ELECTROCHEMICAL DEGRADATION AND CHEMICAL ASSESSMENT OF
AZO DYES IN THE TEXTILE WASTE WATER

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A thesis submitted in partial fulfillment of the requirements for the Degree of
Master of Science in Chemistry of Pwani University

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DECLARATION

Declaration by the candidate

This thesis is my original work and has not been presented for a degree in any other university.

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DEDICATION

This thesis is dedicated to the almighty God. Also to my dear wife Jediliah Mwakisha and our children Georgesmartin Genus, Condoleezzamartins Rice and Anglamartins Brilliant..
ACKNOWLEDGEMENT

I am very grateful to all the people who contributed directly or indirectly to this work.

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To God be the glory.
ABSTRACT

Azo dyes are carcinogenic and if taken would lead to debilitating adverse health effects in animals, man and aquatic organisms. In this study, novel Boron Doped Diamond (BDD) electrodes were the anode while stainless steel served the role of cathode to degrade azo dyes. Iron (11) sulphate was used as a supporting electrolyte and silver nanoparticles as electrocatalyst to enhance the degradation efficiency. A sample of synthetic and real wastewater samples were employed in the electrochemical treatments and the variations studied were; voltage, dye concentration, supporting electrolyte, current density, inter-electrode distance, pH and temperature of the effluent. Degradation efficiency was monitored by UV-VIS spectrometry while some of the Physico-chemical parameters were determined by standard methods for examination of water and waste water as outlined in the APHA (2000). The absorption spectra for the four dyes were determined and their $\lambda_{\text{max}}$ ranged between 470 to 590 nm in UV-VIS spectrum. Colour removal of 100% was achieved at the end of the electrochemical degradation. The BOD and COD of the effluent were lowered below the recommended values by the WHO (2002) of 150mg/l and 250 mg/l before the discharge to water course. The colour levels of the treated textile waste water was found to be BDL. The final treated wastewater was compared with National Environmental Management Authority (NEMA) and World Health Organization (WHO) effluent discharge standards for possibility of re-use or direct discharge to a natural water course.
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AgNPs</td>
<td>Silver nanoparticles</td>
</tr>
<tr>
<td>Aq</td>
<td>Aqueous</td>
</tr>
<tr>
<td>APHA</td>
<td>American public health association</td>
</tr>
<tr>
<td>BDD</td>
<td>Boron doped diamond electrode</td>
</tr>
<tr>
<td>BDL</td>
<td>Below detected limit</td>
</tr>
<tr>
<td>BOD</td>
<td>Biochemical oxygen demand</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>Conc.</td>
<td>Concentration</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DMM</td>
<td>Digital multimeter</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved oxygen</td>
</tr>
<tr>
<td>EC</td>
<td>Electrochemical</td>
</tr>
<tr>
<td>ES</td>
<td>Effluent Sample</td>
</tr>
<tr>
<td>EMCA</td>
<td>Environmental Management Co-ordination Act</td>
</tr>
<tr>
<td>FAS</td>
<td>Standard ferrous ammonium sulphate</td>
</tr>
<tr>
<td>GOK</td>
<td>Government of Kenya</td>
</tr>
<tr>
<td>KEBS</td>
<td>Kenya Bureau of Standards</td>
</tr>
<tr>
<td>LSD</td>
<td>Least significant difference</td>
</tr>
<tr>
<td>ML</td>
<td>Millilitre</td>
</tr>
<tr>
<td>Mm</td>
<td>Millimetre</td>
</tr>
<tr>
<td>Mmol</td>
<td>Millimolar</td>
</tr>
<tr>
<td>OP</td>
<td>Oxidation potential</td>
</tr>
<tr>
<td>PD</td>
<td>Potential difference</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>SE</td>
<td>Standard electrode</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>------</td>
<td>-------------------------------------</td>
</tr>
<tr>
<td>UV-VIS</td>
<td>Ultraviolet visible</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organization</td>
</tr>
</tbody>
</table>
viii

LIST OF FIGURES

Figure 2.1: Structure of reactive blue 5.................................................................7

Figure 2.2: Structure of lithol rubine........................................................................7

Figure 2.3: Structure of disperse black 3.................................................................8

Figure 2.4: Structure of disperse orange 5..............................................................8

Figure 2.5: Structure of acid red dye........................................................................9

Figure 2.6: Schematic representation of reduction-oxidation electrons formation- TiO$_2$ surface with pairs of holes.......................................................................................13

Figure 3.1: Electro-chemical cell set up.....................................................................24

Figure 4.1: A plot of UV Absorbance vs. Wavelength (nm) obtained by scanning the samples in the range of 450nm to 650 nm.................................................................28

Figure 4.3(a): A plot showing the effect of time on the electrochemical degradation of disperse black dye scanned between 520 nm and 670nm....................................................33

Figure 4.3 (b): plots showing the effect of time on the electrochemical degradation of disperse blue scanned between 470 nm and 620nm..............................................................33

Figure 4.3(c): A plot showing the effect of time on the electrochemical degradation of reactive red scanned between 470 nm and 620nm...............................................................34

Figure 4.3 (d): A plot showing the effect of time on the electrochemical degradation of reactive red scanned 470nm and 570nm.................................................................34

Figure 4.4(a): A plot showing effect of dye concentration on electrochemical degradation of reactive red dye scanned between 420nm and 520nm........................................36

Figure 4.4(b): A plot showing effect of dye concentration on electrochemical degradation of disperse black dye scanned between 420nm and 520nm........................................36
Figure 4.4(c): A plot showing the effect of dye concentration on electrochemical degradation of reactive deep dye scanned between 400nm and 600nm..........................37

Figure 4.4(d): A plot showing effect of dye concentration on electrochemical degradation of disperse blue dye scanned between 550nm and 750nm............................37

Figure 4.5(a): A plot showing effect of iron (II) Sulphate concentration on disperse blue dye degradation scanned between 450nm and 600nm in the UV spectrum.........................38

Figure 4.5(b): A plot showing effect of iron (II) Sulphate concentration on reactive deep dye degradation scanned between 470nm and 620nm........................................39

Figure 4.5(c): A plot showing effect of iron (II) Sulphate concentration on reactive red dye degradation scanned between 420nm and 620nm in UV spectrum.........................39

Figure 4.5(d): Plot showing effects of iron (II) Sulphate concentration on disperse black dye degradation scanned between 520nm and 700nm in the UV spectrum....................40
LIST OF TABLES

Table 4.2: Effects of AgNPs concentration, current and power consumption on azo dye degradation .................................................................29

Table 4.6: Effects of variation of potential difference on azo dyes degradation...................................................................................................41

Table 4.7: Effects of inter-electrode spacing on the degradation of the various azo dyes.............................................................................................................43

Table 4.8: Effects of the effluent pH on usage of power at a potential difference of 24 V.................................................................................................46

Table 4.9: Effects of effluent temperature on dye degradation on the samples ES1, ES2, ES3 and ES4.................................................................48

Table 4.10: Determination of colour removal level during effluent electrochemical Degradation........................................................................51

Table 4.11: Determination of biochemical oxygen demand of the effluent before and after electrochemical degradation.........................................................52

Table 4.12: Determination of Chemical oxygen demand before and after electrochemical degradation.................................................................54
LIST OF SCHEMES

Scheme 3.1 Electrochemical cell set up for Azo Dye removal..........................25
TABLE OF CONTENTS

DECLARATION..................................................................................................................ii

DEDICATION..................................................................................................................iii

ACKNOWLEDGEMENT....................................................................................................iv

ABSTRACT.....................................................................................................................iv

LIST OF FIGURES............................................................................................................viii

LIST OF TABLES.............................................................................................................x

LIST OF SCHEMES..........................................................................................................xi

TABLE OF CONTENTS....................................................................................................xii

CHAPTER ONE..................................................................................................................1

INTRODUCTION..............................................................................................................1

1.1 Background information ...........................................................................................1

1.2 Problem statement ....................................................................................................3

1.3 Justification of the study ..........................................................................................3

1.4 Objectives ................................................................................................................4

1.4.1 Overall Objective ...............................................................................................4

1.4.2 Specific objectives ..............................................................................................5

1.4.3 Research hypothesis ...........................................................................................5

CHAPTER TWO..................................................................................................................6
LITERATURE REVIEW

2.1 Textile Dyes

2.1.1 Reactive Dyes

2.1.2 Disperse Dyes

2.1.3 Acid Dye

2.1.4 Naphthol Dye

2.1.5 Basic/ Cationic Dye

2.1.6 Direct Dye

2.1.7 Mordant Dye

2.1.8 Sulphur Dye

2.1.9 Vat Dye

2.2 Catalytic technology in textile dye removal

2.2.1 Photocatalysis behavior

2.2.2 Surface reactions of TiO2

2.2.3 Nanoparticles as electrocatalyst in the dye removal

2.2.4 Silver nanoparticles as electrocatalyst in the textile dye removal

2.3 Methods of wastewater treatment

2.3.1 Biological techniques

2.3.2 Electrocoagulation methods
2.3.3 Natural Mineralization of Organic Pollutants………………………………16
2.3.4 Adsorption of industrial pollutants……………………………………………16
2.3.5 Cationic coagulation and flocculation………………………………………17
2.4 Electrode materials in organic degradation of wastewater…………………..17
2.5 Water quality………………………………………………………………………18
2.6 Experimental design………………………………………………………………19
   2.6.1 Geometry………………………………………………………………………19
   2.6.2 Scale-up issues………………………………………………………………..19
   2.6.3 Current density……………………………………………………………….19
   2.6.4 Electrode material……………………………………………………………..20
   2.6.5 Solution pH……………………………………………………………………20

CHAPTER THREE…………………………………………………………………21

MATERIALS AND METHODS……………………………………………………21

3.1 Chemicals, reagents and electrodes……………………………………………21
3.2 Biochemical oxygen demand……………………………………………………21
3.3 Chemical oxygen demand…………………………………………………………22
   3.3.1. Reagents required for preparation………………………………………22
3.4 Electrochemical cell set-up………………………………………………………24
   3.4.1 Electrochemical measurements……………………………………………25
3.4.2 Effect of voltage..........................................................................................25
3.4.3 Effect of dye concentration...........................................................................26
3.4.4 Effect of Silver Nanoparticles......................................................................26
3.4.5 Effect of current density...............................................................................26
3.4.6 Effect of Inter-electrode distance.................................................................26
3.4.7 Concentration of Iron (II) Sulphate..............................................................26
3.4.8 Effect of effluent pH......................................................................................26
3.5. Degradation efficiency.....................................................................................27
3.6. Data analysis...................................................................................................27

CHAPTER FOUR........................................................................................................28

RESULTS AND DISCUSSIONS................................................................................28

4.1 The determination of the absorption spectra for the four azo dyes (reactive and
disperse dyes)..............................................................................................................28
4.2 Effect of silver nanoparticles on azo dye removal............................................29
4.3 Effect of time on degradation of dyes.................................................................31
4.4. Effect of the concentration on dyes degradation..............................................34
4.5. Effects of addition of iron (II) sulphate on degradation of the dyes.................37
4.6. Effects of variation of potential difference on azo dyes degradation...............40
4.7. Effect of inter-electrode distance, current and power consumption on dye
removal..................................................................................................................43
4.8 Physical-Chemical properties of effluent

4.8.1 Effect of effluent pH on dye degradation

4.8.2. Effect of effluent temperature on dye degradation

4.8.3 Determination of colour removal level during effluent electrochemical degradation

4.8.4 Determination of Biochemical oxygen demand of the effluent before and after electrochemical degradation

4.8.5 Determination of Chemical oxygen demand before and after electrochemical degradation

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.2 Recommendation

REFERENCES
CHAPTER ONE

INTRODUCTION

1.1 Background information

According to (Grierson, 1989) the earliest humans started applying coloration to the organic substances especially to the textile products as their settling occurred from 7000-2000 BC. Dyes have got various usages in fields such as pharmaceuticals, food technology, textile industry products, beautification application, chromatography and printing industries (Rafi, Franklin 1990). More than 10,000 varieties of dyes and over 700,000 tons of the said dyes can be produced within a period of one year. More and beyond 668,000 tons are made of azo dyes (Ollgaard et al., 1998). Of all the azo dyes commonly utilized in the textile industries an amount of not less than 15% are lost and end up in various water bodies (Zollinger, 1987).

The various categories of dyes are listed as; azo, anthraquinon and triarylmethane, acid dyes, disperse dyes, reactive dyes, mordant dyes (Anliker et al, 1981). They have long life and contain carcinogen components. Dyes possess chromophores which constitute delocalized electrons with conjugated double bonds .They also contain auxochromes referring to substances which are either withdrawing electrons or take part in the donation of electrons changing electron components thereby increasing color of the chromophores. Normally chromophores include the following; -C=O, -C=N-, -NO₂, -C=C-, whereas the auxochromes include; -NH₃, -OH, -COOH, -SO₃H (Zee, 2002). Textile effluents contain several components, for instance chlorine based organic compounds, xylene substances which are pollutants in nature (Judd et al., 1994). These azo dyes are easily noted by human eye at a range of 0.1g/l and anything above this level is
considered to be harmful to human health, animals and also aquatic organisms living in the water bodies where these azo dyes are discharged occasionally (O’Neill et al., 1999). Azo dyes are considered to cause other health challenges like allergies and skin dermatoses (Su and Horton, 1998). These textile waste waters if not treated have effects on human liver, the respiratory system, the circulation process, the immunity components and reproduction process in human beings (Deveikis et al., 1995). Azo dyes contain the nitro and the amino groups which are carcinogenic in nature and lead to growth of tumor of the liver and other organ systems in living things (Dipple et al., 1991). The complexity of the pollutant makes the treatment problem more complex. The components that constitute the effluents are many; for instance, xylene, phenol, pH buffer, scouring and discoloration agents, salty water solutes, surfactants, biochemical enzymes, and pH changers (James and Cynthia, 1985). Several components explain the reason for the complicated nature of the effluent (Reid and Green, 1996). The stability of the dyes results from the complexity of the molecules in the materials which are in the form of aromatic structure (Jawabreh et al., 2003). The safe method of dye disposition is by use of natural or artificial light, high temperature, enzymes, and chemical (Aziz, 2007). Note that, the dyes from textile are resistant to the above methods of disposition (Feng and Li, 2003). This makes the process of degrading the said dyes slow and hard (Lin, 2003). The international regulation demands that the manufacturers formulate appropriate measures that allow proper treatment before disposal. Untreated dyes that are released even in small concentrations have been found to introduce strange color into the water body, hence, discourages users (Lai et al., 2003). Essentially, the polluted water is unfit for human use and aquatic animals’ survival (Zawani et al., 2009). In this study only four types of azo dyes were considered and they included; disperse black, disperse blue, reactive red and reactive deep.
1.2 Problem statement

Disposal of textile wastewater is a primary concern as large volumes of untreated waste water (up to 100 m$^3$) is released daily during factory processing procedures. This discharged effluent contain high levels of color, pH, COD and BOD that can pollute water streams when released directly into the streams. The 1999 Environmental Management and Co-ordination Act, (GOK, EMCA 1999) bestowed the responsibility of maintaining good surrounding to every other individual within and outside the country. Therefore, any manufacturing industry that produces waste must strictly follow the laws of environment preservation (The water Act cap 372, section 145-147 of the Laws of Kenya) (GOK, 1972). Part ix section 16 of the Public Health Act (Cap 242), (GOK, 1986), requires every industry to uphold and maintain the natural clean environs around and away from the vicinity. This would reduce the burden of pollution caused diseases, toxicities and dangers. The factories need to have a strategic system of waste water cleaning before releasing to the water bodies. This study was therefore geared towards developing an environmentally friendly electrochemical method that is reliable and efficient, capable of treating industrial textile wastewaters to meet standards for re-use or discharge to a watercourse. This electrochemical method of waste water treatment addresses the shortfall experienced by the textile industries resulting from the use of electrocoagulation which has a problem of electrical polarization and formation of excess flocs.

1.3 Justification of the study

Azo dyes are quite carcinogenic hence wastewaters from textile industries need to be treated before they are discharged to a water course. Colour, inorganic and organic pollutant loads affect the quality of water hence should be removed before discharge to water bodies. Electro coagulation methods have proved to be effective but expensive in
colour removal and treatment of wastewater (Maghanga et al., 2009). The other two methods that are efficient in the treatment of the wastes in the textile industries include the electrochemical method and the chemical oxidation method. The former is recent and mineralizes the organic forms of the pollutants. On the other hand, the latter uses oxidants to dissolve the waste by oxidation. Apparently, the first method is safer than the second because of the use of electricity contrary to chemicals. The complete dissolution of the particles ensures that the waste reaching the environment is particles free, hence, no sludge accumulation at the bottom of the trash pit (Comninellis and Pulgarin, 1991). The most recent and also considered to be greatly effective is the adsorption method (Lefrano et al., 2016). However, the recent discoveries have shown that adsorption method may not actually be cost effective (Rahmani et al, 2018). In this study an attempt is made to find out if the colour of the textile factory wastewater can be removed electrochemically. The studies will also focus on optimizing the conditions of the electrochemical cell so as to understand the effects of electrochemical method on effluent quality and subsequent environmental impacts on the effluent discharged into the surrounding water bodies. The textile dye in the industrial waste waters were electrochemically treated using boron doped diamond electrodes (BDD) with silver nanoparticles to act as an electrocatalyst.

1.4 Objectives

1.4.1 Overall Objective

To optimize an effective electrochemical method that is reliable, efficient and economically viable, capable of treating azoic dyes in textile wastewater to meet standards for re-use or discharge to a water course.
1.4.2 Specific objectives

1. To measure the absorption spectra of the four azo dyes (reactive and disperse dyes)

2. To assess the effect of process parameters: (dye concentration, current density, pH, time, concentration of silver nanoparticles and Iron (II) sulphate) in colour removal.

3. To measure specific physico-chemical properties of effluent before and after electrolysis.

1.4.3 Research hypothesis

$H_0$: Variation of process parameters have no effect on the azo dye removal from the textile waste water.

$H_1$: Variation of process parameters have effect on the azo dye removal from the textile waste water.
CHAPTER TWO

LITERATURE REVIEW

2.1 Textile Dyes

Dyeing industries are of great scale and very crucial world over. The textile effluents to water bodies are the ones considered unwanted in the surroundings due to their polluting effects. Textile dyes have been proven to cause cancer related disorders and alteration of the genetic materials (Golka et al., 2004). It is estimated that hundreds of tons of dyes produced annually are mainly azo dyes which comprise of about 70% of the total yield worldwide (Ollgaard et al., 1998).

2.1.1 Reactive Dyes

These dyes contain reactive group, and in the Color Index, this is the second largest dye class. The bond formed when reactive dyes react with hydroxyl, -NH, or -SH fibres is a strong one because of the formation of the covalent bonds. Salts of chlorine, fluorine, and vinyl sulfur are the substitution molecules for heterocyclic aromatic ring. The hydrolysis of the group during dyeing interferes with the fixation degree of reactive dyes which create the problem of colored effluent. A distinguishing trait of this dye is its ability to dissolve in water and the resistance towards the degradation procedures. This difficulty is complementary to the structure of the molecules constituting the dye. The process of manufacturing the said dye requires a product that can withstand the degradation techniques (Brown and Hamburger, 1987). One positive characteristic of the dye is that in its natural form, the level of toxicity is low and safe for humans. However, when one creates a suitable environment, for instance, deprivation of oxygen, the resultant molecules have aromatic amines. Notably, such can cause cancer and are toxic to one’s health (Pinheiro et al., 2004; Frank and Villaverde, 2005). The component
molecules can react with hydroxylated cellulosic fiber, and the protein fiber in sub-component of amino, hydroxyl, and mercapto, as well as the amine polyamides. The resultant covalent bond is strong (Zollinger, 1991). Therefore, the strength exhibited by these dyes make their application suitable in the textile factory (Waring and Hallas, 1994). The structures of reactive blue 5 and lithol rubine below are some of the examples of reactive dyes.

*Figure 2.1 Structure of reactive blue 5*

*Figure 2.2 Structure of lithol rubine*

2.1.2 Disperse Dyes

This dyes gained popularity in the industry when there was the invention of the
artificially made fibers. The molecules of such fibers do not dissolve in water, hence, the appropriateness. The compounds present are amino chemicals and as the name suggests, the dyes act by dispersion of particles that are very tiny. The solution can act sufficiently in small quantities. The material of choice for the dye is polyester. However, one can also use it in materials containing nylon or acetate (Christie, 2001).

It should be noted that this category of dye applies acetate and polyester which are the only insoluble components. Furthermore, the particles are very microscopic. The structure consists of bonds between azobenzene or anthraquinone and the –NH, -SH, and –OH. These strong bonds ensure durability even in adverse environmental conditions (Kirk 2003). Some of the examples of dyes in this category include: disperse black 3 and disperse orange 5.

![Figure 2.3 Structure of disperse black 3](image)

![Figure 2.4 Structure of disperse orange 5](image)

2.1.3 Acid Dye

The dyes contain acid and function well in polyamide fibers. The category includes many types of stains and has different commercial names. The three most suitable
materials to use such dye include cotton, silk, and nylon. The process involves putting
the elements in water bath that has a temperature of about one hundred degrees.
Moreover, the solution should be neutral one or a strong acid, for instance, chlorine or
sulphuric acid. The different eventual colors are varying according to the design of
desire that the client requires, for example, dull or bright colors (Kirk, 1993).

\[ \text{Figure 2.5 Structure of acid red dye} \]

2.1.4 Naphthol Dye

Unlike the acidic dye, the azoic one is a pigment that is insoluble and not exactly a
complete one. The synthesis of the dye occurs inside the fiber. Evidently, the primary
component, the naphthol, is originally soluble, contrary to the end product. The process
of obtaining the final color requires addition of a salt called diazo. Notably, the original
materials are toxic, and one needs to be careful when mixing (Kirk, 1993).

2.1.5 Basic/ Cationic Dye

The appropriate materials that one can apply such dye include the acrylic fibers, specific
types of nylons, as well as fibers that contain protein. Contrary to the natural fibers, the
Acrylic one works well with the dye. (Kirk, 1993).
2.1.6 Direct Dye

There is increased tendency of such to move onto fibers without the need for other chemicals to bond the dye to the fiber, and this makes them have poor wash fastness (Christie, 2001).

2.1.7 Mordant Dye

Mordant dyes, as the name connotes, originates from a chemical of the similar name. the formulae of working are through creating a strong attachment between the fiber and the dye. A typical example includes the chromium one. The material of choice to apply such is cotton. Note that, the chemical complements the natural dyes, hence, the demand in the textile industry (Kirk, 1993).

2.1.8 Sulphur Dye

Sulfur, after reacting with other chemicals that are organic in nature forms the dye. The primary form of the dye does not dissolve in water. Such is not usable. Hence, the manufacturer has to add other compounds to make the dye soluble. The loss of the color of the dye in the textile is easy, though the fastness is appealing. The preservation method entails putting in alkaline bath the final fabric. Such is because exposure to increasing temperature and humidity leads to production of acid. Therefore, the alkaline condition neutralizes the acid (Kirk, 1993).

2.1.9 Vat Dye

CThe natural form of the dye does not dissolve in water. Therefore, during application, one has to apply reducing agents to change the state. The previous form is long- lasting, consequently, through oxidation, the manufacturer needs to convert the soluble dye to be insoluble again. The commonest color of the dye is indigo. The material that commonly needs the colour is the jeans, especially, the blue one. Chlorine has weak effect on the
color, and the wash fast is encouraging (Kirk, 1993).

2.2 Catalytic technology in textile dye removal

There is increased attention to the use of electrochemical technology in color removal because of the guarantee of not having other new pollutants afterward, convenience as well as simplicity (Cheng et al., 2005). The exact mechanisms are complicated, but both direct and indirect oxidation of the organic effluents is possible through electrolysis using oxidants, for instance, ozone, hydrogen peroxide, chloride, hydroxyl, and ClO⁻. Such is suitable only for large plants because of the large scale use of electrochemical oxidants. The process requires catalysts to make the treatment more efficient. According to Cheng and Zhu 1998, to remove phenols, phenylamine, and dimephthalate, a total of twenty-two dioxides are in demand. In an experiment to investigate the removal of an acidic dye, use of sol-gel method required semiconductor, electrolyte, and elements like Si, Co, Zn, La, Ag, Ce, W, and Bi (Saroha et al., 2013). The resultant reaction led to spiking of nano-powders of TiO₂. Evidently, incorporation of catalysts, ten percent cobalt and 33.1% of TiO₂, contrary to when there was no catalyst, the removal of color was almost twice as fast (Notarnicola et al., 2016). Unlike when one uses pure TiO₂ and not as in the above process, the color removal is less efficient because the latter has a superior activity in absorption of light and photocatalysis. The process was demonstrable using diffuse reflectance spectroscopy (Yangming et al., 2006). However various classes of catalysts, such as the heavy metal based catalysts, have been found to be extremely toxic (Anastas and Warner, 1998).

2.2.1 Photocatalysis behavior

According to (Fujishima and Honda 1972) the discovery of how light catalyzes the process of water splitting when using TiO₂ electrodes promoted the start of studying photocatalysis in heterogeneous form. The procedure is remarkable for in the course of
cleansing the pollutant effluent. The splitting using light destroys the organic compounds, consequently, reducing the toxicity level (Ollis and Al-Ekabi, 1993). The system leads to changes in the molecular constitution and shifting of the reaction paths where the catalysts are present. Such lead to adoption of two pathways of reaction progression. Increasing the speed of the photoreaction involves photo excitation of adsorbent molecule. The resulting compound then reacts with substrate catalyst. Sensitization of the photoreaction refers to the second reaction that occurs after adding the second catalyst. Such indicate that there is shifting of electrons and hence the energy. At the end of the process, the excitation stops, hence the occurrence of reactions that is heterogeneous.

2.2.2 Surface reactions of TiO2

When there is absorption of a photon, there is production of energy of same quantity or more than the semiconductor oxide (TiO2) possesses in the band gap (ca.3.2 eV for anatase). Then, there is production of electron-hole (e−/h+) pairs (Equation 1).

\[ \text{TiO}_2 \text{hv} \rightarrow e^-_{cb} (\text{TiO}_2) + h^+_{vb} (\text{TiO}_2) \]  

Eqn 1

Reduction-oxidation reaction species that are in the solution bind with the electrons and the holes with positive charge. The result indicates radicals that are charged and ready to participate in reaction shown in the figure 2.6 below.
Figure 2.6 Schematic representation of reduction-oxidation electrons formation- $\text{TiO}_2$ surface with pairs of holes.

2.2.3 Nanoparticles as electrocatalyst in the dye removal

Organic dye substances have harmful impacts on the water bodies when released without proper treatment (Lloyd et al., 2003). There have been several attempts to treat these dyes using methods such as incineration, bioremediation and even the ozonation. However, the outlined methods alone have proven to have several demerits like production of severe bad odour in the case of bioremediation technique and release of volatile and harmful substances in the case of incineration method (Miranda et al., 2000). Metal oxide as an electrocatalyst using zinc dioxide semiconductor has facilitated complete removal of the dyes in waste waters (Ziang et al., 2016). The said nanoparticles help in the conversion of these dyes from their organic nature into water, carbon dioxide and less harmful compounds (Mohammad et al., 2018). Semiconductors like $\text{TiO}_2$ and $\text{ZnO}$ are continuously applied to enhance the complete degrading process of the effluents as a result of their friendliness to the surroundings and the ease of their synthesis (Lee et al., 2016).
2.2.4 Silver nanoparticles as electrocatalyst in the textile dye removal

This is an example of a nanoparticle used in the nanotechnologies with their sizes ranging from one nanometer to about a hundred nanometer (1-100 nm). Silver in its pure state occurs in four oxidation numbers, these include 0, +1, +2 and +3 with greatest electrical and thermal conductivity compared to the rest of the metals. This metal also shows the least resistance. Silver in its metallic structure does not dissolve in water, however the salts of the metal for instance silver nitrate dissolves in water (WHO, 2002). The concentration of the free silver ions in nature is way too low to cause health hazards according to the statistics provided by the world health organization (WHO, 2002). Silver nanostructures acted as electrocatalyst in the degradation of the azo dye in the textile wastewater effluent (Khammarnia et al, 2017).

2.3 Methods of wastewater treatment

The effluents from the textile industries are a major challenge to the water courses in the recent past globally Aspland (1991). However, there have been an increasing number of studies related to solving these pollution effluents mainly emanating from the textile waste waters and the proper discharge of the same. All of these industries involve the use of raw materials, water, energy and many other materials that are converted to useful final products, byproducts and wastes. The wastes resulting from these activities of the industrial processes are of concern due to their effects on human health and the environment as a whole (Chen et al., 2004). The application of various technologies has been put in place in order to develop friendlier surroundings to all of the organisms living there. Many methods on how to treat waste effluents from the textile industries have been devised. These include the use of incineration, electrocoagulation, biological treatment and electrochemical mineralization of organic pollutants.
2.3.1 Biological techniques

Typical biological processes accomplish very low colour removal. In tea industry, constructed wetlands are introduced and the effluent passes through a series of ponds containing waterweeds. These waterweeds are selected on the basis of feeding on some nutrients especially nitrates and phosphates and also the ability to oxygenate the effluent through their roots (Pearce *et al.*, 2003). Reduction of COD and BOD are normally achieved, however colour removal remains a big problem for the textile industry Llyod (2003). Biologically various dye elimination process depends on microbe bioremediation of the concerned textile waste effluents. Under natural conditions these substances do not easily disintegrate. (Padmavathy *et al.*, 2003) optimized various methods on how reactive dyes could be degraded. The conclusion drawn from these researches illustrated the efficiency at which the consortium was most efficient in degrading dyes from textile industries. In the presence of the addition of that particular starch, degradation took place within twenty-four hours and when chemical oxygen demand was carried out on the same over 70% colour removal was realized (Kaykhaii *et al.*, 2018).

2.3.2 Electrocoagulation methods

Electrochemical method is applicable in the process of treatment of many effluents. Such include tea wastewater, dye wastewaters, dye wastewater of textile, restaurant wastewater, semiconductor wastewater and distillery alcohol wastewater. Moreover, tannery wastewater, and sewer of dairy require the same technique. Catalysts have also been introduced to make electrocoagulation more efficient in the treatment of dye wastewater (Yangming *et al.*, 2006). Electrochemical treatment combined with wood ash leachate (ELCAS) was effective in Kraft as well as paper mill color reduction in Kenya. However, the electrodes undergo electrical polarization. Such results in damping
effect of the additional voltage, hence, making the technique less reliable (Orori et al., 2005; Etiegni et al., 2007).

2.3.3 Natural Mineralization of Organic Pollutants

Among the many forms of degrading the contaminants, the use of organic materials to treat the effluent saves financial situation because this process does not involve the use of electricity. This is applicable for the organic compounds that are easy to dissolve in the water plants. However, presence of toxic compounds and biological pollutants that are resistant to natural treatment, makes the dissolving process challenging. The resistant forms of organic particles require mineralization as the technique for cleansing. Such entails incorporation of oxygen, increasing temperature, and Ultra Violet rays (Boye et al., 2004).

2.3.4 Adsorption of industrial pollutants

After the processing the synthetic textile wastewater, fly ash appropriately serves the purpose of removing the stains like malachite green, methylene blue, and rhodamine B. The ash is cost friendly, hence, affordable in large volumes (Grassi et al., 2016). The process requires specific conditions regarding the primary saturation, pH, level of heating, and time of contact (Singh, 1999). Also, to obtain other adsorbents, there was a study on husks of rice determining the adsorbing ability to remove methylene blue (MB). The conditions for consideration include pH, salts, rate of flow, nature of the bed, and MB saturation (Prabhakar, 2004). Employing the model of Thomas, one could identify the cutoff curve and the parameters that incorporated a regression that is linear in nature (Han et al., 2006). Alternatively, leaves powder of Ficus religiosa served well as an absorbent for hexavalent chromium and lead metal (Qaiser et al., 2007).
2.3.5 Cationic coagulation and flocculation

Treatment of the pollutants has employed the method for the longest time than the other techniques. Materials of use include ferric chloride or alum as coagulants and polyelectrolytes as additives. The results are large aggregates. Separation of such is easy because of the big size; hence, applying physical methods of separation is satisfactory. Apparently, sufficient land is a requirement to set up the plant so as to accommodate the many cleaning spots. Additionally, the germs cleaning chemicals are essential and in abundance (Holt and Mitchel, 2006). Coagulation and flocculation, using polyamide or cationic coagulants followed by settlement is the physicochemical process most commonly used at full-scale plants to achieve high efficiency of colour removal. Some coagulating cations like Al, Fe (III), and Ca, can be obtained from industrial wastes like fly-ash, cinder or the sludge from some wastewater treatment (Garcia-Heras and Forster, 1989). Mechanisms by which coagulation takes place include; adsorption-charge neutralization, sweep flocs and formation of insoluble salts. These reactions are affected by the solution pH, concentration of coagulant and presence of salts in solution (Garcia-Heras and Forster, 1989).

2.4 Electrode materials in organic degradation of wastewater

There are specific types of anodes that are considered organic material oxidizers since their structure influences the electrochemical effect (Stucki et al. 1991; Feng and Li 2003). Granite and Ni give inappropriate results of the current (James et al. 1999). One effective method of inactivation of the Pt anode is by introduction of phenols. These deposit oligomers, hence, slows the process of organic degradation (Comninellis and Pulgarin 1991). The invention of anodes of BDD in 1996 has contributed to milestone development (Beer, 1976).
2.5 Water quality

Water quality regulations have been set by National Environmental management Authority (NEMA) in Kenya. The Environmental Management and Coordination Act of 2006 lists guidelines for domestic water quality and also monitoring guide for discharge into the environment. According to schedule 4, the parameters most critical to monitor for textile discharge are; biochemical oxygen demand (BOD), Total Suspended Solids (TSS), and Chemical oxygen demand (COD), Colour/dye/pigment, temperature, oil and grease (GOK, 2006).

Table 2.5): A table showing standards for effluent discharge into environment by NEMA

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>Maximum levels permissible</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended solids (mg/L)</td>
<td>250</td>
</tr>
<tr>
<td>Total dissolved solids (mg/L)</td>
<td>2000</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>20 – 35</td>
</tr>
<tr>
<td>pH</td>
<td>6-9</td>
</tr>
<tr>
<td>Oil and Grease (mg/L) - where conventional treatment shall be used</td>
<td>10</td>
</tr>
<tr>
<td>Oil and Grease (mg/L)- where ponds is a final treatment method</td>
<td>5</td>
</tr>
<tr>
<td>Ammonia Nitrogen (mg/L)</td>
<td>20</td>
</tr>
<tr>
<td>Substances with an obnoxious smell</td>
<td>Shall not be discharged into the Sewers</td>
</tr>
<tr>
<td>Biological Oxygen Demand BOD₅ days at 20 °C (mg/L)</td>
<td>150</td>
</tr>
<tr>
<td>Chemical Oxygen Demand COD (mg/L)</td>
<td>250</td>
</tr>
<tr>
<td>colour (mg/L)</td>
<td>0.1</td>
</tr>
</tbody>
</table>
2.6 Experimental design

The design applied throughout the experiment was categorized to involved physical and chemical aspects and the way each would affect the electrochemical cell set up and the reaction process. The design applied included the following factors:

2.6.1 Geometry

Geometry of the reactor affects operational parameters including bubble path, flotation effectiveness, floc formation, fluid flow regime and mixing/settling characteristics. The most common approach involves plate electrodes (BDD or iron). Water is dosed with dissolved metal ions as it passes through the electrochemical cell.

2.6.2 Scale-up issues

One of the cornerstones of chemical engineering is to establish key scale-up parameters to define the relationships between laboratory and full-scale equipment. The surface area to volume ratio (S/V) was anticipated as being a significant scale-up parameter. Electrode area influences current density, position and rate of cation dosage, as well as bubble production and bubble path length. As the S/V ratio increases the optimal current density decreases (Mameri and Yeddou, 1998).

2.6.3 Current density

Current density is the current delivered to the electrode divided by the active area of the electrode and is achieved by varying the current. It determines both the rate of electrochemical metal dosing to the water and the electrolytic bubble density production. Current densities ranging from 10 to 2000 A / m² have been used; however current density in the range 10 to 150 A / m² has proved efficient (Cheng, 2004). Different current densities are desirable in different situations. High current densities are desirable for separation processes involving flotation cells or large settling tanks, while small
current densities are appropriate for electrochemical cell set ups that are integrated with conventional sand and coal filters. A systematic analysis is required to define and refine the relationship between current density and desired separation effects.

2.6.4 Electrode material

The electrode material used impacts a marked performance of the electrochemical reactor. The anode material determines the cation introduced into solution. Several researchers have studied the choice of electrode material. The most common electrodes were BDD or iron plates (Vik et. al. 1984; Novikova and Shkorbatova., 1982).

Comparison of the performance of iron and BDD electrodes for removing colour from dye-containing solutions indicated that optimal electrochemical conditions varied with the choice of electrode, which in turn was determined by: initial pollutant concentration; pollutant type and stirring rate (Do and Chen, 1994).

2.6.5 Solution pH

Solution pH determines the speciation of metal ions. The pH influences the state of other species in solution and the solubility of products formed. Thus, solution pH influences the overall efficiency and effectiveness of electrocoagulation. The pH of the solution can easily be altered. An optimal pH exists for a given pollutant, with optimal pH values ranging from 6.5 to 7.5 (Holt et al., 2006).
CHAPTER THREE

MATERIALS AND METHODS

3.1 Chemicals, reagents and electrodes

Analytical grade was the main credential of consideration before choosing any chemical or reagent. All solutions were prepared in the laboratory using distilled de-ionized water. Novel Boron Doped Diamond (BDD) electrodes were purchased from commercial suppliers while factory wastewater and models azo dyes were obtained from Rivatex, a Textile Factory in Eldoret. synthesized and characterized silver nanoparticles were obtained from Pwani University. Chemical reagents included: Dichloromethane, anhydrous sodium sulphate, propylene glycol, hexane, sulphuric acid, sodium hydroxide, pH buffer, phosphate buffer, magnesium sulphate, calcium chloride, iron (III) chloride, potassium dichromate (VI), silver sulphate, ammonium sulphate, salicylic acid, sodium nitrate, sodium dihydrogenphosphite, copper sulphate, zinc sulphate and 1, 10-phenanthroline monohydrate.

3.2 Biochemical oxygen demand

The BOD analysis was carried out at the Government Chemistry in Mombasa as stated using the standard methods for examination of water and waste water as outlined in the APHA (2000). Standard 20ml of distilled water was siphoned into each of the two BOD bottles, which served as blank for initial dissolved oxygen (control). To the remaining dilution water, 1 ml of the nutrient was added. The nutrients were standard prepared phosphate buffer solution containing magnesium sulphate, calcium chloride and ferric chloride. A 5% of the seed was added to the dilution water and well mixed to avoid air contamination. The 20ml mixed dilution water was then siphoned into one litre volumetric flask containing the sample and filled to the mark. The content of the
The volumetric flask was siphoned into two BOD bottles. One was incubated and the other used for the determination of initial dissolved oxygen in the mixture. The bottles were stoppered tightly and incubated for 5 days at 20 °C. The BOD bottles were later sealed throughout the five-day period.

Equation 2 below was used to determine BOD after determining initial and final dissolved oxygen of the blank and sample.

\[ BOD = (D_1 - D_2) - (B_1 - B_2) \times 1000/V \]

Where

D\textsubscript{1} is dissolved oxygen in sample 15 minutes after preparation.

D\textsubscript{2} is dissolved oxygen in sample 5 days after preparation.

V is the volume (ml) of the sample used

B\textsubscript{1} is concentration of oxygen in the seeded dilution water or blank 15 minutes after preparation.

B\textsubscript{2} is concentration of oxygen in the seeded dilution water after incubation at 20 °C for 5 days.

3.3 Chemical oxygen demand

3.3.1. Reagents required for preparation

1. Standard potassium dichromate digestion solution 0.0167M.

A 4.913 g K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} heated for 2 hours at 103°C was weighed and added to a mixture of 167 ml concentrated H\textsubscript{2}SO\textsubscript{4}, and 33.3 g HgSO\textsubscript{4}. The mixture was then dissolved in a little of pure water. The temperature was allowed to fall to the same level as the one of the room. Distilled deionized water was then topped up to one litre mark.
2. Sulphuric acid/Silver sulphate solution.

Silver sulphate (Ag$_2$SO$_4$) was added to concentrated Sulphuric acid for every 5.5 g Ag$_2$SO$_4$ against 1 kg of concentrated H$_2$SO$_4$ acid. This was let to stand for 2 days for Ag$_2$SO$_4$ to dissolve.

3. Solution of Ferroin indicator.

A 1.4885g of 1, 10-phenantrolin monohydrate and 695 mg FeSO$_4$.7H$_2$O was dissolved in distilled solvent and diluted to 100 ml.

4. Standard ferrous ammonium sulphate (FAS) titrant, 0.10 M

This was prepared by dissolving 39.2 g Fe (NH$_4$)$_2$(SO$_4$).6H$_2$O in 100 ml pure water. There was addition of 20 ml of concentrated H$_2$SO$_4$, cooled and diluted to 1000 ml. For each experiment, there was standardization against standard potassium dichromate: there was mixing of 5 ml distilled water, 3-ml standard potassium dichromate digestion solution and 7 ml of sulphuric acid, and then cooling to obtain same temperature as of the room, then addition of 1-2 drops of ferroin indicator. Then titration with FAS followed.

Procedure

A 2.5ml wastewater sample was measured and transferred into a 100ml glass beaker and 1.5 ml of digestion solution added, followed by 3.7 ml of sulphuric acid also being added to the said sample of digestion solution and the digestion solution formed a layer at the bottom. Contents were stirred thoroughly before applying heat. While on the block digester, the tubes were refluxed for two hours, and then cooled to room temperature. The samples in the tubes were then allowed to settle on the rack. Transferring of the said contents into an Erlenmeyer flask was necessary before placing on a magnetic stirrer. There was addition and stirring of 2 drops of ferroin indicator then titrated with 0.1M FAS. The colour changed from blue to red. Distilled water blank was made and treated
in the same manner. The determination of the chemical oxygen demand was done using the equation below.

\[ \text{COD} = (A-B) \times M \times 8000 \text{ ml of sample} \]

\[ \text{Eqn. 3} \]

Where:

A= ml FAS for blank
B= ml FAS for sample
M= molarity of FAS.

3.4 Electrochemical cell set-up

Figure 3.1: Electrochemical cell set up for azo dye removal
Scheme 3.1 Electrochemical cell set up for azo dye removal

A sample of 80 ml azo dye effluent was measured and placed into a 100 ml glass beaker. Boron doped diamond (BDD) electrode served as the anode while the cathode was made of stainless steel. Electrodes were suspended into the solution and kept apart using an insulator. Electrodes were connected in series with an ammeter. The reaction was carried out to complete colour removal while recording the current and the time taken.

3.4.1 Electrochemical measurements

There was simultaneously switching on of both parameters, that is, timer and source of power as the electrochemical reaction started. The current generated was recorded and after degradation, the two parameters were halted. Then the total time reading documentation followed. The power consumed during the process was determined by;

\[ \text{Power} = \text{Current (A)} \times \text{Potential Difference (V)} \times \text{Time (hours)} \]  

Eqn 4.

3.4.2 Effect of voltage

Direct current was applied using an AC – DC converter and varied at two levels of 12 and 24 volts.
3.4.3 Effect of dye concentration

A stock solution of each dye was made of 100 ppm. The stock solution was diluted to give different concentrations from 10 ppm up to 50ppm using distilled deionized water. The current generated and time taken for complete removal of the dyes was recorded.

3.4.4 Effect of Silver Nanoparticles

Silver nanoparticles were applied to the wastewater sample at 0, 2, 4, 6 and 8 mg/L. A 5 ml of each concentration was added to the 80 ml of waste water effluent sample and reaction carried out at constant conditions. The time taken and current passed was recorded.

3.4.5 Effect of current density

The current density was adjusted in series of 10, 20, 30, 40 and 50 A/m². This was achieved using a stabilized variable rheostat connected in series and addition of SE.

3.4.6 Effect of Inter-electrode distance

The distance was varied at four levels; 2 mm, 4 mm, 6 mm and 8 mm. The reaction was then carried out at constant conditions.

3.4.7 Concentration of Iron (11) Sulphate

Iron (11) Sulphate was added in four different concentrations at 0.2, 0.4, 0.6, 0.8 and 1g/L to the sample at constant conditions. The reaction was carried out and time and current recorded.

3.4.8 Effect of effluent pH

The adjustment of the effluent's pH was done from 4.0, 5.0, and 6.0 up to 7.0 using the pH meter current generated and time taken was recorded.
3.5. Degradation efficiency

Degradation efficiency was monitored by taking a 2-ml treated sample and measuring its absorbance using UV-VIS spectrophotometer at a pre-determined $\lambda_{\text{max}}$. The equation for calculating the quantity of dye removed or degraded;

$$R\% = \left(\frac{(A_o - A_e)}{A_0}\right) \times 100$$

Where;

$R\%$ is the amount of dye removed,

$A_0$ is the initial dye absorbance,

$A_e$ is the final dye absorbance.

3.6. Data analysis

The data derived was subjected to descriptive and inferential statistical analysis using mini-tab software. Data collected from the field and laboratory was managed by Microsoft Excel. Mean and standard deviation was used to relate how the various parameters affect power consumption during the electrochemical process. Analysis of variance (ANOVA) was used to analyze the data. Graphs and tables were used to present data. Levels of significance were tested at a probability level of $P < 0.05$ in all treatments.
CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 The determination of the absorption spectra for the four azo dyes (reactive and disperse dyes)

Figure 4.1: A plot of UV Absorbance vs. Wavelength (nm) obtained by scanning the samples in the range of 450nm to 650 nm.

The results showed difference in the $\lambda$ max of the four dyes; disperse black showed its highest absorption spectrum at a wavelength of 586nm, disperse blue showed its highest absorption spectrum at a wavelength of 532nm, reactive deep showed its highest absorption spectrum at a wavelength of 476nm, and reactive red showed its highest absorption spectrum at a wavelength of 512nm. The above mentioned values of
wavelengths are in line with the findings of (Zee 2002), all aromatic compounds absorb electromagnetic radiation, however, only those that absorb light within the wavelengths in the visible range (400-700 nm) are coloured. Azo dyes have conjugated system i.e. a structure with alternating double and single bonds have at least one chromophore and exhibit resonance of electrons which is the stabilizing force in these organic dye compounds (Abrahart, 1977). The figure 4.1 above shows the λ max for the four dyes obtained by scanning at different wavelengths within the UV-VIS spectroscopy. The disperse blue and black dyes, reactive deep and red are some of the examples of commonly used industrial azo dye types (Anliker, Clarke and Moser, 1981).

4.2 Effect of silver nanoparticles on azo dye removal

Table 4.2): A table showing effects of AgNPs concentration, time, Current and power consumption on azo dye degradation

<table>
<thead>
<tr>
<th>Azo dye type</th>
<th>Conc. of AgNps (mg/L)</th>
<th>Time (hours)</th>
<th>Current (ampere)</th>
<th>Power used (watt-hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive red</td>
<td>0</td>
<td>0.16±0.0100</td>
<td>0.51±0.0107</td>
<td>1.9584</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.08±0.0050</td>
<td>0.57±0.0006</td>
<td>1.0944</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.07±0.0010</td>
<td>0.54±0.0093</td>
<td>0.9072</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.05±0.0076</td>
<td>0.60±0.0057</td>
<td>0.7200</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.031±0.0005</td>
<td>0.64±0.0057</td>
<td>0.47616</td>
</tr>
</tbody>
</table>
The test was carried out at 95% level of significance on the hypothesis whether there is any effect of concentration of the AgNPs on power used, $H_0$: $CE=0$ Vs. $H_1$: $CE\neq 0$. The results from the ANOVA table for the same indicated that the value ($p=0.002349$) is less than ($p=0.05$) hence we reject the null hypothesis and conclude that subjecting the
sample to different concentrations resulted to difference in power used. The table 4.2 above shows that AgNPs has great impact on the azo dye degradation. The greater concentration of 8 ppm of the nanoparticles consumed the least power of 0.4536 watts within the mean values of 0.03±0.0023 time (hours) and 0.63±0.0001 current (amperes) in the case of disperse black. The largest amount of power was consumed in all the four cases of the model azo dyes where the application of the said nanoparticles was not done for instance in the case of the same disperse black with power consumption of 2.3688 watts within the means and standard deviation values of 0.21±0.0100 time (hours) and 0.47±0.0007 current (amperes).Silver nanoparticle has the ability to act as an electro-catalyst due its nano size nature which enhances a large surface area to volume ratio. The explanation is in line with findings of the catalytic properties of silver nanostrutures supported on the silica spheres (Sebastian et al., 2019). In all the four cases where zero (0 mg/L) of the AgNPs was applied low current range of (0.42±0.0105-0.51±0.0107 amps) was generated leading to high power consumption hence not economical. Addition of the AgNPs led to an increase in the current generation thus lowering the power consumption in watt-hour given that the reaction would take the shortest time to degrade the chromophore in the azoic textile dyes. The table 4.2 further illustrates the impact of increasing the concentration of the silver nanoparticles on the reaction rate of each of the azoic dye used in this research. The trend in reaction time was similar to the findings of Chiranjib (2017).

4.3 Effect of time on degradation of dyes

The effect of time was studied by carrying out electrochemical treatments at different time intervals while recording the current in the circuit. Absorbance values were obtained from the UV-VIS spectrophotometer. The determination of the time taken to remove the chromophores of the said dye solutions was done using UV-VIS
Spectroscopic analysis at the determined $\lambda$ max value of the dye. As the removal of dye proceeded, the result was the breaking of bonds holding the chromophores involved, thus the removal of the coloured substances which absorbs UV-VIS radiation at the determined wavelengths, similar observations were made by Guthrie (2003).

In all the four azo dye types it was clear that absorbance decreased with an increase in electrochemical degradation time that resulted in the decrease of the concentration of the dye molecules in the sample solution. This is in line with Beer (1976), who stated that absorbance is directly proportional to the concentration whenever path length and the extinction coefficient are held constant. The figures 4.3(a), (b), (c) and (d) below illustrate a trend in which there was decrease in absorbance as the electrochemical time was varied between zero and 50 minutes. This indicated that time was a major factor in the reduction of coloured chromophores of the dye. As the dyes mineralization proceeded for a longer time, colour chromophores were reduced and the dye absorbance decreased. Therefore, a time of 50 minutes was considered reliable and economically viable because the absorption spectra for the four dyes had been reduced to value $>97.8\pm0.34\%$ as the group mean for the four commonly used textile dyes. The WHO (2002) recommends that treatment of textile waste water should be done to ensure that organic coloured materials are lowered to the levels that human eye cannot detect before discharging to the water course. The results are shown in the figures 4.3(a), (b), (c) and (d).
Figure 4.3(a): A plot showing the effect of time on the electrochemical degradation of disperses black dye scanned between 520 nm and 670 nm.

Figure 4.3 (b): A plot showing the effect of time on the electrochemical degradation of disperses blue scanned between 470 nm and 620 nm.
4.4. Effect of the concentration on dyes degradation

To observe the effect of initial dye concentration on the dye removal efficiency by electrochemical degradation, experiments were carried out for three different dye
concentrations at constant time of 50 minutes. The dye removal efficiency decreased with an increase in the dye concentration. For example within the 50 minutes of operation, the dye removal decreased from 99.87% in 10 ppm to 37.21% in 100 ppm. Hence 100% dye removal was obtained in quick time compared to higher concentration. Hence, it is quite clear that under the present operating conditions, the lower is the dye concentration the better would be the removal efficiency. Kobya et al. (2003) reported similar results for the removal of reactive dye solutions by EC process. Concentration of the four dyes affected the rate at which the degradation took place with the removal efficiency being best at 10ppm of the dye concentration. The more the concentration the longer the time it took for each of the dyes to degrade. The impact of using very high concentrations proved to be otherwise uneconomical due to the high energy consumptions. Spectroscopic analysis using different concentrations for instance. A; 10 ppm, B; 50 ppm and C; 100 ppm was done using the UV-VIS spectroscopy. The dye degradation rate resulted from direct proportionality between the electrochemical reaction time and the concentration of the different dye solutions. The concentration of the dye had consistent effect on degradation trend for the four dyes. The figures 4.4 (a), (b), (c) and (d) below illustrate the effect of different dye concentrations and their removal using an electrochemical process.
Figure 4.4(a): A plot showing effect of concentration on electrochemical degradation of reactive red dye scanned between 420nm and 520nm.

Figure 4.4(b): A plot showing effect of concentration on electrochemical degradation of disperse black dye scanned between 420nm and 520nm.
Figure 4.4(c): A plot showing the effect of concentration on electrochemical degradation of reactive deep dye scanned between 400nm and 600nm.

Figure 4.4(d): A plot showing effect of concentration on electrochemical degradation of disperse blue dye scanned between 550nm and 750nm.

4.5. Effects of addition of iron (II) sulphate on degradation of the dyes

Iron (II) sulphate acts as support electrolyte according to (Omutange, 2007). The salt increases the conductivity of the waste water to be treated by electrochemical method.
Increase in the salt concentration also increases the ion concentration in the solution and hence reduces the resistance between the electrodes (Yue et al., 2003). This was done by taking into account the beginning time and comparing them to the amount of ion concentration as the electron exchange in this chemical reaction proceeded. There is inverse proportionality between the absorbance of the four dyes and the concentration of the iron (II) salt in g/L. Therefore, there was a rise in the level of degradation of the dyes whenever the concentration of the salt was increased. Increase in the salt concentration decreases the cell voltage at constant current density and reduces the power consumption in electrolytic cell (Hameed et al., 2007). This is clearly illustrated by the figures 4.5 a, b, c, d below.

Figure 4.5(a): A plot showing effect of iron (II) Sulphate concentration on disperse blue dye degradation scanned between 450nm and 600nm in the UV spectrum.
Figure 4.5(b): A plot showing effect of iron (II) sulphate concentration on reactive deep dye degradation scanned between 470nm and 620nm.

Figure 4.5(c): A plot showing effect of iron (II) sulphate concentration on reactive red dye degradation scanned between 420nm and 620nm in UV spectrum.
4.6). Effects of variation of potential difference on azo dyes degradation

Variation of the potential difference of the direct current on the DMM at 12 and 24 volts was necessary. The variation allowed for proper determination of required voltage to ensure effectiveness and efficiency of the azo dye removal. Therefore, the total time and the quantity of current that the process of colour removal required was taken into consideration in order to determine the optimal conditions for the whole process. The results of the Potential difference applied; time taken, current and power consumption at 12 and 24 V are as shown in the table 4.6 below. Each of the dye gave different values on power consumption at different potential difference.
Table 4.6: A table showing effects of variation of potential difference, current and power consumption on azo dyes degradation

<table>
<thead>
<tr>
<th>S/N</th>
<th>Dye</th>
<th>Time (hours)</th>
<th>Pd (V)</th>
<th>Current (amps)</th>
<th>Power (watt-hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Minimum</td>
</tr>
<tr>
<td>1(a) R. red</td>
<td>0.83±0.0018</td>
<td>12</td>
<td>0.30±0.0021</td>
<td>2.999</td>
<td>3.0154</td>
</tr>
<tr>
<td>1(b) R. red</td>
<td>0.12±0.0026</td>
<td>24</td>
<td>0.52±0.0003</td>
<td>1.498</td>
<td>1.5309</td>
</tr>
<tr>
<td>2(a) R. deep</td>
<td>1.17±0.0081</td>
<td>12</td>
<td>0.30±0.0014</td>
<td>4.200</td>
<td>4.2609</td>
</tr>
<tr>
<td>2(b) R. deep</td>
<td>0.14±0.0019</td>
<td>24</td>
<td>0.52±0.0033</td>
<td>1.747</td>
<td>1.8972</td>
</tr>
<tr>
<td>3(a) D. blue</td>
<td>0.78±0.0110</td>
<td>12</td>
<td>0.30±0.0009</td>
<td>2.808</td>
<td>2.8562</td>
</tr>
<tr>
<td>3(b) D. blue</td>
<td>0.10±0.0075</td>
<td>24</td>
<td>0.52±0.0017</td>
<td>1.248</td>
<td>1.3459</td>
</tr>
<tr>
<td>4(a) D. black</td>
<td>0.73±0.0027</td>
<td>12</td>
<td>0.30±0.0037</td>
<td>1.0601</td>
<td>2.672</td>
</tr>
<tr>
<td>4(b) D. black</td>
<td>0.16±0.0010</td>
<td>24</td>
<td>0.52±0.0031</td>
<td>1.997</td>
<td>2.0213</td>
</tr>
</tbody>
</table>

In all the electrochemical processes, applied voltage is the most important parameter for controlling the rate of reaction within the electrochemical system (Cocker et al., 2001). The potential difference as a variable determines the production rate of coagulant, adjusts the polarization issues and affects the of formed flocs (Bazrafshan, 2013). The test was carried out at 95% level of significance on the hypothesis whether there is any effect of variation of potential difference on power used, \( H_0 : CE = 0 \) Vs. \( H_1 : CE \neq 0 \). Information from the one way ANOVA showed that there is significant difference between the different concentrations of the silver nanoparticles applied to each of the
dye and the power consumed in each case for instance (P=0.016676) for the reactive red, (P=0.01147) for the reactive deep, (P=0.01750) for the disperse blue and (P=0.01261) for the disperse black. Similar observations were made by (Maghanga, 2009). He stated that subjecting the sample to the Pd of 12V or 24V had significant difference in power used and that more current was produced where greater voltage was applied that acted as a powerful driving force during the removal of textile dye through the electrochemical process. In the table 4.6 a greater potential difference of 24V generated the most current of 0.52±0.0003A in the case of the reactive red dye, 0.52±0.0033A for the reactive deep, 0.52±0.0017A for the disperse blue and 0.52±0.0031A in the case of the disperse black dye compared to that of 12 volts where the current produced by the said azo dyes were as follow; 0.30 ±0.0021A reactive red, 0.30±0.0014A reactive deep, 0.30±0.0009A disperse blue and 0.30±0.0037A for the disperse black dye. The greater voltage normally increases the current intensity which is necessary parameter in electrolysis which increases the degradation rate linearly (Tabarra et al., 2014). Greater potential difference of 24 volts ensured that time taken to remove the textile waste water dyes was smaller for instance, 0.12 ±0.0026hr for the reactive red as compared to 0.83±0.0018 hr at a potential difference of 12 volts. The similar trend is observed in the other dyes : 0.14±0.0019 hr at pd of 24 volts and 1.17±0.008 hr at pd of 12 volts in the case of the reactive deep, 0.10±0.0075 hr at pd 24V and 0.78±0.0110 hr at pd of 12V for disperse blue and finally 0.16±0.0010 hr at pd 24V and 0.73±0.0027 hr at pd of 12V for the disperse black dye. These trends confirmed the previous investigation on the effect of voltage on the reduction rate constants where the applied voltage was considered to be the thermodynamic driving force for any particular chemical reaction whereby the removal of contaminants rate increased with increasing voltage used (Murphy et al. 2006) considering chemical reaction kinetics as the limiting rate path.
4.7). Effect of inter-electrode distance, current and power consumption on dye removal

The stainless steel (ss) electrodes as cathode and boron doped diamond (BDD) electrode as the anode were used at different spacing of 2 mm, 4mm, 6mm and 8 mm. Electrolysis condition entailed a potential difference of 24 volts.

Table 4.7): A table showing effect of inter-electrode spacing, current and power consumption on the degradation of the various azo dyes.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Inter-electrode (mm)</th>
<th>Time (hours)</th>
<th>Current (amps)</th>
<th>Power (watt)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Minimum</td>
<td>Maximum</td>
<td></td>
</tr>
<tr>
<td>R. red</td>
<td>2</td>
<td>0.025±0.0012</td>
<td>1.23±0.0140</td>
<td>0.738</td>
<td>0.7822</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.063±0.0134</td>
<td>0.92±0.0051</td>
<td>1.391</td>
<td>1.4285</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.546±0.0065</td>
<td>0.65±0.0034</td>
<td>8.518</td>
<td>8.6641</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.723±0.0047</td>
<td>0.58±0.0048</td>
<td>10.064</td>
<td>10.2134</td>
<td></td>
</tr>
<tr>
<td>R. deep</td>
<td>2</td>
<td>0.030±0.0087</td>
<td>1.31±0.1204</td>
<td>0.943</td>
<td>1.3286</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.0792±0.0011</td>
<td>0.87±0.0094</td>
<td>1.654</td>
<td>1.6948</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.651±0.0099</td>
<td>0.67±0.021</td>
<td>10.467</td>
<td>10.9604</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.876±0.0047</td>
<td>0.49±0.0039</td>
<td>22.061</td>
<td>22.9231</td>
<td></td>
</tr>
<tr>
<td>D. black</td>
<td>2</td>
<td>0.043±0.0036</td>
<td>0.87±0.021</td>
<td>0.897</td>
<td>0.9965</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.076±0.0082</td>
<td>0.99±0.0118</td>
<td>1.806</td>
<td>2.0224</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.611±0.0032</td>
<td>0.63±0.0243</td>
<td>9.238</td>
<td>9.6449</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.043±0.0033</td>
<td>0.49±0.0245</td>
<td>12.265</td>
<td>12.9197</td>
<td></td>
</tr>
<tr>
<td>D. blue</td>
<td>2</td>
<td>0.039±0.0051</td>
<td>1.18±0.0234</td>
<td>1.104</td>
<td>1.2738</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.064±0.0075</td>
<td>0.88±0.062</td>
<td>1.351</td>
<td>1.6165</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.451±0.0014</td>
<td>0.45±0.0057</td>
<td>4.871</td>
<td>4.9478</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.045±0.0033</td>
<td>0.23±0.0019</td>
<td>5.768</td>
<td>5.8344</td>
<td></td>
</tr>
</tbody>
</table>
As it can be noted from the table 4.7 above, the electrode spacing affects the rate of azo dye degradation. In all the four experiments using different kinds of dyes, it was clear that an increase in the inter electrode distance from 2mm to 8 mm led to a decrease in the current production from $1.23\pm0.0140A - 0.58\pm0.0048A$ which resulted into a lot of time taken from $0.025\pm0.0012$ hr - $0.723\pm0.0047$ hr. Therefore, to degrade the reactive red azo dye a lot of power ranging from 0.738-10.2134 watts was utilized in the process. From the ANOVA (P=0.00231) revealed that there were statistically significant differences in the mean inter- electrode distance and power consumption in the reactive red dye. The same trend in the power consumption by the other azo dye types was noted as follows: Reactive deep the current produced decreased from $1.31\pm0.1204A - 0.49\pm0.0039A$ since time taken to remove the said textile dyes increased from $0.030\pm0.0087hr - 1.876\pm0.0047hr$. The disperse blue dye had its current generated decrease from $1.18\pm0.0234 - 0.23\pm0.0019A$ as the spacing of the electrodes increased, for the disperse black the decrease in current production was from $0.87\pm0.021 - 0.49\pm0.0245A$. These trends were similar to the findings of (Crespilho, 2004). He stated that the distance between electrodes is an important variable to optimize operating cost. The greater the distance between the electrodes, the greater is the difference in the applied potential because the solution presents higher resistivity to the electrical current. The best distance for efficient degradation in all the four cases was at 2 mm inter-electrode distance. The power consumption at this spacing in all the cases was significantly lower compared to the rest. These results on the interelectrode spacing agrees with the findings of (Mallah , 2014) which indicated that a smaller interelectrode distance as a parameter increases the rate of the said textile waste water with a reliable factor The reduced distance facilitates increased conductivity and the concentration of the electrolyte (Zeng et al., 2006). According to (Daneshvar, 2004) increasing the electrode spacing reduces the treatment efficiency which can be attributed to the fact
that at constant voltage, electrical resistance increases with the increased distance between the electrodes while current passed through decreases. Therefore, decreasing of current lead to lower production of hydroxyl ions and dye removal efficiency decreases (Presanna et al., 2005).

4.8 Physical-Chemical properties of effluent

4.8.1 Effect of effluent pH on dye degradation

It has been established that the initial pH of solution is one of the important factors affecting the performance of electrochemical processes (Kuokkanen et al., 2013). Most of the pollutants in the textile waste water are weak organics acid or base, so the pH value of the water influence the property of pollutants available in waste water (Chen, 1997). All experiments were done at room temperature of 25± 5°C by varying the pH of effluent samples solutions. The adjustment of the effluent's pH was done from 4.0, 5.0, and 6.0 up to 7.0 using either 0.5M solution of hydrochloric acid or alkaline solution of the same concentration of potassium hydroxide at the potential difference of 24 volts as the point of reference for electrolysis. The reaction was carried out mainly in the acidic medium because electrochemical process on dyes in the textile waste water exhibit some buffering capacity in alkaline medium, which prevents pollutant removal efficiency (Bayramoglu et al., 2004). Table 4.8 below shows the effect of effluent pH on power consumption at a potential difference of 24 V.
Table 4.8: A table showing effect of effluent pH on usage of power at a potential difference of 24 V.

<table>
<thead>
<tr>
<th>Effluent samples</th>
<th>Dye pH</th>
<th>Time (hours)</th>
<th>Current (amps)</th>
<th>Power (watt –hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Minimum</td>
</tr>
<tr>
<td>ES1</td>
<td>7.0</td>
<td>0.53±0.0130</td>
<td>0.24±0.0014</td>
<td>3.058</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>0.54±0.0040</td>
<td>0.22±0.0021</td>
<td>3.057</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.71±0.0023</td>
<td>0.21±0.0007</td>
<td>3.578</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>0.83±0.0010</td>
<td>0.21±0.0005</td>
<td>4.183</td>
</tr>
<tr>
<td>ES2</td>
<td>7.0</td>
<td>0.56±0.0024</td>
<td>0.32±0.0003</td>
<td>4.301</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>0.61±0.0077</td>
<td>0.31±0.020</td>
<td>4.538</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.67±0.0078</td>
<td>0.29±0.0057</td>
<td>4.663</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>0.78±0.243</td>
<td>0.29±0.0008</td>
<td>5.429</td>
</tr>
<tr>
<td>ES3</td>
<td>7.0</td>
<td>0.51±0.0044</td>
<td>0.35±0.0411</td>
<td>4.284</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>0.60±0.0087</td>
<td>0.34±0.0032</td>
<td>5.067</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.73±0.0011</td>
<td>0.34±0.0066</td>
<td>5.957</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>0.75±0.049</td>
<td>0.34±0.0024</td>
<td>6.120</td>
</tr>
<tr>
<td>ES4</td>
<td>7.0</td>
<td>0.46±0.0097</td>
<td>0.33±0.0067</td>
<td>3.643</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>0.49±0.0004</td>
<td>0.29±0.0099</td>
<td>3.363</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.68±0.0084</td>
<td>0.31±0.0056</td>
<td>5.059</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>0.89±0.0089</td>
<td>0.30±0.0078</td>
<td>6.408</td>
</tr>
</tbody>
</table>
From the ANOVA (P=0.00731) revealed that there were statistically significant differences in the pH used and power consumption in all the dyes. As the pH increased from 4.0 to 7.0, current production increased from (0.21±0.0005-0.24±0.0014 A) in the effluent sample ES1, ES2 (0.29±0.0008-0.32±0.0003A), ES3 (0.34±0.0024-0.35±0.0411A) and ES4 (0.30± 0.0078 - 0.33±0.0067A). The current being generated was greater where strength of acidity was low but not neutral. These findings were similar to that of (Sozbir, 2004). He stated that current efficiencies are higher at either acidic or alkaline conditions than at neutral.

The results obtained from these analyses in the table 4.8 above showed that electrochemical removal was greater in the dye solutions with pH higher than 5. The pH of the medium changes during the process, depending on the type of electrode material and initial pH (Kobya, 2003).

(Jawabre, 2003) established that the rate of the azo dye discoloration depended on the acidic medium which was one of the determining factor. The acidic pH medium, higher removal efficiencies are obtained during electrolysis probably because of the liberation of H₂ gas at the cathode and the formation of OH⁻ (aq) ions (Budiyon et al., 2010). The boron doped diamond (BDD) electrode loses the electrons during the electron transfer since it acts as the electron donor. The dye molecule being electron acceptor combines with the H⁺ ions to bring about a transition product. The transition product combines again with H⁺ ions to end up forming the final product thus facilitating the faster removal of the coloured dyes in the effluent waste waters (Zongo et al., 2012).

4.8.2. Effect of effluent temperature on dye degradation

Temperature is another important operating condition that can affect pollutant removal efficiency in the waste water treatment generally. The efficiency of turbidity removal
from abattoir waste water in the electrochemical process increases by increasing solution temperature (Katal, 2011).

The effluent temperature was adjusted from 30°C, 35°C, 40°C to 45°C using a thermostatic heated plate. These temperatures are within optimal range for the semi conductivity and anodic oxidation properties of the BDD electrodes (Stucki et al., 1991; Feng and Li 2003). There were electrochemical reactions at each temperature using the optimized conditions. The current passed and the time taken to degrade the various textile waste water samples was recorded. The effects of effluent temperature on power consumption in all the textile waste water samples showed a similar general trend in the table and figure 4.9 below.

Table 4.9): A table showing effect of effluent temperature on dye removal from the effluent samples ES1, ES2, ES3 and ES4

<table>
<thead>
<tr>
<th>Effluent type</th>
<th>Temp. (°C)</th>
<th>Time (Hours)</th>
<th>Current (Amperes)</th>
<th>Power (watt –hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Minimum</td>
</tr>
<tr>
<td>ES1</td>
<td>30</td>
<td>0.23±0.0022</td>
<td>0.40±0.0068</td>
<td>2.208</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.21±0.0110</td>
<td>0.40±0.0092</td>
<td>2.016</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.19±0.0002</td>
<td>0.40±0.0053</td>
<td>1.824</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>0.17±0.0071</td>
<td>0.40±0.0089</td>
<td>1.632</td>
</tr>
<tr>
<td>ES2</td>
<td>30</td>
<td>0.34±0.040</td>
<td>0.38±0.0006</td>
<td>3.101</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.29±0.0008</td>
<td>0.38±0.0075</td>
<td>2.645</td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.26±0.0033</td>
<td>0.38±0.0310</td>
<td>2.371</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>0.16±0.0051</td>
<td>0.38±0.0001</td>
<td>1.459</td>
</tr>
<tr>
<td>ES3</td>
<td>30</td>
<td>0.39±0.0140</td>
<td>0.35±0.0011</td>
<td>3.276</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.37±0.047</td>
<td>0.35±0.0023</td>
<td>3.108</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.31±0.0120</td>
<td>0.35±0.0013</td>
<td>2.604</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>0.24±0.035</td>
<td>0.35±0.0044</td>
<td>2.016</td>
</tr>
<tr>
<td>ES4</td>
<td>30</td>
<td>0.29±0.0141</td>
<td>0.42±0.0012</td>
<td>2.923</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.23±0.0006</td>
<td>0.42±0.0007</td>
<td>2.318</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.16±0.0095</td>
<td>0.42±0.0047</td>
<td>1.613</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>0.11±0.0018</td>
<td>0.42±0.0014</td>
<td>1.109</td>
</tr>
</tbody>
</table>

The four temperature levels were significantly different (P=0.023) in power consumption, due to the increase in current generation as temperature increased steadily.
from 30-45 °C. Effluent samples current production ES1 (0.40±0.0068-0.40±0.0089A), ES2 (0.35±0.0011-0.38±0.0001A). At temperatures of 45 °C, power consumption was the lowest and highest at 30°C. The increase in removal efficiency with temperature in the electrochemical process can be explained by the fact that increasing solution temperature can improve ion transfer from the anode and/or cathode surface to the solution bulk resulting in a solution viscosity and consequent ion diffusivity (Vasudevan et al., 2009). Increasing the temperatures led to low power consumption in all the effluents ES1, ES2, ES3, ES4. The amount of power necessary for the process to proceed had an inverse relationship with the rise in temperature from 30°C to up to 45 °C. Increasing the temperature of the molecules leads to an increase in the kinetic energy which leads to effective and successful collisions of the particles. The power consumption group mean was lowest with 1.554 watts-hour at the highest temperature of 45°C and the highest power consumption group mean was 2.877 watts-hour at the lowest temperature of 30°C. The trend clearly showed that the operation of electrochemical process at higher temperature significantly reduces electrical energy consumption and fluid conductivity increases (Chaturvedi, 2013).

4.8.3 Determination of colour removal level during effluent electrochemical degradation

Sample ES1, ES2, ES3, and ES4 colors were determined by the use of standard method that the APHA platinum-cobalt offers (APHA, 1989). The HACH DR 2000 spectrophotometer was used to measure colour concentration in the samples. The colour levels before and after electrochemical degradation of the effluents ES1, ES2, ES3 and ES4 were determined. The results of the experiments were as tabulated below. From the table the results indicated that the effluent samples had almost consistent trend in their Pt-Co colour units both before and after electrochemical degradation.
Table 4.10: A table showing determination of colour removal level during effluent electrochemical degradation

<table>
<thead>
<tr>
<th>Effluent samples</th>
<th>Colour, Pt-Co colour units before electrochemical degradation</th>
<th>Colour, Pt-Co colour units after electrochemical degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES1</td>
<td>2005±0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>ES2</td>
<td>1989±1.5</td>
<td>0.0</td>
</tr>
<tr>
<td>ES3</td>
<td>2010±2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>ES4</td>
<td>2013±0.2</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The highest value recorded was with the sample ES4 with the Pt-Co colour units of 2013±0.2 and the lowest being ES2 with 1989±1.5 Pt-Co colour units before electrochemical degradation. The colour unit levels after electrochemical degradation was 0.0 indicating the efficiency with which anodic oxidation effluents was. Therefore, this meant that there was 100% colour removal from the waste effluent after the treatment. One way ANOVA showed that there was a significant difference (P=0.0135) between the colour level of textile waste water effluent before treatment and acceptable value by the WHO (2002) of 0.1 mg/L. On the other hand there was no significant difference (P=0.0612) between the colour level of textile effluent and the WHO value limit after treatment.

4.8.4 Determination of Biochemical oxygen demand of the effluent before and after electrochemical degradation

Biochemical oxygen demand is the measure of the quantity of the oxygen that bacterium will consume while breaking down organic compounds in the aerobic conditions. The major concern of textile wastewater treatment is to remove or even lower the BOD in
the effluent before release to the major water course. This reduction of the BOD before discharge will ensure less competition for the dissolved oxygen for the aquatic organisms for instance fish and planktons for their respiratory activities. The table below shows the BOD of the textile wastewaters before and after the electrochemical degradation.

**Table 4.1**: A table showing Biochemical oxygen demand of the effluent before and after electrochemical degradation.

<table>
<thead>
<tr>
<th>Effluent samples</th>
<th>BOD, mg/L of effluent before electrochemical degradation</th>
<th>BOD, mg/L of the effluent after electrochemical degradation</th>
<th>% Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
<td>Maximum</td>
<td></td>
</tr>
<tr>
<td>ES1</td>
<td>179±5.22</td>
<td>23±1.58</td>
<td>85.15</td>
</tr>
<tr>
<td></td>
<td>88.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ES2</td>
<td>176±4.8</td>
<td>22±3.20</td>
<td>83.54</td>
</tr>
<tr>
<td></td>
<td>87.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ES3</td>
<td>171±2.60</td>
<td>19±1.74</td>
<td>85.89</td>
</tr>
<tr>
<td></td>
<td>89.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ES4</td>
<td>181±6.31</td>
<td>25±2.26</td>
<td>84.82</td>
</tr>
<tr>
<td></td>
<td>86.79</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

One way ANOVA showed that there was a significant difference (P=0.0212) between the BOD of textile waste water effluent before treatment and acceptable amount by the (WHO 2002) of 150±5 mg/L. On the other hand there was no significant difference
(P=0.835) between the BOD of textile effluent after treatment and the WHO value limit. The effluent BOD in all the four samples ES1, ES2, ES3 and ES4 was much higher before the electrochemical degradation. The BOD of the effluent was even highest in the sample ES4 at about 181±6.31mg/L before treatment and 25±2.26 mg/L after treatment and lowest in ES3 with 171±2.60 mg/L before electrochemical degradation of the textile waste waters and 19±1.74 mg/L after degradation. The above table 4.11 shows that biochemical oxygen demand was greatly reduced after electrochemical degradation of the effluents. This treatment of the textile effluent ensured higher BOD reduction which was safe for discharge to the water course similar to the findings of (Sasani, 2017).

### 4.8.5 Determination of Chemical oxygen demand before and after electrochemical degradation

Chemical oxygen demand (COD) refers to the quantity of oxygen that is used during a reaction process. COD gives the amount of the organics in water, the basis of the test is to ensure that nearly all if not completely all organic compounds in the effluent are fully oxidized to carbon dioxide, ammonia and water under acid conditions. The potassium dichromate used in the COD as an oxidizing agent would not otherwise oxidize the ammonia produced into nitrate. From all the samples done it is very clear that COD values of the textile wastewater are much greater compared to the BOD of the same effluent. The table below gives the COD of the effluent before and after electrochemical degradation.
Table 4.12: A table showing Chemical oxygen demand before and after electrochemical degradation.

<table>
<thead>
<tr>
<th>Effluent type</th>
<th>COD, mg/L of the effluent before electrochemical Degradation</th>
<th>COD mg/L of the effluent after Electrochemical degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES1</td>
<td>709 ±5.78</td>
<td>92.8±3.84</td>
</tr>
<tr>
<td>ES2</td>
<td>693±8.74</td>
<td>96.6±7.25</td>
</tr>
<tr>
<td>ES3</td>
<td>693±6.47</td>
<td>97.2±2.26</td>
</tr>
<tr>
<td>ES4</td>
<td>692±3.79</td>
<td>98.0±4.96</td>
</tr>
</tbody>
</table>

One-way ANOVA showed that there was a significant difference (P=0.0142) between the COD of textile waste water effluent before treatment and acceptable value by the WHO (2002) of 250±5 mg/L. On the other hand, there was no significant difference (P=0.635) between the COD of textile effluent and the WHO value limit. The figure and table 4.13 above illustrate the COD of the effluent before electrochemical degradation which proved to be very high and if released in this form to the water course without any treatment, would lead to over utilization of the dissolved oxygen (DO) which would in turn destroy the aquatic life in that area of jurisdiction. In the four different effluent samples ES1, ES2, ES3 and ES4 there was very insignificant difference in their COD values determined. The greatest COD value was found to be in the sample ES1 with 709 ±5.78 mg/L and after electrochemical degradation of the effluent sample the percentage reduction was 86.91%. The lowest COD value was in the case of effluent sample ES4 with the COD value of 692±3.79 mg/L with percentage reduction of 85.83%. Therefore, in all the four effluent samples accuracy in the treatment was achieved on the basis of the difference being < 1.5% . The table 4.14 above shows COD values of the four effluent samples after the electrochemical degradation. In all the samples of the effluent,
COD was reduced to the levels below 100 mg/L bearing in mind that the acceptable levels should not go beyond COD>250 mg/L (Maiga, 2012). Therefore, it means that the electrochemical degradation as a method for waste water treatment was very much effective in lowering the COD in the textile waste water effluent (Dieng, 2004).
CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

All the objectives of this study were achieved. This method of electrochemical colour removal proved to be sufficient in the determination of how the variation of the process parameters affected the textile effluent removal. The absorption spectra of the four dyes were determined and ranged between the wavelengths of 470 up to 590 nm in UV-Vis spectrum. The disperse black and blue had their highest absorbance at 586 nm and 532 nm wavelengths respectively. The reactive red and deep had their maximum absorption at the wavelengths of 512 nm and 476 nm respectively. Increasing time from 0 to 50 minutes showed consistency in the reduction of the peaks in terms of their respective absorbance within the same wavelengths. The concentration of the dyes considered efficient for colour removal was 10 ppm since there was less power consumption thus economical. Increased concentration from 0.1 to 0.5 g/l of FeSO₄ was added to act as support electrolyte to enhance quick removal of the dye. As the concentration of silver nanoparticles increased from 0 to 8 ppm lowest power of 0.4536 watts within the group mean value of 0.03±0.0023 time (hours) and 0.63±0.0001 current (amperes) was recorded. Therefore, it was concluded that greater concentration of AgNPs acted effectively as the electrocatalyst to eliminate the barrier during the dye removal process. The interelectrode spacing was 2mm with a potential difference of 24 V which enabled most efficient current flow, thus realistic and economical in the power consumption recorded. In all the four experiments using different kind of textile dyes, it was worth noting that an increase in the inter electrode distance from 2mm to 8 mm led to a decrease in the current production from 1.23±0.0140 A - 0.58±0.0048 A which resulted to a lot of time taken from 0.025±0.0012 hr -0.723±0.0047 hr. The aspect of temperature
was also considered under the above optimal conditions, and at 45°C the removal was faster as there was an increase in the chemical kinetics of the particles in the reaction system. As the pH increased from 4.0 to 7.0, current production increased from (0.21±0.0005-0.24±0.0014 A). From the group means analyzed pH range of 6.5±0.5 was noted to be enhancing better removal of the studied azo dye from the textile waste water effluent. The electrochemical azo dye removal also lowered the BOD and COD of the waste water effluent to way below the acceptable levels recommended by WHO of 150mg/l and 250mg/l respectively. The textile azo dye colour was removed to below detectable levels (BDL) thus could not be detected by human eye after treatment.

5.2 Recommendation

This electrochemical method of the azo dyes removal using boron doped diamond electrodes and silver nanoparticles has proven to be one of the most efficient ways of removing components of the textile dyes electrochemically. Indeed, the reactions where silver nanoparticles were used, the degradation was very fast as opposed to where nanoparticles were not applied. I therefore recommend that more studies to be carried out on the electrochemical removal of dye using other types of electrocalysts.
REFERENCES


Feng, Y. J. and Li, X.Y. (2003) Electro-catalytic oxidation of phenol on several metal-


