°C for 26 hours. Yellow equal to or greater than the comparator is positive for total coliforms, Yellow and fluorescent equal to or greater than the comparator is positive for *E.coli* and colourless is negative for both.
3.2.3 Characterisation of Nanomaterials

3.2.3.1 X-ray diffraction

The usage of X-ray diffraction was for attaining organizational data of the crystalline solids. Bragg and Bragg (1913) established a correlation analysis to describe the appearance of the cleavage in the crystals and to imitate X-ray beams at definite angles of incidence (theta). X-ray diffraction technique is most useful in the characterisation of crystalline materials such as ceramics, metals, intermetallic, minerals, and inorganic compounds. When X-rays interrelate with a crystalline substance (phase), a diffraction pattern is attained.

X-ray diffraction (XRD) was used for the arrangement of atoms in the crystals, diffractometer with Cu-Ka radiation at $\lambda \approx 0.154$ nm operating at 40 kV and 40 mA over the 2 range 0–80. The XRD measurements were carried out using an E’xpert Philips apparatus at room temperature coupled with Cu Kalph radiation beam (0.1540 nm) polychromatic beam. The diffraction pattern was recorded by the scan ratio of $5^\circ$/min over the array of $5^\circ \leq 2\theta \leq 90^\circ$, with the power source of 40 mA and 40 KV.

![Bragg's law diagram](image)

**Figure 3.1:** Bragg’s law showing atomic planes of a crystal cause an incident beam of X-rays to interfere with one another as they leave the crystal.
3.2.3.2 Transmission electron microscopy

The (Fe$_3$O$_4$@TiO$_2$ nanocomposite and Fe$_3$O$_4$) powder samples were primed by scattering the constituents in isopropyl alcohol; positioned onto a sample vessel with a carbon-coated copper grid and were analysed using the Transmission Electron Microscopy (TEM JEOL, JEM-2010, Japan) at an accelerating voltage of 200kv. Samples disseminated at an applicable concentration and were cast onto a carbon-coated copper grid to study the growth of layers, their composition and defects in semiconductors on the calcined powder.

3.2.3.3 The Fourier transform infrared spectroscopy

The usage of Fourier transform infrared (FTIR) spectroscopy was to analyse and observe microstructure of nanoparticles. FTIR propose quantitative and qualitative analysis for organic and inorganic samples by detecting a chemical bond in a molecule by creating infrared radiation. This analysis was done by using the KBr pellet technique on a PerkinElmer spectrum 100 Fourier Transform Infrared Spectrometer, in the range of 4000-400 cm$^{-1}$.

![Figure 3.2: FTIR Sample analysis](image-url)
3.2.3.4 Brunauer Emmett -Teller (BET)

The Brunauer-Emmett-Teller (BET) specific surface area analyzer (Nova Quantachrome 1200e) was used to govern the precise surface area and pore size dispersal of TiO$_2$ and Fe$_3$O$_4$@TiO$_2$ nanoparticles.

Specific surface area is imperative in photocatalysis processes, because a greater surface area can lead to more active sites per unit area, leading to an increase in activity. BET was adapted from Langmuir theory which describes the monolayer absorption of a gas on a solid and multilayer adsorption.

3.2.3.5 X-ray fluorescence (XRF)

X-ray spectrometry (XRF) was used to find the elemental configuration of Fe$_3$O$_4$TiO$_2$ composite. Samples were prepared by making a pallet using a wax binder whose mass was from 1% to 7% of the sample mass. The XRF analysis was done by the use of the AXIOS spectrometer (P Analytical) fortified with an Rh-anode X-ray pipe. The quantifiable examination of the spectra was achieved by the use of the P Analytical analytical Omnian method.

3.2.4 Coagulation/Flocculation using laboratory jar tests

A series of bench scale experiments were made using a completely stirred jar test to investigate the effectiveness of preliminary settling, coagulation and flocculation on the removal of suspended solids, COD and colour from wastewater. The study considered different types of coagulants, to include alum. Before addition of any chemicals, samples from the raw water inlet were collected and turbidity, pH and temperature were analysed. Approximately 400 mL, aliquots of raw water were measured into several beakers on the jar test machine. The solution was subjected to rapid mixing, followed by slow mixing using the flash mix speed and stirrer at different times. The supernatant was drawn below water surface without disturbing the sediment. Approximately 25 mL of the supernatant was collected for the measurement of turbidity, chemical oxygen demand and final pH in the wastewater.
3.2.4.1 Effect of pH.

Table 3.2: summarizes the volume and concentration of coagulant dose added to 200 mL of coffee wastewater, pH adjusted to 6.5 using 0.1 M NaOH.

<table>
<thead>
<tr>
<th># 500 ml Beakers</th>
<th>Volume of coagulant added(mL)</th>
<th>Concentration of coagulant added(mg/L)</th>
<th>pH(@25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>6.5</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>10</td>
<td>6.5</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>50</td>
<td>6.5</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>100</td>
<td>6.5</td>
</tr>
<tr>
<td>5</td>
<td>7.5</td>
<td>150</td>
<td>6.5</td>
</tr>
</tbody>
</table>

500 mL volumetric beakers were used to facilitate 200 mL of wastewater and at 25°C since the wastewater is sent to the municipality at room temperatures. The following calculation was used to get the final volume of the coagulant:

\[ C_1V_1 = C_2V_2 \]

3.2.5 Synthesis and application of \( \text{Fe}_3\text{O}_4 \) composite

The magnetic nanoparticles were arranged by the use of co-precipitation. Synthesis of Nano-Iron powder was done following a method reported by (Zou, Peng & Tang, 2014). In a typical procedure, Iron (III) chloride tetra hydrate (\( \text{FeCl}_2.4\text{H}_2\text{O} \)) was mixed with Iron (III) chloride hexahydrate (\( \text{FeCl}_2.6\text{H}_2\text{O} \)) and was dissolved with de-ionized water. The preparation of Ammonia and Hydrazine solution was done by combining ammonia, hydrazine and diluted with de-ionized water. \( \text{FeCl}_2.4\text{H}_2\text{O} \) & \( \text{FeCl}_2.6\text{H}_2\text{O} \) were added in a dropwise form. The solution was subjected to stirring. The products were collected via a magnetic separation, and calcined at 450°C. After complete precipitation, the solids were detached from the liquid medium using magnetic decantation and then washed numerous periods with deionized water. The \( \text{Fe}_3\text{O}_4 \) was used to make the hybrid catalyst \( \text{Fe}_3\text{O}_4@\text{TiO}_2 \).

3.2.5.1 Effect of the reaction time (1-8hours) using \( \text{Fe}_3\text{O}_4 \) nanomaterial

Eight samples were prepared with a ratio of 1:10 using 2g Nano-iron and 200 mL coffee wastewater. From the prepared samples, the longest removal time was further
analysed for TOC and COD including coliforms removal in a period from 60 to 480 minutes.

Adsorption experiments were done in the laboratory by changing the parameters that affect adsorption of coffee wastewater onto magnetite and Titania nanoparticles. The outcome of adsorbent dosage, pH, and time was considered. The dosage was changed from 1 to 5 g/l by enchanting all other parameters as constant. Initial pH varied from 4-8 which was adjusted using 0.1M HCl and 0.1M NaOH. After the prearranged time was attained, the ascorbate solvent was withdrawn and strained out to isolate the adsorbent. Cellulose nitrate membrane filter paper (0.2 μm) was used for filtration of the solution after adsorption. Magnetic field was moreover applied for the exclusion of magnetic nanoparticles. The filtrate solution from wastewater was determined using UV-Vis spectrophotometer between 200-500 nm, TOC and coliforms.

3.2.6 Synthesis and application of Fe₃O₄ and TiO₂ composite
Photocatalytic degradation was assessed by the use of Fe₃O₄@TiO₂ under 3W LED light radioactivity. The radiation experimentations were carried with the usage of a homemade reactor where photo-radiation spectrum of the LED perceptible light was in the variety of 400–800 nm. The detachment among the light basis and the resolution at the end was 15 cm. An amount of 200 mL of wastewater and TiO₂ composite were placed in 500 mL glass beakers and stimulated using the magnetic stirrer, temperature being kept constant at 25°C. The samples were placed in the reactor and aliquots for analysis with numerous time interludes (60min-480min). The samples were centrifuged at 1000 rpm and analysed for pH, COD, TOC and coliforms.
The influence of pH (4,6 and 8) on the removal of pollutants from wastewater was examined.

**Figure 3.3**: Homemade reactor for the photodegradation study

According to (Mondal & Sharma, 2016), photocatalysis is when TiO$_2$, ZnO, ZrO$_2$, and CdSe others. Photocatalyst semiconductors absorb infrared energy from the rays or an exposed artificial source of light such as light-emitting and diodes fluorescent lamps. Photocatalysis then produces an electron–hole duo when the energy becomes more than the bandgap energy of the material. The transmission band electron (e$_{CB}$) of this photocatalyst re-joins the illuminated light energy. The positive electric hole of the photocatalyst in valance band (h$_{VB}$) separates the water molecule into high energetic hydroxyl free radical and hydrogen gas (**Figure 4**).
3.2.7 UV-VIS spectrophotometer

A shimadzu UV-2450 UV Vis Spectrophotometer was used to measure the concentration of coffee wastewater after the photodegradation studies. Ultra-visible spectra of the wastewater was recorded in using the Shimadzu spectrophotometer in a range between 200-800 nm regions.

3.2.8 Cost benefit analysis

Cost-Benefit Analysis (CBA) is an analytical tool that was be used for judging the economic advantages or disadvantages of the proposed wastewater treatment method by assessing its costs and benefits. This enabled an assessment on the welfare change attributable to it. This monetary value to all the positive (benefits) and negative (costs) effects verifies that the project is appropriate to the context in which it takes place.
The following figure is the approach that was used for the costs and benefit analysis of the project under study.

Figure 3.5: The methodology used for the costs and benefits of the project under study

1. Description of the context:
   - The current operating costs for the current wastewater (falling film evaporator) method was calculated.

2. Financial analysis
   - The cost analysis for all nanomaterials used in the study were calculated.
   - The expenses calculated were only product/ material’s costs.

3. Technical feasibility, environmental sustainability and Risk assessment
   - Impacts of the project on climate.
   - Current demand based on wastewater regulations.
Figure 3.6: The table showing the assessment of each nanomaterial in terms of the severity and probability ratio (Gu-18.045-01).

3.3 References


CHAPTER FOUR

Results & Discussions

4 Introduction

The handling of waste effluent from the food and beverage manufacturing processes includes variable treatment steps that depend on the quality and requirements for the final water. Coffee wastewater is an environmental problem because it possesses high polluting power due to the amount of pollutants such as pectin, proteins, caffeine, soluble salts, and sugars present (Kulandaivelu & Bhat, 2012).

A number of research methods have reported the use of coagulants for the handling of coffee wastewater. However, limitations exist through the amount of excess sludge that is produced within this process (Garde, et.al., 2017).

Research studies for the treatment of coffee wastewater using magnetic catalyst and magnetic catalysts with core–shell conformations are scarce. In the handling of wastewater using magnetic catalysts, the surface of catalytically active particles can consist of TiO$_2$ to remove organics. While the core-shell consisting of magnetic particles such as Fe$_3$O$_4$, provide the means to address the recovery of the catalysts. Magnetic particles have therefore been effectively used as recyclable supporting to span the opening between heterogeneous and homogeneous catalysis (Yao, et.al., 2015).

In this study, coagulation and nanotechnology studies were conducted to assess their effectiveness in reducing the amount of organic, inorganic and microbiological content in coffee wastewater from Nestle Estcourt.

This chapter presents the results on the characterisation of the prepared iron and titanium composite using TEM, XRD, FTIR, BET, XRF and the application of coagulants, the prepared iron, and the titanium composite on the coffee wastewater. The wastewater studied was from the coffee processing plant since it comprises of 80% of the total factory wastewater.

Table 4.1: Estcourt factory daily water consumption

Water is used for the different operational requirements, in the services department it is where steam is generated and where water is distributed to different departments.
About 65% of this water coming from the services is used by the coffee processing plant (Table 4.1) and the resulting effluent is mainly coffee, this leads to this project’s focus on the coffee plant.

<table>
<thead>
<tr>
<th>Water consumption %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Departments</td>
</tr>
<tr>
<td>Services(Boilerhouse)</td>
</tr>
<tr>
<td>Coffee</td>
</tr>
<tr>
<td>Dairy</td>
</tr>
<tr>
<td>Utilities</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

4.1 Characterisation of coffee wastewater before treatment

Complete quality analysis on wastewater samples from Nestle’ Estcourt was done by an external vendor and outcomes are represented in (Table 4.2-Table 4.5).

4.1.1 Physical parameters of the coffee wastewater

Table 4.2 presents the physical parameters; specifically, turbidity, electrical conductivity, pH and colour.

It is evident from (Table 4.2) that wastewater generated from Estcourt coffee processing plant contains high amount of physical pollutants if it remains untreated. The coffee wastewater’s physical appearance is dark brown to black indicating a high concentration of undissolved components which result in elevated levels of turbidity, and high colour content. Another physical property that was not measured, but determined qualitatively is the smell or odour. Typically, the wastewater entering the wastewater evaporator in the boiler house has a strong foul smell associated with it. To determine the sources of these foul smells is beyond the scope of this study, however they can be associated with the period the water stays, product being produced and the cleaning frequency of the wastewater evaporator system. This has been attributed to the deoxygenated state of this wastewater, which causes ammonia and fermentation to form that results in foul smells (Iqbal, et.al., 2017).

Results obtained (Table 4.2) show an average pH value of 4. One possibility is the various organic groups present such as carboxylic acids, phenols, sugars and other carbon-oxygen functionalities that contributes to the low pH. Typically, the low pH indicates the active decomposition of coffee organic substances. Coffee wastewater
additionally contains high levels of soluble salts and tannins that further lowers the pH value. Thus the acidity of the coffee wastewater is usually attributed to the fermentation process that occurs during the production of coffee, forming alcohols and carbon dioxide that quickly converts into aceatic acid in the fermented water. This acidification of sugars drops the pH.

A study by Von Enden (2010) presented that sugar fermentation during wet coffee processing could reduce the pH of the wastewater to low values up to 3.

**Table 4.2:** Physical parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>SA standard norms (DWA,2013)</th>
<th>Coffee wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>&lt;100</td>
<td>17100</td>
</tr>
<tr>
<td>Electrical Conductivity [25°C])</td>
<td>150</td>
<td>949</td>
</tr>
<tr>
<td>pH (pH units [25°C])</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>&lt;500</td>
<td>&gt;800</td>
</tr>
</tbody>
</table>

### 4.1.2 Chemical characterisation of the coffee wastewater

The coffee wastewater’s non-metal chemical results revealed a high TOC, TOC, TDS, COD and sulphate content, this was due to a range of organic complexes that are present in the coffee wastewater. A high anti-oxidant capacity is caused by the presence of phenolic compounds, and aromatic compounds that arises from ingredients (coffee beans).

**Table 4.3:** Chemical characterisation of the coffee wastewater (Non-metals)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>SA standard norms (DWA,2013)</th>
<th>Coffee wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia Nitrogen (mg/L)</td>
<td>1</td>
<td>5.7</td>
</tr>
<tr>
<td>Chemical Oxygen Demand(COD) (mg/L)</td>
<td>5000</td>
<td>14454</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>0.1</td>
<td>320</td>
</tr>
<tr>
<td>Chlorine (free) (mg/L)</td>
<td>1.0</td>
<td>&lt;0.020</td>
</tr>
<tr>
<td>Nitrate Nitrogen (mg/L)</td>
<td>1</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td>Phenols (mg/L)</td>
<td>0.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Sodium (mg/L)</td>
<td>50</td>
<td>3992</td>
</tr>
<tr>
<td>Sulphate (mg/L)</td>
<td>0.05</td>
<td>777</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>75</td>
<td>6652</td>
</tr>
<tr>
<td>Total Organic Carbon (mg/L)</td>
<td>220</td>
<td>12310</td>
</tr>
</tbody>
</table>
Corroborating results were found in a study conducted by Dadi, et.al. (2018) on the effluent quality from wet coffee processing mills. The results showed that the coffee processing mills studied were not compliant with either US-EPA or Ethiopian EPA guidelines and also were found to be polluting water streams with their high acidity, organic load (BOD and COD), nutrients (nitrate and phosphate).

4.1.3 Heavy Metal characterisation of coffee wastewater

Lead, zinc, copper, chromium, mercury, and arsenic were present beyond the South African permissible limits in the coffee wastewater during this study (Table 4.4). These may enter a municipal water supply and lead to fines and penalties. Heavy metals bioaccumulates and are transferred by both anthropogenic, for example industrial and domestic activities and natural sources.

These metals, often in the form of complex ions, are present due to the erosion of natural materials and anthropogenic sources (industrial wastewater). Arsenic and lead could be part of the machinery enamel, meaning they are coming from additives that were used in the manufacturing of the pipes, frictional and corrosion reactions within the process (Siu, et.al., 2007).

Iron along with manganese were present in high concentrations and this was due to the fact that these are natural minerals that are found in coffee. Their presence in coffee wastewater could be a result of coffee Agro-industry since coffee bean is one of the raw materials used. Other compounds that were present in the coffee wastewater included phenols that are formed by the Maillard reaction arising from the roasting process (Novita, 2016).

The presence of copper and zinc in water is complex and influenced by pH and dissolved oxygen concentration. Aluminum occurs naturally in water and its toxicity is influenced by the organic content of the water, the higher the organic content, the more aluminum will be found in the water and the results from coffee wastewater were high in the organic content. Chromium arises naturally from the boiling of oil, coal and petroleum and gets released into the atmosphere over sewage (Jaishankar, et.al., 2014). Within the coffee processing (boilerhouse), there is a mini coal processing plant where this coal is used in the boilers and this chromium might be coming from the remains.
Similar results were found by Zuluag (1989) when he conducted a study on coffee wastewater and it was concluded that high iron content present in coffee wastewater was due to the wear and tear off of machinery and the corrosion of pipes within the process.

**Table 4.4**: Chemical characterisation of the coffee wastewater (Heavy metals)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>SA standard norms (DWA,2013)</th>
<th>Coffee wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (μg/L)</td>
<td>0.1</td>
<td>7.8</td>
</tr>
<tr>
<td>Boron (mg/L)</td>
<td>0.5</td>
<td>0.16</td>
</tr>
<tr>
<td>Cadmium (μg/L)</td>
<td>0.05</td>
<td>0.50</td>
</tr>
<tr>
<td>Chromium (μg/L)</td>
<td>0.05</td>
<td>41</td>
</tr>
<tr>
<td>Copper (μg/L)</td>
<td>0.02</td>
<td>653</td>
</tr>
<tr>
<td>Lead (μg/L)</td>
<td>0.1</td>
<td>21</td>
</tr>
<tr>
<td>Mercury (μg/L)</td>
<td>0.02</td>
<td>0.29</td>
</tr>
<tr>
<td>Zinc as Zn (μg/L)</td>
<td>0.3</td>
<td>2469</td>
</tr>
<tr>
<td>Manganese (μg/L)</td>
<td>0.1</td>
<td>154</td>
</tr>
<tr>
<td>Iron (μg/L)</td>
<td>0.3</td>
<td>8259</td>
</tr>
<tr>
<td>Aluminium (μg/L)</td>
<td>5</td>
<td>3199</td>
</tr>
</tbody>
</table>

These metals can bio accumulate, affect the water’s appearance and its physico-chemical characteristics. When iron levels are high, the iron poses a risk to pipes, pumps and machinery since it can either corrode or easily deposit and block pipes and clog up machinery. They may also badly affect the soil ecology, agricultural production, ground water quality and will eventually cause destruction to health of living organism by food chain. Their pollution in aquatic environments is a growing problem globally and currently it has reached an alarming rate. Contamination of water bodies by copper could lead to chronic anemia, since copper collects in the brain and liver, its toxicology is a vital cause of Wilson diease (Nazir, et.al., 2015).

**4.1.4 Microbial characterisation of coffee wastewater**

Waste effluent produced from coffee manufacturing revealed the high levels of total coliforms, *Lactobacillus* and *Escherichia coli* (Table 4.5). These organisms are found in many foods such as fruits and the coffee fruit is used for the manufacturing of coffee beans that are further used for coffee processing. The coliform bacteria favours warm
temperatures and the coffee wastewater’s temperature was between 25-30°C. The lactic acid bacteria grows in nutrient-rich environments. Deoxygenation of this coffee wastewater leads to fermentation which in-turn increases bacterial growth (Von Enden & Calvert, 2010). Studies conducted at Nestle R&D have shown that *Lactobacillus* species, yeasts and moulds have the ability to grow in coffee extracts. The presence of high levels of *Lactobacillus* spp. during coffee processing and finished products indicates that the hygiene conditions are not satisfactory. Mould such as *Aspergillus* species are able to grow on green coffee when given the right conditions. Bacteria found may include *Bacillus*, *Lactobacillus*, *Pseudomonas*, *Streptococcus* species (GI-31.019).

The strains of *Lactobacillus* and *Pediococcus* are found to readily grow in any environment with pH values of 3.8 or lower in a study conducted by Kulandaivelu & Bhat (2012) in coffee wastewater.

Another study was conducted by Novita, (2016) on coffee wastewater and he found that microorganisms were able to adapt in acidic conditions. The contamination levels were however found to be much less in wet processed green coffee (washed Arabica and washed Robusta) when compared with wastewater coming from dry processing.

**Table 4.5: Microbiological characterisation of the coffee wastewater**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>SA standard norms</th>
<th>Coffee wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Escherichia coli</em> (count per 100ml)</td>
<td>&lt;100</td>
<td>32000</td>
</tr>
<tr>
<td>Somatic Coliphages ( count per 100ml)</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Total Coliforms(count per 100ml)</td>
<td>1000</td>
<td>140000</td>
</tr>
<tr>
<td>Biological chemical mg/L (BOD)</td>
<td>5000</td>
<td>4350</td>
</tr>
<tr>
<td><em>Lactobacillus</em></td>
<td>&lt;10</td>
<td>10000</td>
</tr>
</tbody>
</table>

**4.1.5 Chemical characterisation of coffee wastewater: Summary and implications**

**Table 4.5** shows the applicable norms that are regulated in South Africa. Section 2 of Department of Water Affairs (DWA, 2013), states that if complex industrial wastewater contains mixtures that are hard and impossible to chemically characterise and enumerate, the limits in **Table 4.6** applies. The wastewater discharged to the
municipality or rivers needs to be fully compliant with the stated municipal requirements.

A study on the reduction of COD and BOD concentrations using discarded carbon-based material made up of Avocado Peel Carbon (APC) in coffee wastewater reached conclusions that complement the findings from this study. The COD and BOD concentrations were found to be very high compared to world health organization (WHO) acceptable parameters for discharge or irrigation and agricultural uses (Devi, et.al., 2008).

The World health organisations (WHO) and United States Environmental Protection Agency (Roll & Fujioka, 1997), states that wastewater must be disposed off into the public or integrated waste effluent handling systems that have adequate capacity to meet local regulatory requirements for treatment. The pre-treatment of wastewater to meet regulatory requirements before discharging from the site is required if the municipal or centralized wastewater treatment system receiving wastewater from the project does not have adequate capacity to maintain regulatory compliance (EPA, 2007).
Table 4.6: South African wastewater limits (DWA, 2013 & NWA 36 OF 1998)

<table>
<thead>
<tr>
<th>ELEMENTS</th>
<th>GENERAL LIMIT</th>
<th>SPECIAL LIMIT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faecal coliforms (per 100ml)</td>
<td>1000</td>
<td>0</td>
</tr>
<tr>
<td>Chemical Oxygen Demand (mg/L)</td>
<td>75(i)</td>
<td>30(i)</td>
</tr>
<tr>
<td>pH</td>
<td>5.5-9.5</td>
<td>5.5-7.5</td>
</tr>
<tr>
<td>Ammonia (ionised and un-ionised as Nitrogen (mg/L)</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>Nitrate/Nitrite as Nitrogen (mg/L)</td>
<td>15</td>
<td>1.5</td>
</tr>
<tr>
<td>Chlorine as Free Chlorine (mg/L)</td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td>Suspended Solids (mg/L)</td>
<td>75</td>
<td>10</td>
</tr>
<tr>
<td>Electrical Conductivity (mS/M)</td>
<td>70ms/m above intake to a maximum of 150ms/m</td>
<td>50ms/m above background water to a maximum of 100ms/m</td>
</tr>
<tr>
<td>Ortho-Phosphate as Phosphorus (mg/L)</td>
<td>10</td>
<td>1 (median) and 2, 5 max.</td>
</tr>
<tr>
<td>Fluoride (mg/L)</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Soap, Oil or grease (mg/L)</td>
<td>2.5</td>
<td>0.01</td>
</tr>
<tr>
<td>Dissolved Arsenic (mg/L)</td>
<td>0.02</td>
<td>0.001</td>
</tr>
<tr>
<td>Dissolved Cadmium (mg/L)</td>
<td>0.005</td>
<td>0.02</td>
</tr>
<tr>
<td>Dissolved Chromium (VI) (mg/L)</td>
<td>0.05</td>
<td>0.002</td>
</tr>
<tr>
<td>Dissolved Copper (mg/L)</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Dissolved Cyanide (mg/L)</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Dissolved Iron (mg/L)</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Dissolved Lead (mg/L)</td>
<td>0.01</td>
<td>0.006</td>
</tr>
<tr>
<td>Dissolved Manganese (mg/L)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Mercury at its compounds (mg/L)</td>
<td>0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>Dissolved Selenium (mg/L)</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Dissolved Zinc (mg/L)</td>
<td>0.1</td>
<td>0.04</td>
</tr>
<tr>
<td>Boron (mg/L)</td>
<td>1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

These pollutants can result in numerous severe health problems such as abdominal complications, eye, ear and skin irritation, nausea including breathing problems if it is directly discharged to nearby waterbodies (Alemayehu & Devi, 2008).
4.2 Characterisation of the Nanomaterials and the Composites Synthesised

Nanoparticles have become the most recognised and studied materials for wastewater treatment because of their high surface area to volume ratio, superior physical-chemical characteristics, and adsorption capacity (Savage & Diallo, 2005).

The predominant magnetic materials that are studied are iron oxides and these are low-priced, easy to prepare, strongly magnetic and suitable for technical and biomedical applications (Tran, et.al., 2010). The zero-valent iron and titanium dioxide are mostly used as hybrid material in the degradation of dyes and pharmaceuticals. These studies usually look at single or simple binary mixtures, and there are very few studies looking at wastewater.

In this study, iron oxide (Fe₃O₄) and titanium dioxide (TiO₂) were used since they are inexpensive and eco-friendly (Tan, et.al., 2015).

4.2.1 X-ray diffraction

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer equipped with a copper source (λ = 1.541 Å). XRD was used to identify the phases present in the prepared catalyst. The results for iron oxide were the same as those of magnetite, indicating that the material is magnetic, and this is similar to what has been reported in the literature (Giri & Das, 2013).

The XRD patterns of the synthesized Fe₃O₄ showed six characteristic peaks for magnetite (2θ = 30.1°, 35.4°, 43.2°, 53.5°, 57.2° and 62.5°), marked by their indices (220), (311), (400), (422), (511) and (440). This indicated that the adsorbent had an iron element core and iron oxide shell which indicates that magnetic properties could be used for magnetic separation.

The titanium composite (Fe₃O₄TiO₂) showed peaks at (101), (004), (200), (105), (211), (204), (116), (220) and (215) crystal planes at 2θ values of 21.8°,30.1°,35.4°,37.0°,43.0°,53.4°,56.9°,62.5°,70.9°,73.9° and 74.9°. Two broad peaks were observed at 25.48° and 48.18° and these were allocated to (101) and (200) of anatase phase. Thus, anatase was determined to be the main crystalline phase of the TiO₂ coated-magnetite.
The nanocrystalline size of titanium broad peak was calculated using the Debye-Scherrer equation below:

\[ D = K \frac{\lambda}{(\beta \cos \theta)} \]  

Where \( D \) is the crystal size; \( \lambda \) is the wavelength of the X-ray radiation (\( \lambda = 0.1540 \text{nm} \)); \( K = 0.89 \); \( \theta \) is Bragg’s diffraction angle and \( \beta \) is the full width half-maximum height using (101 & 200) peaks (Vijalahalakshmi & Rajendran, 2012).

Similar results were observed in a study investigating organic pollutant degradation using magnetic TiO\(_2\) nanocomposite by (Zhiqiao, et al., 2012).

**Figure 4.1**: X-ray diffractograms for Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4\)TiO\(_2\)

Transmission electron microscope (TEM) images were obtained using a TEM, JEOL JEM-2010 FE-TEM equipped with a post-column Gatan imaging lter (GIF-Tridium) at an acceleration voltage of 200 kV. TEM was used for the size distribution, particle size and to understand the microstructure of the prepared nanoparticles.

Spheres were observed for Fe\(_3\)O\(_4\). The magnetic iron core was observed as a high contrast component (almost black) while the iron oxide coating was observed as a grey/low contrast shell (**Figure 4.2a**). The composite consisted of Fe\(_3\)O\(_4\) nanoparticles covered by small, coherent coated layer of spherical dispersed TiO\(_2\) nanoparticles (**Figure 4.2b**).
This is consistent with results obtained by Tana, et.al. (2005) who conducted a study aimed at adsorption of uranium (VI) from aqueous solution by Fe$_3$O$_4$@TiO$_2$ composites was studied by batch experiments. Their findings showed that a novel sorbent, Fe$_3$O$_4$@TiO$_2$, has been synthesized and was used to adsorb uranium (VI) from aqueous solution by batch experiments.

![TEM results for Fe$_3$O$_4$ and Fe$_3$O$_4$TiO$_2$](image)

**Figure 4.2**: Transmission Electron Microscope (TEM) results for Fe$_3$O$_4$ and Fe$_3$O$_4$TiO$_2$

### 4.2.2 Fourier transform infrared spectroscopy
A Shimadzu IR spectrophotometer was used to analyse the infrared spectra bands for iron oxide and titanium nanocomposite. These bands were recorded between 400 and 4000 cm\(^{-1}\) using the Fourier transform infrared (FTIR) spectroscopy. The iron oxide (Fe\(_3\)O\(_4\)) and (Fe\(_3\)O\(_4\)TiO\(_2\)) Titania nanocomposites were analysed by the means of the FTIR with the intention to confirm the presence of magnetite recovered through the addition of TiO\(_2\) (Figure 4.3). The characteristic band of magnetic iron ore was recognized at 560 cm\(^{-1}\) assigned to Fe–O stretching vibrations of the magnetite in the range of Fe\(_3\)O\(_4\). In this region, TiO\(_2\) absorbed more than magnetite (due to Ti–O Ti stretching vibrations), thereby covering the magnetite band. The presence of water is shown by the appearance of the bending mode at 1640 cm\(^{-1}\) and the stretching mode at 3400 cm\(^{-1}\).

![Figure 4.3: The results showing Fe\(_3\)O\(_4\) & Fe\(_3\)O\(_4\)TiO\(_2\) spectra bands.](image)

### 4.2.3 X-ray fluorescence spectrometry

X-ray fluorescence spectroscopy (XRF) was used for the elemental composition of Fe\(_3\)O\(_4\) and TiO\(_2\) nanocomposite. The elemental analysis gave information for the following elements (Al, Ca, Cl, Cr, Cu, Fe, K, Na, Ni, O, Rb, S, Si, Ti,) in a wide range of concentration. The results of the quantitative analysis for main elements were TiO\(_2\)
and Fe₂O₃ (Table 4.6). The ratio of Fe₃O₄ : TiO₂ was 1 : 4.65, which was in accordance with the mixing ratio for the composite preparation which was 1 : 5.

**Table 4.7**: Crystalline sizes and texture measurement for Fe₃O₄ TiO₂ composite.

<table>
<thead>
<tr>
<th>Elemental analysis</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>0.387</td>
</tr>
<tr>
<td>CaO</td>
<td>0.014</td>
</tr>
<tr>
<td>Cl</td>
<td>0.813</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.055</td>
</tr>
<tr>
<td>CuO</td>
<td>1.551</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>16.956</td>
</tr>
<tr>
<td>K</td>
<td>0.025</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.987</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.601</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.042</td>
</tr>
<tr>
<td>TiO₂</td>
<td>78.903</td>
</tr>
</tbody>
</table>

4.2.4 **Textural Properties of the nanomaterials synthesised**

The introduction of TiO₂ nanoparticles to the surface of Fe₃O₄ nanoparticles showed an increase in the surface area (Table 4.8). The surface area for the titania nanocomposite was 121.5 g/m², and this was higher than iron oxide surface area 79.13 g/m²). This can be attributed to the titania coating the iron oxide nanoparticles, and preventing some agglomeration of the magnetic particles, and thus increasing the surface area. The pore volume decreased from 1.258 mL/g, with the iron oxide nanoparticles, to 0.8618 cm³/g, with the nano-composite.
Table 4.8: Textural properties for Fe$_3$O$_4$ and Fe$_3$O$_4$@TiO$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pore radius (nm)</th>
<th>Total pore volume (cm$^3$ g$^{-1}$)</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$</td>
<td>63.58</td>
<td>0.8618</td>
<td>79.13</td>
</tr>
<tr>
<td>Fe$_3$O$_4$TiO$_2$</td>
<td>28.37</td>
<td>1.258</td>
<td>121.5</td>
</tr>
</tbody>
</table>

The pore size distribution (PSD) data was attained by the use of desorption curve of isotherm data, using the BJH (Barrett–Joyner–Halenda) technique (Figure 4.4 - 4.5). The nitrogen adsorption-desorption isotherms showed an isotherm type IV with a hysteresis loop of H3 according to IUPAC classification (Wang, et.al., 2012) that is correlated with the previous TEM results showing some spaces between the nanoparticles.

![Figure 4.4: N$_2$ adsorption-desorption isotherm of Fe$_3$O$_4$.](image-url)
Figure 4.5: N₂ adsorption-desorption isotherm of Fe₃O₄TiO₂.

4.3 Coagulation/Flocculation using laboratory jar tests on the Coffee Wastewater

Coagulation is described as the weakening of colloidal particles through disabling the powers that keep them separately using coagulating agents and coagulant aids. Flocculation is the usage of polymers for the formation of bonds amongst the flocs and bind elements to create large agglomerates or clusters (Chowdhury, et.al., 2018).

According to effluent discharge standards, the following discharge parameters are required within various industries (Table 4.9). This rationalises why the wastewater from coffee processing was analysed for the impervious organic materials that can only be broken down by chemical means, commonly known as COD during coagulation. COD is one of the wastewater release criterias required by the South African wastewater discharge standards and one of the problematic parameter within the coffee processing plant since make up about 80% of the pollution load in the coffee wastewater.

According to wastewater discharge standards, COD, pH and BOD are the most crucial test methods that are required for wastewater to be discharged into a municipality sewer.
Most large water treatment plants use coagulation/flocculation methods to purify wastewater. Colour in water is usually connected to aromatic compounds formed from falling-off of anthropogenic and natural organic constituents (Malakootian & Fatehizadeh, 2010).

**Table 4.9**: The list of required parameters for certain industrial activity (National Environmental Act, 2002)

<table>
<thead>
<tr>
<th>INDUSTRIAL ACTIVITY</th>
<th>PARAMETERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dairy Processing</td>
<td>Temperature, pH, COD, BOD₅, TSS, Selenium, Oil &amp; Grease, Detergents, ammoniac Nitrogen.</td>
</tr>
<tr>
<td>Soft Drink Bottling</td>
<td>Temperature, pH, COD, BOD₅, TSS, Sodium, Zinc, Detergents.</td>
</tr>
<tr>
<td>Breweries &amp; Distilleries</td>
<td>Temperature, pH, COD, BOD₅, TSS, Nitrate as N, Selenium, Zinc, Oil &amp; Grease, Detergents, Ammoniac Nitrogen.</td>
</tr>
</tbody>
</table>

**4.3.1 Effect of the dosage of coagulants & flocculants**

Coagulation/flocculation was found to be effective when the concentration of the dosage was at its minimum values (Figure 4.6). As the dosage increased, the COD removal rate decreased. There are many factors that facilitate the coagulation/flocculation process: the pH is very important because a coagulant with a contrasting charge is added to water to overwhelm the revolting charge and subvert the suspension and the lower the pH, the less effective the destabilisation process will be (Šostar-Turk, et.al., 2005).

Overdosing or insufficient dosages results in poor performance in flocculation, as well as mixing speed, and retention time influence the colour removal efficiency (Patel, et.al., 2006).

In this study, the pH was adjusted to 6.5 using 0.1 mol L⁻¹ NaOH or 0.1 mol L⁻¹ HNO₃ before coagulation/flocculation experiments were carried out and lime was excluded since an excess sludge was produced when it was used for adjustment. BUFLOC 5170 (Aluminium hydrochloride) was the most effective flocculant in terms of COD removal and alum being the least effective. The flocculants (BUFLOCs) were the most effective in removing pollutants from coffee wastewater when compared with
coagulants (BULABs). These results showed that coagulation alone could not completely remove pollutants. Alum is the most common coagulant, although it was found to produce an excess sludge when it was used as a coagulant for removing pollutants in coffee wastewater which was highly acidic. Waste treated with this coagulant must be neutralized before being discharged. The overall findings demonstrated that the use of coagulants/flocculants alone to remove pollutants that are found in coffee wastewater cannot be a feasible solution. The higher dosage resulted in poor performance.

![Figure 4.6](image-url)

**Figure 4.6:** The effect of dosage of coagulants and flocculants.

4.3.1.1 **Effect of pH on functionality of coagulants and flocculants.**

Optimum pH was kept at 6.5 for the test results and all the other experiments were done at this pH. *(Table 4.10)* shows studies that were studied to determine the consequence of diverse pH values for the highest removal coagulant (BUFLOC 5170), starting with 4 which is an average result obtained for coffee wastewater, 6 for the pH regulated value as well as at alkalinity value of 8 for COD, TOC, TDS and coliforms.
which are one of the parameters that were found to be present at higher concentrations before coffee wastewater treatment.

The determined elimination efficiency remained at pH (6) for COD and TOC, whereas TDS was greatly removed at pH 8, however, as the pH further increased to 8, the efficiency decreased. Chemical parameters showed a 28% removal efficiency of pollutants at the studied pH values (6-8). These results showed an overall decrease of on the pollutants that were present in coffee wastewater. For coliforms, the maximal removal percentage was at pH 8 but these microbiological results also showed that coliforms removal was fluctuating, this is due to the amount of nutrients that are available.

**Table 4.10:** Results for COD, TOC, TDS and coliforms analysis of coffee wastewater at pH 4-8 after treatment using commercial BUFLOC5170 flocculant at pH 4-8

<table>
<thead>
<tr>
<th>Parameters</th>
<th>pH 4</th>
<th>pH 6</th>
<th>pH 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (mg/L)</td>
<td>7000</td>
<td>8000</td>
<td>10000</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>8900</td>
<td>8800</td>
<td>8900</td>
</tr>
<tr>
<td>Coliforms (cfu/g)</td>
<td>11000</td>
<td>9000</td>
<td>8500</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>9200</td>
<td>9500</td>
<td>9300</td>
</tr>
</tbody>
</table>

These results are consistent with those of Ghawi, He found that it is possible to improve the reduction of organic matter of highly polluted water samples by altering the pH of the treatment system. However, the increase in the dosage concentration was not operational and cost wise. Thus, several studies to alter the coagulation process through changing pH that have been performed in recent years.

**4.3.1.2 UV-Vis analysis of waste water before and after treatment with Coagulants/flocculants**

The wastewater from coffee treatment plant did not show sufficient sharp and distinguished absorption maxima. The absorbance of the raw wastewater before treatment showed two peaks at a band under this UV region (0-200 nm) of 3.3 at pH 8 and an absorbance of 2.8 at pH 4, a peak of 1.4 at pH 8 and 1.1 at pH 4 in this UV
region 200-300 nm was observed (Figure 4.7). The peak between pH 6-8 were located in one points and the absorbance appears as one graph.

**Figure 4.7**: UV-Vis Scan on the coffee wastewater before treatment (Dilution used was 10mL of wastewater diluted in 100 mL deionised water)

The optical density of all the solutions were proportional as stated by the Beer-Lambert law. After coagulation treatment, a sharp band was observed for coffee wastewater at pH 4 & 6 showing a 54% decrease (0-200 nm) and a 58% decrease at 200-300 nm and at 450-600, the band remained constant. The results at pH 8 were similar with a 30% decrease (**Figure 4.8**).
Figure 4.8: UV-Vis spectral scanning curve of Coffee wastewater after coagulation treatment

4.4.1 Treatment of Coffee Wastewater using Fe$_3$O$_4$ nanomaterial

The simple partition of the magnetic nanoparticles from the reaction medium by means of an external magnetic field is the most effective widely used method (Figure 4.9).

As the time of adsorption changed from 60 to 240 minutes, efficiency first increased slowly from 10% to 16% and after 360 to 480 minutes, it was at standby with a 20% adsorption efficiency. This was due to the surface coverage of the adsorbent that rises when time increases and further no adsorption was observed taking place.
4.4.1.1 The effect of the reaction time (60-480 minutes) on Fe₃O₄ adsorption efficiency

The effect of time was studied on the removal of coffee particles using the Fe₃O₄ material. The COD absorption efficiency decreased at 60 minutes to 360 minutes, from 5000mg/L - 4300 mg/L and further at 480 minutes remained constant. This indicates that photocatalytic degradation increases with time. From this data (Figure 4.10), it can be proposed that the reaction time should be controlled within 60-360 minutes, as there is no unforeseen change that subsequently occurred.
4.4.1.2 Effect of pH on functionality of \( \text{Fe}_3\text{O}_4 \) on coffee wastewater.

It is well known that pH affects adsorption, therefore the effect of initial solution pH has on the removal of pollutants in wastewater with \( \text{Fe}_3\text{O}_4 \) was studied for the adsorption after 360 minutes. Studies for \( \text{Fe}_3\text{O}_4 \) were done at different pH values (4, 6 & 8). Results show that a molecular form of \( \text{Fe}_3\text{O}_4 \) changed wastewater’s solution in the pH range between 6-8. The increase to pH 6, gave the greatest removal potential for all the studied parameters and as pH further increased to 8, the amount of the removal efficiency slowly decreased. The greatest TOC removal percentage at pH 4&6 was at (35%) and for COD, it was at (45%), while coliforms’ removal rate was greatest at pH 8 with (45%) (Table 4.11).

The microbiological results showed that coliforms can be greatly removed when pH decreases (pH8-6), this is due to that at acidic concentrations, there is less availability of the nutrients and this inhibits microbial growth. Chemical parameters showed a slight difference in the removal efficiency of pollutants at the studied pH vaues (6-8). these results showed an overall decrease of 28% on the pollutants that were present in coffee wastewater.

**Figure 4.10:** The effect of time (60-480 minutes) on \( \text{Fe}_3\text{O}_4 \) adsorption efficiency.
Table 4.11: Results for COD, TOC, TDS and coliforms analysis of coffee wastewater at pH 4-8 after treatment with Fe₃O₄ nanoparticle

<table>
<thead>
<tr>
<th>Parameters</th>
<th>pH 4</th>
<th>pH 6</th>
<th>pH 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC(mg/L)</td>
<td>7500</td>
<td>7500</td>
<td>8000</td>
</tr>
<tr>
<td>COD(mg/L)</td>
<td>8500</td>
<td>8100</td>
<td>8100</td>
</tr>
<tr>
<td>Coliforms(cfu/g)</td>
<td>5600</td>
<td>5500</td>
<td>6000</td>
</tr>
<tr>
<td>TDS(mg/L)</td>
<td>8500</td>
<td>8500</td>
<td>8300</td>
</tr>
</tbody>
</table>

A study conducted by Raghubeer, et.al. (1994) showed that the presence of chlorogenic acids found in roasted coffee beans that are further broken down to acetic, caffeic, and quinic acid acted as inhibitors for bacterial growth and this lessened coliforms growth at pH values less than 6.

4.4.1.3 UV-Vis analysis of coffee waste water before and after treatment with Fe₃O₄

The optical absorption properties of Fe₃O₄ was measured on the removal of TOC, COD and coliforms in the coffee wastewater. The results indicated that Fe₃O₄ treatment has a good removal effect on those types of organic matters studied when compared with coagulants/flocculants. The coffee wastewater’s band was found to be at (75%) at pH 4 between this wavelength (200-300nm) and further decreased to (35%) with an increasing pH (6-8). The wavelength further increased to (400-600nm). However, the absorbance remained constant (Figure 4.12).
4.5.1 Photo degradation of Coffee Waste Water using Fe₃O₄TiO₂ nanocomposite

The photocatalysis method using TiO₂ is the far and wide studied as well as preferred photocatalytic method for wastewater treatment. This is relatively due to its low cost, non-toxicity, chemical and biological stability, and electronic properties (Li, et.al., 2016). The results from this study demonstrated that successful deposition of uniform monodispersed Fe₃O₄ nanoparticles into the surface of titanium dioxide matrix allows the dispersion of light by multiple pathways. This improved light collection and greater photocatalytic activity. Furthermore, the deposition of magnetic nanoparticle (Fe₃O₄) onto the surface of the photocatalyst (TiO₂) proved to be an effective way to separate the photocatalyst from the photocatalytic system with an external magnetic field which allowed for reuse in multiple cycles. This approach prevented the agglomeration of the catalyst particles during recovery and could increase the durability of the catalysts.

The removal efficiency increased with the extension of time within 30-60 minutes. The increasing rate slow down after 60 minutes. This was mainly because the photocatalytic process usually performs as a first-order reaction and its reaction rate
is proportional to organic substrate concentration, that is, the reaction rate lessens with the prolong of time. In addition, the decrease of organic substrate concentration in the iron oxide used for the preparation of the Fe$_3$O$_4$TiO$_2$ nanocomposite acts as recyclable support to bridge the gap between heterogeneous and homogeneous catalysis and allows easy separation with a magnetic field. The surface of magnetite nanoparticles became more negatively charged as the pH increased. This caused an increase in repulsion between coffee wastewater and magnetite nanoparticles. (Figure 4.12).

Similar results were observed in a study conducted for the degradation of particles in dyestuff using titanium silicate (Zhang, Jet.al., 2015).

A study by Jin-hui (2012) showed that pH was conductive to increasing the yield, and this would make a slight decline of pH value. Thus, the greater pH value might also act as a buffer in water during photocatalytic process to prevent fast decreasing of pH. The decrease in absorption might be due to the degree of repulsion forces.

Similar results were found for the photocatalytic degradation of methylene blue under visible light irradiation TiO$_2$ and Ag-modified TiO$_2$ coating on magnetic Fe$_3$O$_4$ nanoparticles. In a dark environment, the concentration of methylene blue was found to slightly decrease for the sample of bare Fe$_3$O$_4$TiO$_2$ nanocatalysts while abruptly decreasing for the sample of Fe$_3$O$_4$TiO$_2$ nanocomposites (Tedsreea, et.al., 2017).
4.5.1.1 Effect of the reaction time (1-8 hours)

The effect of the contact time of the adsorbed Titania nanocomposite on coffee wastewater was studied and COD was used for measurement. The COD absorption efficiency decreased at 60 minutes to 360 minutes, from 5000 mg/L - 4000 mg/L and further remained constant (Figure 4.13). This indicated that photocatalytic degradation increases with time.

![Figure 4.13: The effect of time (60-480 minutes) on Fe₃O₄TiO₂ adsorption efficiency.](image)

4.5.1.2 Effect of pH on functionality of Fe₃O₄TiO₂ on coffee wastewater

It is well known that pH affects adsorption, therefore the effect of initial solution pH has on the removal of pollutants in wastewater by Fe₃O₄TiO₂ was studied. Studies for the nanocomposite were done at different pH values. Results obtained (Table 4.12) showed that a molecular form of Fe₃O₄TiO₂ changed wastewater's solution in the pH range between 4-8. Thus in this section, the solution pH values were kept between 4-8. The photodegradation of coffee wastewater was done at diverse levels from the above mentioned pH values. The rate of degradation was studied in terms of changes
in the concentration of pollutant removal and reduction in TOC, COD and coliforms. It has been observed that with an increase in pH the percentage removal for the organic molecules (COD&TOC) decreases while for the bacterial growth (coliforms) was increasing.

The microbiological results showed that coliforms can be greatly removed as pH decreases (pH8-6). This is due to that bacteria cannot tolerate environments that are cold and that are acidic, within this environment, there are less nutrients for bacteria to feed on. Chemical parameters showed a better removal efficiency at pH 6-8. All these results showed an overall decrease of 35% on the pollutants that were present in coffee wastewater.

**Table 4.12:** Results for COD, TOC, TDS and coliforms analysis of coffee wastewater at pH 4-8 after treatment with Fe$_3$O$_4$TiO$_2$ nanocomposite

<table>
<thead>
<tr>
<th>Parameters</th>
<th>pH 4</th>
<th>pH 6</th>
<th>pH 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (mg/L)</td>
<td>7400</td>
<td>7200</td>
<td>7200</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>8300</td>
<td>7900</td>
<td>8100</td>
</tr>
<tr>
<td>Coliforms (cfu/g)</td>
<td>5400</td>
<td>5500</td>
<td>6000</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>8500</td>
<td>8000</td>
<td>8100</td>
</tr>
</tbody>
</table>

The Fe$_3$O$_4$TiO$_2$ nano composite showed strong optical absorption properties over both visible regions (200–300 nm). The coffee wastewater band for colour removal was found to be (65%) at pH 8 between the wavelength of 200-300 and further increased to (85%) colour removal with decreasing pH from 4-6 and later remained constant at wavelength of 450-600nm.

The absorbance showed a decrease that indicated that photocatalytic process had a tremendous removal effect on the studied organic matters. It is shown in (Figure 4.15) that a decrease in the concentration was faster with Fe$_3$O$_4$TiO$_2$ nano composite treatment under LED light than with Fe$_3$O$_4$ and coagulants/flocculants treatment studied under the same experimental conditions.

In all the studied chemicals (Coagulant, Fe$_3$O$_4$ and Fe$_3$O$_4$TiO$_2$), the colour absorbed was found to be in this decreasing order: photocatalytic degradation activity of Fe$_3$O$_4$TiO$_2$ removed more colour under LED light irradiation, followed by Fe$_3$O$_4$ and lastly coagulants were least effective in the colour removal.
A study by Jin-hui (2012) for the elimination of trace organic pollutants in water using a photo catalytic process with TiO$_2$ showed absorption characteristics within this range (190-240 nm). Light intensity and dissolved oxygen were found to be the main factors that affected the UV/TiO$_2$ photo catalytic removal efficiency of organic matter in the filtered water. When the light intensity was increased, more of photons were found to spread to the surface of the catalyst and the more strong oxidizing free radicals were generated, resulting in a resilient oxidation capability of organic matter. The costs associated with this material are also low. It is also a preferred photocatalytic method for wastewater treatment. LEDs are small, do not contain mercury, have a longer life span than conventional light sources, and can operate on a direct current and are environmentally friendly. These are becoming a promising alternative light source (Jo & Rajesh, 2014).

![UV-Vis spectral scanning curve of the filtered water after photocatalytic treatment with Fe$_3$O$_4$TiO$_2$.](image)

**Figure 4.14:** UV-Vis spectral scanning curve of the filtered water after photocatalytic treatment with Fe$_3$O$_4$TiO$_2$.

### 4.5.1.3 The effect of the reaction time (60-480 minutes) on Fe$_3$O$_4$ & hypochlorite adsorption efficiency

As time of adsorption changed from 60 to 240 minutes, efficiency first increased slowly from 12% to 18% and after 360 to 480 minutes, it was standby with 24% adsorption efficiency. This was due to the surface coverage of the adsorbent that was high when
time increased and further no adsorption was found taking place. From this data (Figure 4.15), it can be proposed that the reaction time be controlled within 60-360 minutes, as there is no unforeseen change that occurs after that time interval.

Figure 4.15: The effect of time (60-480 minutes) on Fe$_3$O$_4$ and hypochlorite adsorption efficiency.

4.6.1 The effect of pH on the functionality of Fe$_3$O$_4$ & hypochlorite on coffee wastewater

Results obtained (Table 4.13) show that a molecular form of Fe$_3$O$_4$ and hypochlorite changes wastewater’s solution in the range from 4-8. The chemical parameters removal was greatest at pH 6 with 42% reduction, and at pH 4 with 36% reduction of coffee wastewater pollutants. For the coliforms, there was less removal rate at pH 8 with (20%) and at lower pH ranges (>6) the removal rate increased to (30%). The microbiological results showed that coliforms can be greatly removed with a decreasing pH. This is due to that bacteria cannot tolerate environments that are cold and that are acidic, within this environment, there are less nutrients for bacteria to feed on. All these results showed an overall decrease of 35% on the pollutants that were present in coffee wastewater.
Table 4.13: Fe₃O₄ and hypochlorite results for COD, TOC, TDS and coliforms analysis at pH 4-8.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>pH 4</th>
<th>pH 6</th>
<th>pH 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (mg/L)</td>
<td>7500</td>
<td>7000</td>
<td>7200</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>8050</td>
<td>7700</td>
<td>8000</td>
</tr>
<tr>
<td>Coliforms (cfu/g)</td>
<td>5000</td>
<td>5500</td>
<td>6500</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>8800</td>
<td>8500</td>
<td>8600</td>
</tr>
</tbody>
</table>

4.6.1.1 UV-Vis analysis of coffee wastewater before and after treatment with Fe₃O₄ and hypochlorite.

The results for the UV-Vis spectral scanning curve of the filtered water after treatment with Fe₃O₄ and hypochlorite showed an analogous decline pattern in all the pH ranges (Figure 4.16), more absorbance (70%) was noted from 400nm-800nm. The spectral curve shows a broad spectrum at pH 4. However, results obtained in all three pH values were similar and appeared as one curve.

![Figure 4.16](image)

**Figure 4.16**: UV-Vis spectral scanning curve of the filtered water after treatment with Fe₃O₄ and hypochlorite.
4.7.1 Photo degradation of Coffee Waste Water using Fe₃O₄TiO₂ nanocomposite with hypochlorite.

As time of adsorption changed from 60 to 240 minutes, the efficiency firstly remained constant and slowly changed from 5000-4300 mg/L and at 360 to 480 minutes and remained constant. This was due to the surface coverage of the adsorbent that was high when time increased and further no adsorption took place. From this data (Figure 4.17), it can be proposed that the reaction time should be controlled within 60-360 minutes, as there is no unforeseen change that occurs after that time interval.

4.5.1 The effect of the reaction time (60-480 minutes) on Fe₃O₄TiO₂ nanocomposite with hypochlorite adsorption efficiency.

![Graph](image)

**Figure 4.17**: The effect of time (60-480 minutes) on Fe₃O₄TiO₂ nanocomposite with hypochlorite adsorption efficiency.

The results for the UV-Vis spectral scanning curve of the filtered water after treatment with Fe₃O₄TiO₂ and hypochlorite showed an analogous decline pattern that is similar with the previous results for iron and hypochlorite in all the pH ranges, the more absorbance (70%) was noted from 400nm-800nm. The spectral curve showed a broad spectrum at pH 4. However, results obtained in all three pH values were similar and appeared as one curve.
According to wastewater regulations and the content of the coffee wastewater from Nestle that was studied, the below chemical and microbiological characteristics were studied.

4.7.1.1 The effect of pH on the functionality of Fe₃O₄TiO₂ nanocomposite with hypochlorite on coffee wastewater.

The results for the chemical and microbiological parameters showed that coliforms can be greatly removed at pH (pH8). The chemical parameters showed a better removal efficiency at pH 6. In all these studied parameters (TOC, COD, TDS and coliforms), a 40% reduction of the coffee wastewater pollutants was observed.

Table 4.14: The effect of pH on the functionality of Fe₃O₄TiO₂ nanocomposite with hypochlorite on coffee wastewater

<table>
<thead>
<tr>
<th>Parameters</th>
<th>pH 4</th>
<th>pH 6</th>
<th>pH 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (mg/L)</td>
<td>7500</td>
<td>7000</td>
<td>7800</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>6850</td>
<td>6800</td>
<td>5700</td>
</tr>
<tr>
<td>Coliforms (cfu/g)</td>
<td>4000</td>
<td>3500</td>
<td>3300</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>9000</td>
<td>7000</td>
<td>7500</td>
</tr>
</tbody>
</table>

4.5.3 UV-Vis analysis of coffee wastewater before and after treatment with Fe₃O₄TiO₂ with hypochlorite

The comparison was based on the moles of free radicals formed per unit reactant volume by LED illumination of hypochlorite and Fe₃O₄TiO₂ composite on the coffee wastewater. The results showed a similar decline pattern in all the pH ranges (Figure 4.18). More absorbance (70%) was noted from 400nm-800nm.

Advanced oxidation processes (AOPs) could play an important part due to their ability to produce highly oxidative hydroxyl radicals (•OH), which is capable of destroying the emerging organic pollutants (for example endocrine disrupters, pesticides and pharmaceuticals (Li, et.al., 2005).
The concentration of heavy metals after treatment with the different metals represented in (Table 4.14) showed that removing metals in wastewater is still a challenge. The coagulants had the lowest removal percentage (5%). The iron and the titanium composite removed metals at similar ranges but the titanium composite showed a 30% removal difference copper and lead, there was when compared with the other metals. If the effluent, however is sent to the municipal sewer for secondary treatment, these metals are not part of the industrial wastewater discharge requirements.

**Figure 4.18:** UV-Vis spectral scanning curve of the filtered water after photocatalytic treatment with Fe$_3$O$_4$ with hypochlorite.
Table 4.15 Heavy metals results after treatment with Bufloc 5170, Fe₃O₄ and Fe₃O₄TiO₂ nanocomposite using ICP-OES

<table>
<thead>
<tr>
<th>Parameters</th>
<th>BUFLOC 5170</th>
<th>Fe₃O₄</th>
<th>Fe₃O₄TiO₂ nanocomposite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic(μg/L)</td>
<td>100</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>Boron (mg/L)</td>
<td>5.6</td>
<td>0.25</td>
<td>0.20</td>
</tr>
<tr>
<td>Cadmium (μg/L)</td>
<td>2</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Chromium (μg/L)</td>
<td>41</td>
<td>38</td>
<td>35</td>
</tr>
<tr>
<td>Copper (μg/L)</td>
<td>650</td>
<td>500</td>
<td>410</td>
</tr>
<tr>
<td>Lead (μg/L)</td>
<td>900</td>
<td>400</td>
<td>300</td>
</tr>
<tr>
<td>Mercury (μg/L)</td>
<td>1500</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td>Zinc as Zn (μg/L)</td>
<td>300</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>

4.8 Cost benefit analysis

The amount of wastewater produced is correlated to financial losses and profitability of industries today (Shan-Ganai, 2011). The costs associated with maintenance, breakdowns of the current wastewater system were evaluated for the past three years and data are represented in Table 4.16.

Table 4.16: The expenses trend for the maintenance costs of the wastewater evaporator system for 2013-2016

<table>
<thead>
<tr>
<th>Expenses</th>
<th>2013</th>
<th>2014</th>
<th>2015</th>
<th>2016</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM01®</td>
<td>3 889.09</td>
<td>31 233.00</td>
<td>24 042.91</td>
<td>26 022.65</td>
<td>85 187.65</td>
</tr>
<tr>
<td>PM02®</td>
<td>28 989.08</td>
<td>1 328 345.87</td>
<td>537 532.64</td>
<td>376 321.02</td>
<td>2 271 188.61</td>
</tr>
<tr>
<td>PM03®</td>
<td>4 472.72</td>
<td>67 819.46</td>
<td>33 607.31</td>
<td>30 892.39</td>
<td>136 791.88</td>
</tr>
<tr>
<td>Total®</td>
<td>R37 350.89</td>
<td>1 427 398.33</td>
<td>595 182.86</td>
<td>433 236.06</td>
<td>2 493 168.14</td>
</tr>
</tbody>
</table>

The pie chart in (Figure 4.19) shows a trend for the breakdown costs in percentages that occurred in the past four years on the wastewater evaporator system. These include replacing stators on lime dosing pump, unblocking Hotwell pumps, replacing pumps, and motors. The trend fluctuates yearly and the main challenge with the system is maintenance.
Figure 4.19: Graph showing estimation of breakdowns (PMO1) report per annum from 2013-2016

The below pie chart (Figure 4.20) shows the maintenance costs for the inspections that are conducted weekly on the wastewater evaporator system. These include, changing faulty flow switch, repairing balance tanks, high pressure cleaning of drains and replacing contactors as well as gaskets. From the percentages in the trend, it is observed that, the walkabout inspections decreased yearly which could be one of the reasons why PMO1 (Figure 4.20) increased as these inspections are meant to prevent breakdowns.
**Figure 4.20:** Graph showing estimation of inspections (PMO2) report per annum from 2013-2016

The graph in (Figure 4.21) shows planned maintenance costs for the wastewater evaporator. The main goal of maintenance costs is to prevent having to pay for overnight delivery parts, saving company money, improving safety and decreasing equipment downtime. These include checking the entire system in the factory during shutdown and checking mechanical seals, motor bearings and many others. The above trend also shows a percentage decrease which might be good in terms of cost savings but in the end, it would cost the company more money to fix the system once it is faulty.

**Figure 4.21:** Graph showing estimation of planned maintenance (PMO3) results per annum from 2013-2016.

The evaluation for the current study that was conducted on coagulants and nanoparticles did not include the labor and maintenance costs (Table 4.17). Only the costs for the chemicals used, the risk level and the wastewater discharged hourly were taken into account. Coagulants were found to be cheaper when compared with the nanoparticles but they were found to be less efficient in the coffee wastewater treatment. In terms of the risk level, the studied nanoparticles were found to be less toxic in terms of the toxicological classification. The recovery of the Nano composite
via the magnet is environmentally friendly which is positive to aquatic systems and the exposed environment. The wastewater discharged hourly was however found to be very high including the costs associated to it. The proposed treatment method could be further studied in a pilot plant to see the feasibility of the process in a large pool.

Table 4.17: The estimation of momentary value for the proposed methods

<table>
<thead>
<tr>
<th>Material</th>
<th>Price/g®</th>
<th>Risk level</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Coagulants/Flocculants(Total)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 BULAB 5160</td>
<td>R1.645,00</td>
<td>Low</td>
</tr>
<tr>
<td>1.2 ALUM</td>
<td>R525,00</td>
<td></td>
</tr>
<tr>
<td>1.3 BUFLOC 5170</td>
<td>R420,00</td>
<td></td>
</tr>
<tr>
<td>1.4 BUFLOC 5181</td>
<td>R350,00</td>
<td></td>
</tr>
<tr>
<td>2. Fe₃O₄ (Total)</td>
<td>R 2.236,00</td>
<td>Low</td>
</tr>
<tr>
<td>2.1 FeCl₂.4H₂O (97%)</td>
<td>R1.050,00X5g</td>
<td></td>
</tr>
<tr>
<td>2.2 FeCl₂.6H₂O (97%)</td>
<td>R766,00X5g</td>
<td></td>
</tr>
<tr>
<td>2.3 NH₂.NH₂(35WT)</td>
<td>R420,00</td>
<td></td>
</tr>
<tr>
<td>3. TiO₂ (Total)</td>
<td>R3.540,00</td>
<td>Low</td>
</tr>
<tr>
<td>3.1 Ti (OBU)₄(97%)</td>
<td>R1.240,00X5g</td>
<td></td>
</tr>
<tr>
<td>3.2 NH₄OH (25%)</td>
<td>R800,00</td>
<td></td>
</tr>
<tr>
<td>3.1 C₂H₂O (99%)</td>
<td>R1.500,00x50mL</td>
<td></td>
</tr>
<tr>
<td>4. LED light</td>
<td>R32.50E.A</td>
<td>Low</td>
</tr>
<tr>
<td>5. Wastewater discharge costs(per kL)</td>
<td>R5.09 x 30m³= R 152700 per hour</td>
<td>High</td>
</tr>
</tbody>
</table>

4.9 Discussion

The coagulants, flocculants have been found to be the most used methods in the treatment of coffee wastewater, however drawbacks are due to that diverse operational conditions need to be explored to improve the treatment efficiency of the coffee wastewater. The amount of sludge produced with the treatment of coffee is another challenge.
There are numerous research studies that have been done on nanoparticles and they denote that, the distribution of nanoparticles and particle size have an extensive effect on their distribution and their performance as catalysts. The minor the particles are, the greater their range per unit mass and, subsequently, the more vigorous sites are (Vu, et.al., 2017).

Controlling the viscosity of TiO$_2$ shell of core-shell structures by guiding the hydrolysis and condensation of TBOT in ethanol/ammonia mixtures ensures the shell width of the composite is between 20 nm and 45 nm. These were one of the findings in a study conducted by Li, et.al., (2012).

There are bacterial strains that are found to be present in acidic environments and some can only be deactivated after a long period while lactic acid bacteria, *lactobacillus* are the most prevalent bacteria that are found to be present in an acidic environment. A study by Glass, et.al. (1992) on the effects of pH on *E. coli* 0157:H7 showed that a mixed inoculum of five strains of *E. coli* 0157:H7 was inactivated within 10 days and 17 days at pH 3.5 and 4.0.
CHAPTER FIVE

5.1 General conclusion and recommendations for future work

This work involved the application of coagulants/flocculants and nanoparticles. The main aim of this study was to synthesize and characterize nanoparticles (iron and titanium) and compare them with coagulants/flocculants to discover the most efficient method in removing pollutants present in the coffee wastewater. These characterization techniques (XRD, FTIR, TEM, BET and XRF) were used to study the magnetic properties of the prepared magnetic iron and magnetic titanium photocatalyst for the degradation of coffee wastewater under LED light irradiation.

Based on the observations from this study on coagulants, magnetite iron and titanium nanocomposite, titanium nanocomposite was found to be the most promising treatment technology. However, since Titania cannot be completely recovered from the reaction medium, this poses an environmental concern. The risk level is intolerable (Table 4.10) if the system is used in a large scale industry. The solution to this recovery problem is to combine this nanoparticle (TiO$_2$) with iron (Fe$_3$O$_4$) as the recovery medium, which has been the most studied material and found to be eco-friendly and cheap and this study followed this approach.

There are other similar studies that have been studied for the degradation of dyes using magnetite iron oxide in photocatalytic experiments and the iron was found to have less photocatalytic properties.

This study can further be modified by combining all the methods in one treatment system where all the studied chemicals can be recovered and reused in the treatment process. The combination of flocculants with iron magnetic particles can serve as an environmentally friendly approach in removing organic pollutants in the coffee wastewater since these chemicals are not released to the environment but are recovered through the use of the magnetic field.
The ultra-fine titanium dioxide anatase powder mostly shows remarkable photocatalytic performance due to greater specific surface area that they possess, and greater dispersion in aqueous solutions. Yet, practically, there are difficulties of parting and reprocessing of the photocatalyst particle from wastewater and water. There have been studies of titanium placed on crystal, zeolite, pottery, silica, and fibre crystal but the photo activity in these fixed-bed systems is limited to a significant point coming from the immobility of titania as well as the low mass transfer rate.

A study done by (Bera & Belhaj, 2016) on magnetic flocculants was studied and were found to act as an alternative patterns for nanoparticle recycling by magnetic separation, since they have applications not only for nanocatalysts recycling, but also in remediation of nanoparticle pollution, algae dewatering. This similar approach can be adopted for future work in the treatment of coffee wastewater.
6.1 References


Environmental, Health, and Safety (EHS) Guidelines.


*National Environmental Act, 2002*


