ELECTROCHEMICAL TREATMENT OF TEXTILE DYE WASTEWATER BY ALUMINIUM AND STAINLESS-STEEL ELECTRODES

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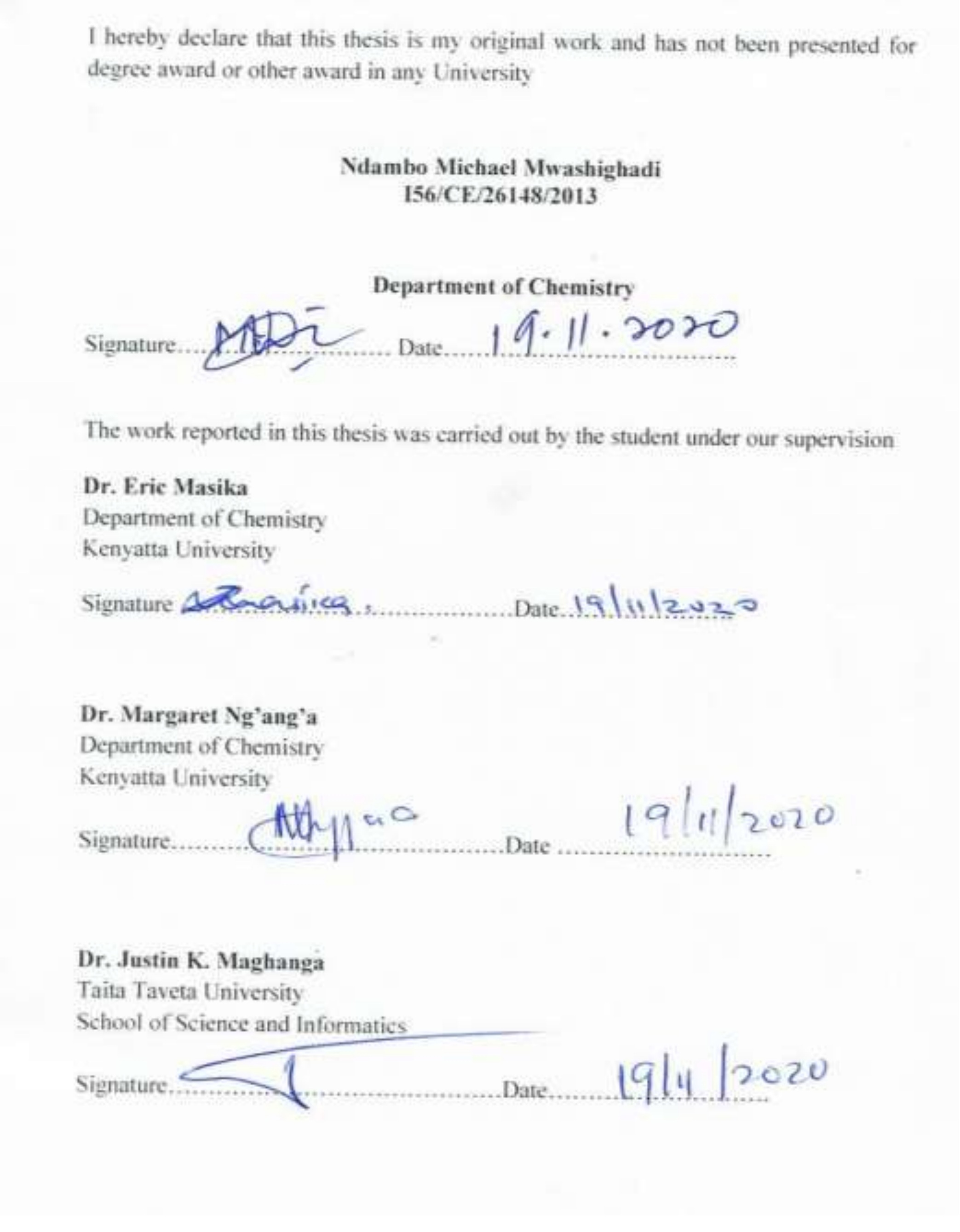
I56/CE/26148/2013

A Thesis Submitted in Partial Fulfilment of the Requirements for the Award of the Degree of Masters of Science (Chemistry) in the School of Pure and Applied Sciences of Kenyatta University

NOVEMBER, 2020

DECLARATION



I hereby declare that this thesis is my original work and has not been presented for degree award or other award in any University

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DEDICATION

I dedicate this work to my wife Frida, my daughters Anne, Joy, Favour and Precious. Their presence, encouragement, moral support and supplications gave nuggets of power throughout my research period.

ACKNOWLEDGEMENTS

First and foremost, I give all honour to Almighty God for well-being, good health, strength and his provision throughout my entire period of study. I sincerely thank my supervisors Dr. Eric Masika, and Dr. Margret Ng’ang’a from the Department of Chemistry, Kenyatta University and Dr. Justin Maghanga from the School of Science and Informatics, Taita Taveta University (TTU). Their mentorship, encouragement, personal involvement in research and preparation of this thesis is highly appreciated. I wish to express my gratitude to Prof. Hamadi Boga of Taita Taveta University for granting me bench space at TTU Chemistry laboratories where all the Lab work was carried out.

I acknowledge the technical assistance from Mwandogo Omari Chigodi of Chemistry department of Pwani University and Mr. Koti Matata the Chemistry Technician at TTU for his commitment and dedication, enduring long working hours while assisting in laboratory work. I also thank Mr. George Nzai of Government Chemist Mombasa for his technical assistance in chemical analysis.

Lastly but not the least, I extend my sincere gratitude to my wife Frida Wakesho, my daughters Anne Wachenje, Joy Wakesho, Favour Wachia and Precious Lewo for their cooperation, bearing with me during my tight research schedule and their prayers will always be valuable.

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ABBREVIATIONS AND ACRONYMS

APHA:	American Public Health Association
ANOVA:	Analysis of Variance
BOD:	Biological Oxygen Demand
COD:	Chemical Oxygen Demand
EC:	Electro-coagulation
IED:	Inter-Electrode Distance
LC-MS:	Liquid Chromatography – Mass Spectrometer
NEMA:	National Environment Management Authority
POME:	Palm Oil Mill Effluent
SS:	Stainless Steel
SEC:	Specific Energy Consumption
UV-VIS:	Ultra-Violet/ Visible spectrophotometer
WHO:	World Health Organisation

DEFINITION OF TERMS

Chemical Oxygen Demand (COD): Is a measurement of the oxygen required to oxidize soluble and particulate organic matter in water. This in SI units is expressed in milligrams per litre (mg/L).

Coagulation: Is the chemical water treatment process used to remove solids from water, by manipulating electrostatic charges of particles suspended in water. This process introduces small, highly charged molecules into water to destabilize the charges on particles, colloids, or oily materials in suspension.

Contact time: Its electrocoagulation time starting with switching on of the current.

Electro-coagulation (EC): A process in which the anode material undergoes oxidation with the formation of various monomeric and polymeric metal hydrolyzed species. These metal hydroxides remove the colour from wastewater by sweep coagulation and colloidal aggregation.

Flocculation: Refers to the process by which fine particulates are caused to clump together into a floc. The floc may then float to the top of the liquid (creaming), settle to the bottom of the liquid (sedimentation), or be readily filtered from the liquid.

Specific Energy Consumption (SEC): The ratio of kWh of energy consumed to the unit volume of dye water treated by this energy consumption. It is represented by kilowatt hour per cubic meter (kWh/m^3).

ABSTRACT

Pollution of water resources due to the increasing growth in industrialization continues to pose a great challenge to the rapidly growing population. Textile industries are among the principal polluters of surface water. The development of these textile industries has resulted in severe water pollution due to discharge of dye wastewaters to natural water courses. This laboratory scale study was aimed at establishing an eco-friendly wastewater treatment method dubbed electro-coagulation (EC) method. The main objective of the study was to establish an electrochemical and efficient method that would effectively remove COD and colour from azo dye wastewater using aluminium (Al) and stainless steel (SS) electrodes. Increasing current density and contact time significantly increased the removal of colour and COD. Increase in current density increased both COD and colour removal. When current density was increased from 15 to 47 A/m^2 the colour removal increased from71 to 99 % for the case of disperse blue with SS electrode. Increase in contact time 5- 20min. caused increase in colour and COD removal from below 50 to 98 and 78 % respectively for disperse blue with SS. When inter-electrode distance (IED) and dye concentration was increased the colour and COD removal declined significantly. As the IED increased from 1-3cm the percentage removal of colour decreased from 99 to 45 % for the case of disperse blue with SS. Addition of sodium chloride enhanced the electrocoagulation process. Addition of NaCl from 0 - 0.4g enhanced colour removal from 15 to 80% for disperses black with SS. Under optimum operating conditions (current density 47.2 A/m^2, Inter-electrode distance 1cm, SE 0.2 g/L, 0.1 g/L dye concentration and 25 minutes contact time) the performance of stainless steel on removal of colour recorded the highest removal at 97% compared to that of aluminium of 90%.the physio-chemical parameters where reduced to NEMA disposable levels making it possible for treated water fit for re-use. COD reduced by 81%, conductivity by 89% and turbidity by 88%. Operating cost was evaluated by adding cost of electrode per Kg at the market price and the cost of electricity per (kWh/m^3) for SS= 50.56 KES/m^3 and Al =50.55 KES/m$^{3.}$ This confirms the viability and a cost-effectiveness of the process.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Freshwater scarcity remains a limiting problem in economic development globally. Increasing population and industrial growth are major factors escalating the problem. Natural water sources are under threat not only due to deforestation as more land is reclaimed for agriculture but also by human settlement and ever-increasing industrialization (Cairncross, 2014). One of the key steps in industries such as paper, textile, cosmetics, leather, plastics, and food, is a dyeing process using organic dyes and water (Chequer *et al*., 2013). Besides, they consume copious amounts of freshwater and exhaust as dye wastewater (Pang and Abdullah, 2013). The resultant wastewater contains a substantial range of chemicals and other undesirable constituents including suspended solids, high COD, heat, colour, acids and soluble substances (Demirci *et al*., 2015).

The textile industry is among the leading polluters of surface water. Processing one tonne of textile product consumes between 200 –270 tons of water of which over 70% goes to waste (Alkaya and Demirer, 2014; Verma *et al*., 2012). In Kenya, textile factories produce large amounts of wastewater that is alkaline, coloured and with high chemical oxygen demand (COD). This leads to eutrophication, subjecting mankind and aquatic life to adverse conditions (Maghanga, 2016). Textile dyes contain heavy metals ions such as Cd^{2+}, Cr^{6+}, Pb^{2+}, Zn^{2+} and Cu^{2+} inform of the non-biodegradable chromophoric group which accumulate in body organs leading to diverse diseases (Dadi *et al*., 2017). Also untreated or partially treated textile effluent is both harmful to terrestrial and aquatic lives which interfere with the ecosystem causing health problems (Chung, 2016).

This has greatly reduced freshwater sources, threatening the life of the future generation (Cairncross, 2014). The public perception of water quality is greatly influenced by the colour, which is the first contaminant to be recognized in wastewater (De França, 2010; De França *et al*., 2009). The global demand for potable drinking water is on the rise making regulation of wastewater management of immediate priority (Rahm *et al*., 2013; Bogardi *et al*., 2012). Therefore, there is an urgent need for effective treatment of wastewater to decrease or fully eradicate the waste products to achieve an acceptable limit for its re-use in industrial and agricultural sectors to promote economic development (Akanksha *et al*., 2013).

Industrial effluents are treated by three major methods namely; biological, physical and chemical methods. Biological methods for industrial effluent treatment involve removal of dye waste by use of degrading enzymes from white-rot fungi. However, sometimes the enzyme is not effective (Gupta *et al*., 2015). Microbial adsorption method involving living and dead biomass has been used to remove only dyes with higher affinity for binding with microbial species (Adegoke and Bello, 2015). Anaerobic textile dye remediation system has also been in use. This allows azo dyes and other polar dyes to be decolourized. These processes have been reported to yield methane and hydrogen sulphide leading to secondary pollution (Wijannarong, 2013).

Physical methods include; adsorption by activated carbon, membrane filtration, ion exchange, irradiation process and electro-kinetic coagulation. Adsorption by activated carbon removes a wide range of dyes but it is expensive. Membrane filtration removes all types of dye but leads to more concentrated sludge production (Adegoke and Bello, 2015). Ion exchange dye waste removal without an adsorbent also been employed but it’s not effective for all type of dyes. Irradiation process has equally been done and found effective at laboratory scale but requires a lot of dissolved oxygen (Hossain *et al.*, 2013).

The chemical method involves an oxidation process by a simple application of oxidising agents but also requires the use of other chemical agents to generate hydrogen peroxide (Geraldino, *et al.*, 2015). Photochemical methods exist but they lead to the formation of by products that pollute the environment (Nawaz and Ahsan, 2014). The use of sodium hypochlorite (NaOCl) has been employed but it releases aromatic amines (Wijannarong, 2013). Electrochemical destruction has an advantage over other methods as it uses no chemicals and forms no sludge but its high flow rate may decrease dye removal efficiency (Takdastan *et al*., 2015).

Detection techniques of dye pollution are costly and ineffective. Dyes are known to change chemically to stronger toxic compounds than parent molecules due to environmental conditions (Ratna and Padhi, 2014). This makes them stable to oxidising agents and aerobic digestion. The treatment of dye effluents becomes difficult particularly azo dyes (Nguyen and Juang, 2013). Many synthetic dyes are resistant to light and their molecules are non-biodegrade (Kariyajjanava *et al.*, 2013)). This is as a result of the complex aromatic structure of the dyes (Flayer and Hasan, 2014).

Industrial effluents with synthetic organic dyes cannot be treated by conventional means, hence the need for environmentally friendly technologies to mineralize non-biodegradable compounds (Brillas and Martínez-Huitle, 2015). Due to these challenges on the existing methods of treatment for industrial dye waste, it’s important to develop other systems. In this context, azo dye wastewater treatment requires a more effective alternative method.

Electrocoagulation technology is the preferred option. This method can successfully degrade aromatic organic compounds (Li *et al.*, 2010). Dye removal by electrocoagulation is increasingly becoming a method of choice because it is economical and requires simple equipment (Vidal *et al.*, 2017). Furthermore, there is less sludge production which can be dewatered by simple common methods (Singh *et al.*, 2016).

1.2 Problem statement and Justification

From the literature reviewed, electrocoagulation has been applied to a number of industrial wastewaters, such as diary, tannery, textile, pulp and paper among many. There are a number of individualized optimisation studies like pH and current density to maximise efficiency of removal. However, it has been reported that the electrocoagulation process has been empirically optimised because onsite optimisation and case studies has achieved limited success (Kabdasli *et al.*, 2012).

The optimised condition sometimes conflict with local ones as the operation parameters vary by one or more magnitude.

There is need for more studies to be undertaken especially on laboratory scale study for more fundamental understanding. For different kind of wastewaters, optimizations of operating parameters are at varying levels depending on the composition of the effluent and type of electrode used. It has been reported by some scientific researchers that electrocoagulation process as an alternative wastewater treatment is yet to be fully realized (Gicevic *et al.*, 2019). That's why this research has been undertaken to establish an electrochemical and efficient method that would effectively remove COD and colour from azo dye wastewater using aluminium (Al) and stainless steel (SS) electrodes.

This was made possible by first investigating the effect of process parameters (such inter-electrode distance, dye concentration, current density, pH and time) on colour and COD removal using Al and SS electrodes and secondly effectiveness of aluminium and stainless steel electrodes. The data from this study provides more information on the performance of stainless steel and aluminium electrode and the optimised parameters for maximum removal of colour and COD. Consequently, this may lead the way to potentially realizing the process as the alternative emerging wastewater treatment.

1.3 Objectives of the Study

1.3.1 General objective

The main objective of the study was to establish an electrochemical and efficient method that would effectively remove COD and colour from azo dye wastewater using aluminium (Al) and stainless steel (SS) electrodes.

1.3.2 Specific Objectives

i. To optimise the effect of process parameters (inter-electrode distance, support electrolyte, dye concentration, current density, pH and time) for colour and COD removal using Al and SS electrodes.
ii. To study the efficiency of electrochemical treatment using Al and SS electrodes in terms of colour and COD removal.
iii. To determine selected physico-chemical parameters of both raw and electrochemically treated dye water.

1.4 Hypotheses

i. Inter-electrode distance for SS and Al electrodes does not have significant effect on colour removal.
ii. Current density and pH have no significant effect on specific energy consumption
iii. Addition of supporting electrolyte (NaCl) does not enhance the performance of the electrocoagulation process.

1.5 Significance of the study

The outcome of this research will be used to design an EC unit for the treatment of dye wastewater to reduce their concentration to permissible limits. The system can be applied to treat other types of wastewater such as domestic, dairy and leather industries after optimization of process parameters. The water treated by such a process can be reused for industrial processes or irrigation purposes hence reduce challenges of water scarcity.

1.6 Scope and limitation of the study

The study only focused on the electrochemical treatment of wastewater from azo dyes, using Aluminium and Stainless Steel. Effects of operational parameters such as dye concentration, support electrolyte, contact time, inter-electrode distance, current density and pH on dye removal were investigated. However, the effects of temperature and flow rate on colour and COD removal were not determined in this study

CHAPTER TWO

LITERATURE REVIEW

2.1: Classification of Dyes

Dyes are organic chemicals that confer colour to materials such as plastics, clothes, cosmetics, waxes, paper and pharmaceuticals when they are added to them (Uday *et al.*, 2016). Dyes are classified into different classes basing on their chemical structure, colour index (C.I) and their uses (Adegoke and Bello, 2015). The main classes of dye include; reactive dyes, vat dyes, azo dyes, disperse dyes, mordant dyes, direct dyes, acid dyes and basic dyes (Charoenlarp and Prabphane, 2015). There are over 10,000 textile dyes in use of which 70% are synthetic azo dyes with complex structures (Hassaan and El Nemr, 2017).

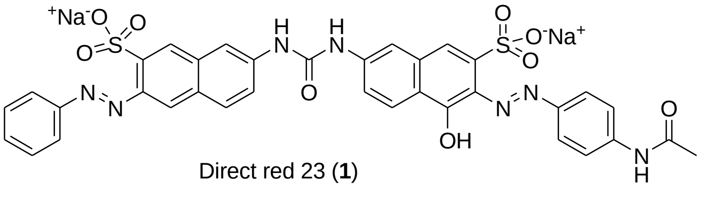
These dyes have electron-withdrawing groups with one or more azo bonds (-N=N-) making them electron-deficient xenobiotic (Singh *et al.*, 2015). The reactive azo dyes give quality dyed materials and are preferred by the textile industry. However, the impact of these on the environment is severe (Deb and Majumdar, 2013). Their presence in water even in a small amount is harmful and toxic to aquatic life (Haddal *et al*., 2014).

2.2 Structure of the azo dyes

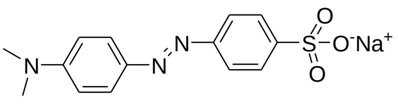
Azo dyes are synthetic nitrogen-based class of dyes that are the widely used groups of dyes. They're cheaply produced, but some can be dangerous and have carcinogenic and toxic effects. They have nitrogen-nitrogen bond (-N=N-) in the centre and they are highly electron deficient. They are complex in nature and show carcinogenic evidences of reductive cleavage (Ratna and Padhi, 2014). Toxicity of ingredients grows with the increase of benzene rings in their structure. Carcinogenicity depends on mechanism of degradation and on the structure of molecule. (Gicevic, *et al.,* 2019)

Nitro-compounds especially Azo are degraded in aquatic bodies resulting to carcinogenic amines. Degradation Products of azo dyes are mainly aromatic amines with different structures and have carcinogenic properties. Carcinogenicity of many azo dyes is due to their cleaved products such as benzidine. Benzidine is known as a carcinogen for the human urinary bladder (Ismail *et al.,* 2019)

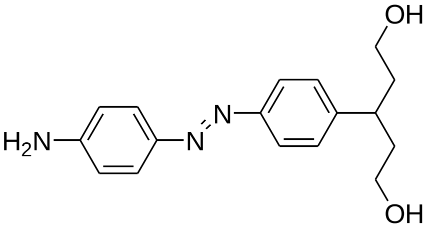
The chemical structure of dyes is comprised of a conjugated system of double bonds and aromatic structures (Bhatia *et al.,* 2018). These structures allow strong π→ π* transitions in the UV-visible area, with high extinction coefficients that making them dye chromophores. Of all these structures, the azo aromatic is the widely spread class of dyes. The chemical structures **1-4** shows some of the common azo dyes (Nikhil, *et al.,* 2012)



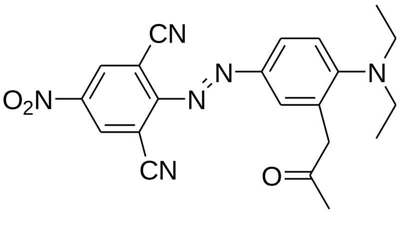
Direct red 23 (**1**)



Methyl orange (**2**)



Disperse black 9 (**3**)



Disperse blue 165 (**4**)

2.3 Environmental Impacts of Industrial dye Wastewater

In textile industries, several processes are involved during the conversion of natural-based fibres (such as wool, cotton and silk) and synthetic-based fibres such nylon into fabrics. These processes include pre-treatment, dyeing, printing and finishing. They involve the use of chemicals such as dispersing agents, emulsifiers, salts and levelling agents. A huge amount of fresh water is used during the finishing stage, this leads to the discharge of substantial volumes of wastewater effluents that is unsafe for consumption (Chollom, 2014).

The textile effluents contain a large number of dyes that get washed from fabrics during processing. The continuous discharge of these effluents to water sources increases their concentration (Ghaly *et al*., 2014). The effluents contain chemicals that are non-biodegradable and carcinogenic posing a major threat to public health and the environment (Uday *et al.,* 2016). It has been found from the toxicity study of several industrial wastewaters that besides dyes contamination, heavy metal ions like $Cd^{2+,}$ Cr^{6+}, $Pb^{2+,}$ Zn^{2+}, Cu^{2+}also significantly contribute towards the toxicity of textile effluents (Ismael *et al.,* 2019) Azo and nitro compounds have been found to be re-duced/degraded in aquatic bodies by giving rise carcinogenic amines. Numerous dyes, especially azo dyes are known to be formed from well known carcinogenic precursors benzidine and get reduced to toxic molecules in the body.

2.4 Dye Removal Techniques

The treatment processes are classified into three major techniques namely physical, biological and chemical techniques (Parma and Shukla, 2019). The choice a technique depends on the chemical nature of the dye, the cost of chemical required, equipment, environment, and maintenance (Parma and Shukla, 2019).

2.4.1 Physical methods

2.4.1.1 Adsorption

Adsorption has been described to take place by concentrating materials on solid body surfaces (Vital *et al*., 2016). Materials that are used as absorbents are known to have porous surface because the method utilizes surface forces of attraction to bring materials to the solid surface. These adsorbents can be from among other sources like charcoal, zeolites, clays, sugar industry waste, peat moss and sawdust (Vital *et al*., 2016).

The method has been used by Saeidi *et al*., (2017), who prepared an adsorptive from tea waste to remove acid orange 7 from wastewater. The dye adsorbent was prepared at different condition to improve the absorptive abilities. The results indicated that the nature of the particles of an adsorbent determines the amount of the dye adsorbed. The concentration range of 50 to100 mg/L achieved 90 to98% dye removal. However, at a concentration of 500 mg/L concentration the removal decreased to 72%. At a higher dye concentration, the number of adsorptive sites decreases hence decline in dye removal. This is a limiting factor in the performance of this mode of dye removal. Besides, the pre- and post-treatment of adsorbents do not make them any better in fully removal of dye waste (Nawaz and Ahsan, 2014).

2.4.1.2 Coagulation–flocculation

In coagulation-flocculation, coagulants are added to dye effluents to decolourize the dyes (Charoenlarp and Prabphane, 2015). These coagulants include Ferric sulphate, Calcium chloride, Aluminium sulphate and Ferric chloride. Other coagulant agents include copolymers such as hexamine, dichloride and penta ethylene (Gadekar, and Ahammed, 2016). Their working mechanisms are based on the formation of flocs when added to dyes making it easier to separate the by either filtration or sedimentation.

Coagulation–flocculation method has been used for colour removal of disperse and sulphur dyes (Puchana *et al*., 2018). Investigations made on coagulation /flocculation process using aluminium based water treatment residuals indicated that the highest colour removal of disperse dye solution was at lower pH. Colour removals of 88, 87 and 76% were attained for an initial dye concentration of 25, 50 and 75 mg/L respectively at pH 3.0 with water treatment dose of 3000 mg/L (Gadekar, and Ahammed, 2016).

Combination of the two techniques; absorption and coagulation using *Hibiscus sabdariffa* seeds as the natural coagulant and activated carbon as the absorbent was employed in studying the removal of Congo red dye from wastewater (Hoong and Ismail, 2018). It was observed that at optimum operating conditions PH 2, the concentration of 385 ppm, adsorbent dosage of 209 mg/L and coagulant dosage of 150 mg/L, led to dye removal of about 96.67% (Hoong and Ismail, 2018).

Removal of reactive dyes from wastewater by the use of inorganic and organic coagulants has been researched (Ashtekar *et al*., 2015). In the study, synthetic reactive dye solution was prepared by mixing 100mg of dye with 500ml of water. When a coagulant poly aluminium chloride (PAC) was used it was observed that a coagulant below 100 ppm led to a lower colour removal while above 100 ppm resulted in almost 100% colour removal.

It was also observed that raising the coagulant dose to 150 ppm had a negligible effect on colour removal. Addition of alum coagulant increases the efficiency of colour removal. The use of ferrous sulphate as a coagulant at different concentrations did not affect colour removal. In addition, the technique has low efficiency, leads to high generation of sludge and require both pre- and post-treatment of the adsorbent. The adsorbent material requires regeneration making the process expensive. Inorganic coagulant such as aluminium results in high residual aluminium concentration, which causes Alzheimer’s disease and senile dementia (Hung *et al*., 2012).

2.4.1.3 Ion Exchange

Ion exchange is a technique that involves interchange of ions reversibly between a solid (ion exchange material) and a liquid (effluent). The complex ion exchangers are made of functionalized porous or gel-like polymer that removes the exchanged ions from an aqueous mixture (Arslan *et al*., 2016). In treatment of dye wastewater, the ion containing dye solution is passed through a column containing the solid resin to remove unwanted ions (Khan *et al*., 2015).

The dye wastewater is passed over the ion exchange resin until the available sites are all used up (Atul *et al*., 2012). The method is employed for both cationic and anionic dyes. Cationic ion exchanger is used to exchange the positively charged ions (cations) formed from weak acid cation exchange resins. The anionic exchangers contain weak base resins which exchange with negatively charged ions (Arslan *et al*., 2016). Anion exchange resins have been recommended due to their adsorption abilities and regeneration properties in the removal of reactive dyes (Atul *et al*., 2012). However, in particle form, the anion exchange resins are limited in packed-bed operations that have slow pore diffusion, high pressure drops, low accessible flow rates and flow channelling. This process is costly and ineffective in removal of disperse dye from wastewater (Khan *et al*., 2015).

2.4.1.4 Membrane Technology

A membrane is a barrier that selectively allows the movement of substances across it (Nqombolo *et al*., 2018). The membranes are porous or permeable, making it easy for them to clarify, concentrate and separate dye from effluents (Chollom, 2014). This method is used at the point of effluent collection, to purify the wastewater during textile processing (Chollom, 2014). However, this technique is not effective in the treatment of concentrated dye effluents and removal of dissolved solid content from wastewater (Thamaraiselvan and Noel, 2015).

Several pressure membrane processes are available which include microfiltration, ultrafiltration, reverse osmosis, and nanofiltration. These membranes only differ in pore size of which, microfiltration membranes have the largest pore size that allows particles size of more than 0.1-0.2 µm to be removed. (Thamaraiselvan and Noel, 2015; Nqombolo *et al*., 2018). They are pressure-driven making them suitable for pre-treatment during nanofiltration and reverse osmosis (Nqombolo *et al*., 2018). Microfiltration is not efficient in the removal of large contaminant solid particles less than 1 mm in size, viruses and organic matter (Nqombolo *et al*., 2018).

Ultrafiltration membranes are made from polyelectrolyte complexes cellulose acetate and inert polymers (Thamaraiselvan and Noel, 2015). Their pore size ranges from 0.005 µm to 1 nm (Nqombolo *et al*., 2018). They are suitable for removal of suspended solids and macromolecules, but not bacteria and soluble macromolecules such as proteins. They have a limitation because they allow salts, solvents and low molecular weight organic solutes to pass through (Atul *et al*., 2012).

Nanofiltration membranes have a typical pore size of 0.5-5 nm. They are suitable in the removal of ions that cause osmotic pressure at low pressures, unlike reverse osmosis. Due to low pressure in the open network structure, low molecular weight solutes such as glucose, pesticides and dyes are retained and removed from the wastewater. This process is subject to fouling that blocks the membrane pores reducing their performance (Chollom, 2014).

Reverse osmosis technique is pressure-driven with pores smaller than ultrafiltration (Atul *et al*., 2012). The Pressure applied must be sufficient to enable the water molecules to overcome the osmotic pressure. This technique removes soluble solids, smaller particles, organic and bacteria (Nqombolo *et al*., 2018). This method is expensive, require high pressure and prone to fouling (Nqombolo *et al*., 2018)).

2.4.2 Biological methods of degradation

This method involves degradation of the dyes using materials such as algae, yeast bacteria fungi for the treatment of dye wastewater (Gupta *et al*., 2015). Such materials have the ability to breakdown and absorb various synthetic dyes (Uday *et al*., 2016). The method has been found to degrade the dyes by breaking the bond on the chromophoric group releasing inorganic compounds that are less toxic (Bhatia *et al*., 2018). Bioremediation biological technique, involves removal of dye waste by use of microbes or/and their products (Gupta *et al*., 2015). The activity of the micro-organism can then be used for large scale treatment of textile dye waste (Bhatia *et al*., 2018).

Biodegradation of textile azo dyes and its bioremediation potential using seed germination efficiency was performed (Ebency *et al*., 2013). The results indicated that the reactor removed up to 90% of colour from1000 mg/L of dye-containing mixed cationic dye (Ebency *et al*., 2013). The results also showed that the removal efficiency decreased as the effluent concentration increased. Increase in hydraulic retention and organic loading time led to increase of removal efficiency (Ebency *et al*., 2013).

Several dyes used in the textile industry do not biodegrade aerobically because the enzymes are dye specific (Gupta *et al*., 2015). Azo dyes anaerobic degradation may be satisfactory but carcinogenic aromatic amines are formed as intermediates (Karim *et al*., 2018). Due to the limitations of these techniques, further research is of paramount necessity to come up with a more efficient, cost-effective and environmentally friendly process.

2.4.3 Chemical Methods

Chemical dye wastewater treatment uses oxidising agents such as chlorine, ozone, potassium permanganate and hydrogen peroxide (Wijannarong *et al*., 2013).

2.4.3.1 Ozonation

Ozone has been noted to be a strong oxidising agent in treating drinking water and industrial dye effluents (Hassaan and El Nemr, 2017). Dye molecules are known to possess a chromophore group that is an organic cyclic compound with a single or a double bond (Wijannarong *et al*., 2013). The process of ozonation involves oxidising double bonds at the chromophore group with ozone (Malik *et al*., 2018). In chemical oxidation, the dye is removed when cleavage of the aromatic ring of the dye molecule takes place (Hassaan and El Nemr, 2017).

The study of the extent of dye removal by ozonation was done, at the reaction time of 5 minutes and 120 minutes had the efficiency of 32.83% and 56.82% of dye removal respectively (Wijannarong *et al*., 2013). When the process was carried out for 1hour colour removal was 48.51 %. Further increase in reaction time to 4 and 6 hours led to an increase in efficiency to 78.29 % and 92.20 % respectively. Limitation of this process is that it achieves 100% colour removal but the product is toxic. It is an expensive process and has a short half-life. The stability of ozone is affected by temperature, salt and pH (Wijannarong *et al.*, 2013).

2.4.3.2 Fentons process

Fenton reaction is an advanced oxidation process that involves degradation of organic substrates by H_2O_2/Fe^{2+} (Palit, 2012). Fenton reagent is made up of hydrogen peroxide (H_2O_2) and iron (II) sulphate (Patil and Raut, 2014). This solution is used as a catalyst during the oxidation of organic solvents. The mixture reacts to produce hydroxyl radical which makes it a strong oxidising agent for a wide range of organic dye effluents (Palit, 2012).

The performance of the Fenton process was evaluated for the removal of COD and colour from textile dye wastewater. The efficiency of colour removal was 98% at H_2O_2 0.1ml/L,0.2g/L $FeSO_4$ at pH 3 and for COD the removal efficiency was 85% at H_2O_2 0.6ml/L,1.2g/L $FeSO_4$ at pH 3 (Patil and Raut, 2014). Although the process can remove the colour from textile effluents, it introduces anion in high levels of concentration in the treated wastewater and large amounts of ferrous sludge (Palit, 2012).

2.4.3.3 Electrochemical process

Electrochemical process is a reduction-oxidation chemical process that takes place when an electric current pass through an electrolyte (Kuokkanen *et al.*, 2013). It can also be referred to as the electrocoagulation process, where dissolution electrode is the anode (Deb and Majumdar, 2013). This so-called “sacrificial anode” (Iron, Stainless steel or aluminium) goes into solution producing metal ions which act as coagulant agents in the aqueous solution in *situ* (Sharma, 2014).

During the process formation of highly charged cations (Al^{3+}, Fe^{2+}) at the anode destabilize colloidal particles by the formation of monomeric and polymeric hydroxo complex species. Due to the high adsorption properties the metal hydroxo-complexes posses, they form strong aggregates with pollutants (Prakash *et al.*, 2011). The extent of metal hydrolysis depends upon the total metal cation concentration and the pH, as well as the type and concentration of other species present in solution.

Electrocoagulation (EC) has been defined as a process in which the anode material undergoes oxidation with the formation of various monomeric and polymeric metal hydrolyzed species (Prakash *et al.*, 2011). These metal hydroxides remove the colour from wastewater by sweep coagulation and colloidal aggregation. The wastewater then forms big size flock particles which are removed by settling thus decolourize dyes (Shivayogimath and Rashmi, 2013). This is a straightforward and proficient method for wastewater treatment containing dyes. In recent years, many investigations focused on the use of electrocoagulation owing to an increase in environmental restrictions on effluent wastewater (Karthik *et al.*, 2014).

Electro-coagulation requires simple equipment and is easy to operate (Nandi and Patel, 2017). The electrolytic processes in the Electrocoagulation are cell controlled electrically with no moving parts, thus requiring less maintenance (Le *et al*., 2017). Wastewater treated by Electrocoagulation gives palatable, clear, and odourless water. It is a low sludge producing technique (Madhusudhan *et al*., 2015). The sludge formed by electrocoagulation tends to readily settle and easy to de-water because it is composed of mainly metallic oxides/hydroxides (Le *et al*., 2017).

This technique depends on many operational factors such as dye concentration, inter-electrode distance, current density and contact time. For the removal of colour and total organic carbon in reactive dyes from textile wastewater by electrocoagulation showed that the removal efficiency was influenced by reaction time, IED, support electrolyte concentration and initial dye concentration (Deb and Majumdar, 2013). Most dye treatment techniques have been found are costly and not economically viable due to high energy and chemical consumptions (Verma *et al*., 2012). Electrocoagulation technique therefore stands as the effective method.

The present study seeks to investigate the influence of process parameters on colour and chemical oxygen demand removal. The study will involve the removal of azo dye from wastewater by EC using Al and SS electrodes. The removal of disperse blue and disperse black dyes from dye effluent using Al and SS electrodes is investigated at different operation conditions.

2.5 Electrochemical reactions in wastewater treatment

According to Santhosh *et al*., (2015) the three major reactions in Electrocoagulation process are;

i) Coagulants form at the anode by dissolution (sacrificial electrode),

ii) Coagulation of contaminants and particulate suspension and breaking of emulsions.

iii) Aggregation of the destabilized by flocculation or adsorption on the metal hydroxide flocs or its polymers.

The study further defined; “electro-coagulation is a process consisting of creating metal hydroxide flocs inside the wastewater by electro-dissolution of a soluble anode made of Iron or Aluminium”

Reaction equations during electrolysis using Iron electrode are

Anode:

$4Fe(s) \rightarrow 4Fe^{+2}(aq) + 8e$ ………….. (2.1)

$4Fe^{+2}(aq)+10H_2O(l)+O_2(g) \rightarrow 4Fe(OH)_3(s) + 8H^+(aq)$…………………………...... (2.2)

Cathode:

$8H^+ (aq) + 8e \rightarrow 4H_2 (g)$ ………………………………………………………..(2.3)

Overall:

$4Fe(s) + 10H_2O (l) + O_2 (g) \rightarrow 4Fe(OH)_3(s) + 4H_2 (g)$………………………… (2.4)

(Ghalwa *et al.*, 2016).

During electrolysis, Iron electrode is oxidised to produce different monomeric and polymeric hydroxyl ions such as $Fe(H_20)_5^{2+}$, $Fe(H_2O)_6^{3+}$, $Fe_2(H_2O)_6(OH)_4^{4+}$ and $Fe(H_2O)_8(OH)_2^{4+}$(Karthik *et al.*, 2014). These complexes depend on the pH of the solution.

The Fe(OH)n(s) remains in the aqueous phase as a gelatinous suspension, which can remove the pollutants from the wastewater by either complexation or by electrostatic attraction followed by coagulation. In the surface complexation mode, the pollutant acts as a ligand (L) to chemically bind hydrous iron (Kabdasli *et al.*, 2012).

L-H $_{(aq)}$ + (OH)OFe$_{(S)}$→L-OFe(s) + H_2O $_{(l)}$---(2.5)

While for the case of aluminium, the electrodes reactions are as follows;

Anode:

Al(s) →Al^{3+} (aq) +3e…………………………………………………………… (2.6)

Cathode:

$3H_2O$ (l) +3e-→$3/2H_2$ (g) +$3OH^+$ (aq)……………………………………….. (2.7)

(Ghalwa *et al.*, 2016).

For the aluminium electrodes, Al^{3+} (aq) ions immediately undergo a further spontaneous reaction to generate corresponding hydroxides and polyhydroxides. Due to hydrolysis of Al^{3+}, the $Al(H_2O)_6^{3+}$, $Al(H_2O)_5OH^{2+}$, and $Al(H_2O)(OH)_2$+ are generated. These products produce many monomeric and polymeric substance such as, $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$, $Al(OH)^{4-}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, and $Al_{13}(OH)_{34}^{5+}$ (Karthik *et al.*, 2014). The polyhydroxides, hydroxides, polyhydroxymetallic compounds have the power to attract dispersed particles of pollutants as well as counter ions leading to coagulation (Uzoh, 2014). The hydrolyzed Al ions form large networks of Al-O-Al-OH that can chemically bind pollutants. For example the structure of dimeric and polymeric Al^{3+} hydroxo complexes are shown equation 10 and 11.The gelatinous charged hydroxo cationic complexes can effectively remove pollutants by adsorption to produce charge neutralization. $Al(OH)_3$ flocs remove the dye molecules present in the solution by the following reaction mechanism according to Deb and Majumdar, 2013

Precipitation

$\text{Dye} + \text{Al}_m = [\text{Dye Al}_m]_s$---(2.8)

$\text{Dye} + \text{Alp} = [\text{Dye Al}_p]_s$---(2.9)-

Adsorption

$\text{DYE} + \text{Al (OH)}_3 = \text{Al(OH)}_{3\ s}(\text{DYE})$---(2.10)

$(\text{DYE Al}_p)\text{s} \quad + \text{Al(OH)}_{3s} = [\text{Al(OH)}_3\text{DYE Al}_p]_s$--------------------------------(2.11)

Effluents from the textile industry are known to possess high-density colour levels. This leads to high chemical oxygen demand and a wide range of pH (Tyagi *et al*., 2014). Electro-coagulation is becoming a method of choice for wastewater treatment in removing valuable chemicals from the sludge (Le *et al*., 2017). Treatment of dye waste by electro-coagulation has been reported not only to be a very successful and effective tool but also with high efficiency of COD and colour removal (Akanksha *et al*., 2013). This method (EC) has been recommended for use due to its simplicity, easy to operate, effectiveness, ability to handle large volumes of wastewater and environmentally friendly (Nandi and Patel, 2017).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Electrochemical experimental set-up

The electrochemical experimental set-up represented in Figure 3.1 was used for the study. It comprised of electrochemical cell, magnetic stirrer (85-2 China), an AC-D.C variable power supply unit (MCP Lab electronics M10-350-02, 0-24 V, and 0-2 A), a digital multi-meter (V and A True RMS VA140103613 model) and electrode plates (Stainless Steel and Aluminium) of size 6 cm x 2 cm x 0.1 cm

3.2 Preparation of dye water sample

The dye water used in this study was prepared by dissolving disperse blue in four 100ml beaker at different concentration (0.1 g/L, 0.2 g/L, 0.3g/L and 0.4 g/L). The same procedure was repeated for disperse black dye. The two-commercial azo disperse blue and disperse black were sourced from Kenyan textile industry. A 0.2 g/L of NaCl supporting electrolyte was added depending on the experiment to increase the conductivity.

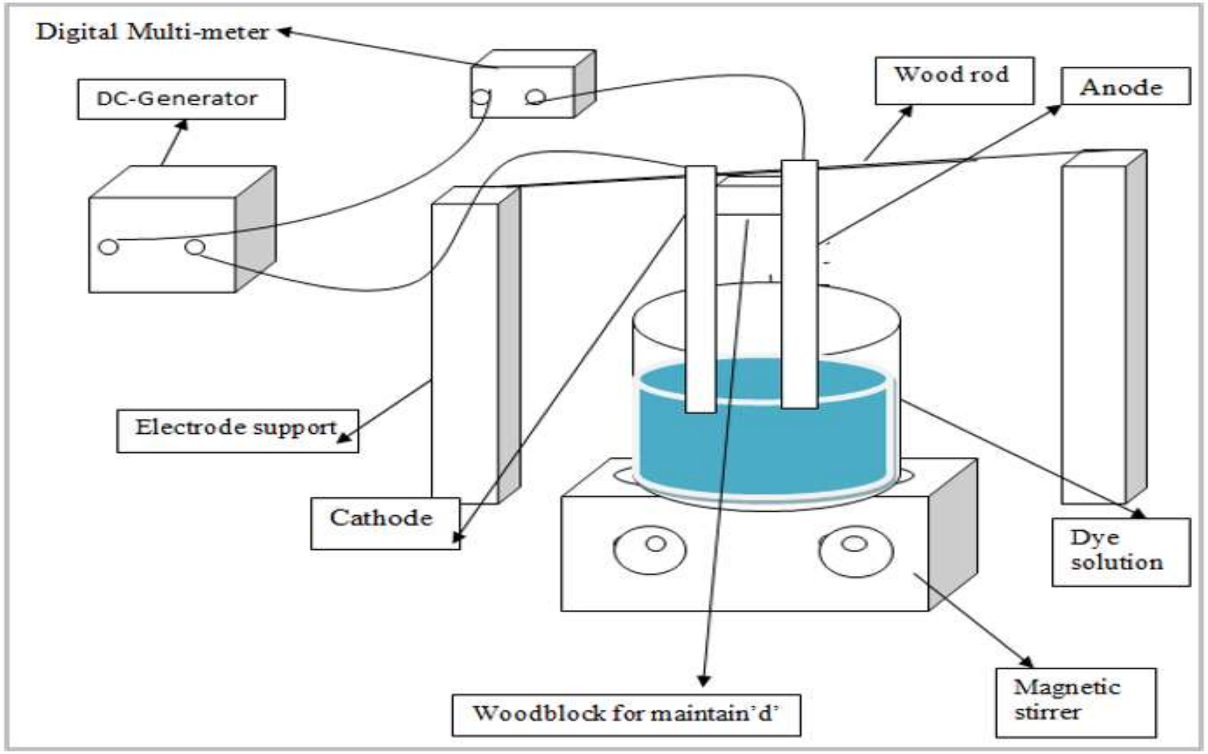


Figure 3.1: A schematic diagram of the electrochemical experimental set-up

3.3 Experimental procedure

The test reagents of disperse blue and disperse black were separately prepared in four different dye concentrations (0.1, 0.2, 0.3 and 0.4 g/L) according to Nandi and Patel, (2017) with modification. The modifications were made on concentration from the 0.05-0.2 g/L for Nandi and Patel (2017) to 0.1-0.4 g/L for the present study and the electrolytic cell capacity adjusted from1L to 100 mL.

A sample of 100 mL of each test solution was transferred into a 100 mL glass beaker this ensured maximum surface of the electrode was immersed in the dye waste and with electronic stirring most of the solution was in contact with the surface of the electrodes. Al electrodes were vertically positioned, with a space of 1cm between them. The Anode and cathode were supported above the beaker and dipped vertically into the solution. An insulator was placed between the electrodes to maintain the desired inter-electrode distance. The sample solution was stirred at 80 rpm by a magnetic stirrer to maintain uniformity of the electrolyte concentration and constant temperature.

Direct current of 12 V and timer were switched on simultaneously and the current passing through them recorded. The reaction continued to complete removal of colour while recording current. Measurements absorbance was taken at an interval to monitor colour removal progress. This was repeated using stainless steel electrodes. The electrodes were mechanically polished underwater with abrasive paper, cleaned in 0.2 M HCl solution for 2 minutes and rinsed with distilled water to eliminate any interference and ensure surface reproducibility during EC.

3.4 Effect of Process Parameters

The removal of COD and colour from test reagents by electrocoagulation was investigated basing on the parameters described on the table 3.1 (Nandi and Patel, 2017).

Table 3.1: Experimental range of test parameters studied

Parameter studied	Ranges	Parameters kept constant during the study
pH	2, 4, 6,7, 8 and 10	C_O=0.2 g/L, Cd =47 A/$m^{2,}$ SE=0.2 g/L t=25 min, IED=1 cm
Current density (Cod)	15, 26, 36 and 47 A/m^2	C_O=0.2 g/L, SE=0.2 g/L, t=25 min IED=1cm, pH=4
Dye initial concentration (C_0)	0.1, 0.2, 0.3 and 0.4g/L	SE=0.2g/L, t=25min, IED=1cm, pH=4, CD=47A/m^2
Support electrolyte (SE)	0.1, 0.2, 0.3 and 0.4	C_O=0.2g/L, t=25min, IED=1cm, pH=4, Cd=47A/m^2
Inter-electrode distance (IED)	1,1.5, 2, 2.5, and 3	C_O=0.2g/L, t=25min, SE=0.2g/L, pH=4, Cd=47A/m^2
Contact time (t)	5, 10, 15, 20, 25 and 30 min.	C_O=0.2g/L, IED=1cm, SE=0.2g/L pH=4, Cd=47A/m^2

3.4.1 Effect of dye concentration on colour removal

The effect of dye concentration was done in accordance to Deb and Majumdar, 2013 with modifications of range of initial dye concentration made from 0.05-0.3 g/L to 0.1-0.4 g/L to cater for slightly concentrated effluent. Contact time and voltage were also modified from 30 to 20 min and 15 to 12 V respectively since the present study used a smaller volume of dye solution of 100 mL compared to 2.5.L

To investigate the influence of initial dye concentration on SEC and removal efficiency test reagents were prepared in four different initial dye concentrations (0.1, 0.2, 0.3 and 0.4 g/L). Each solution was subjected to electro-coagulation at a voltage of 12V, optimum current density of 47 A/m^2 for 25 minutes contact time. The initial concentration that produced the highest removal efficiency was then taken as optimum and used for studying other factors.

Dye concentrations were determined by the absorbance of treated samples and the standards using a UV-visible spectrophotometer (Fenway, Model 6850, Double Beam), at 574 nm and 304.5 nm against blank solutions for disperse blue and disperse black respectively. Absorbance values were then converted to concentrations by using calibration curves obtained from dye standards using formula 7(Figure3.3 and 3.4)

$$\text{Colour removal (\%)} = \frac{C1-C}{C1} X100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.1)$$

Where

C_1 and C are concentrations of dye before and after electro-coagulation in mg/L respectively (Daneshvar *et al*., 2006).

3.4.2 Effect of Current density on colour removal

The effect of current density was investigated using electrocoagulation accordance with to Nandi and Patel, (2017) with of current densities varied from 15 to 47 A/m^2 in this study. The choice of parameters was made according to the rating of the dc power supply generator used and the size of the electrode active surface. During the experiment, the electrode of height 4.5cm was dipped into the test solution. The electrodes were connected to a DC supply with galvanostatic operational options for controlling the constant current density. The effective surface area and current density were calculated following equation 13;

Current density = $^{I}/_{2S}$………………………………..………………….. (3.2)

where;

I = current through the solution in amperes (A)

S = area of the electrode (m^2)

The current density was altered by changing the amount of support electrolyte sodium chloride solution. The optimal electrical current density was found out by conducting experiments in various current densities keeping other operational conditions constant. Application of four current densities (15, 26, 37 and 47A/m^2*)* was applied to determine the effect of current density on the electro-coagulation treatment of test reagents. The current density that produced the best percentage removal in colour in the shortest time was assumed as the optimum.

3.4.3 Effect of Inter-Electrode Distance (IED) on colour and COD removal

To assess the effect of inter-electrode distance the electrocoagulation was performed as described by Deb and Majumdar, (2013) with modifications on the IED range from 0.5-2 cm and voltage of 15 V to 1- 3 cm and voltage of 12 V. The gap between the anode and the cathode was maintained by placing different wooden blocks of varying size from 1 to 3cm. The batch experiments were carried out at different inter-electrode distance (1, 1.5, 2, 2.5 and 3 cm) at an optimized current density of 47 A/m^2. The dye removal efficiency was then calculated at each electrode distance and comparison made to come up with the inter-electrode distance that gives the least power consumption

3.4.4 Effect of Contact Time on dye removal efficiency

The effect of contact time on dye removal efficiency was determined by electrocoagulation method as described by Hamaadi *et al.*, (2016) with modifications, made on time range from 2-12 min to 5-30 min for this present study. In addition, operating conditions for Hamaadi *et al.*, (2016) were pH= 4, conductivity= 6ms/cm, IED= 0.6cm, current density = 250 A/m^2, initial dye concentration=100mg/L and for this study are as stated in table 3.1. The dye removal efficiency was determined by the variation of the reaction time (5, 10, 15, 20, 25 and 30 mins) while keeping other parameters constant, The experimental time of 25 minutes was taken as the optimum time because it led to complete decolourisation of wastewater.

3.4.5 Effect of pH on dye removal and power consumption

The effect of pH on dye removal and power consumption was performed as described by Bazrafshan *et al.,* (2014) with modification of initial pH from (3, 5, 7, 9, 11) to (2, 4, 6, 7, 8 and 10) .Choice of the pH was arrived at from preliminary work in this research that showed that EC performance at highly acidic and highly alkaline conditions was very low, for this reason, the pH range of 2-10 was selected. The adjustment of pH was done by addition of small amounts of dilute 0.1M NaOH or 0.1M HCl. The pH of the solutions was measured by a pH meter. The initial pH that resulted in the highest dye removal and lower power consumption was taken as the operational pH.

3.4.6 Effect of supporting electrolyte on dye removal

The effect of supporting electrolyte on dye removal and electrical energy consumption was conducted according to the method developed by Nandi and Patel, (2017) with modifications of additional range of NaCl from 0.1-1 g/L to 0.1-0.4 g/L in this study. The choice of the concentration was derived at by preliminary tests that showed a higher concentration of NaCl had no much effect on the removal efficiency. The conductivity of solutions was then adjusted by the addition of different concentrations of NaCl (0.1, 0.2, 0.3 and 0.4 g/L) and their efficiency determined.

3.4.7 Effect of electrode type on colour and COD removal

The effect of electrode type was investigated by performing the process at optimised parameters. (pH 4, IED 1cm, SE 0.2g/L, current density 47A/m^2). 10 samples 100mL of dye solution were prepared at concentration of 0.1g/L of the dye all subjected to electrocoagulation at the optimised conditions using Aluminium electrodes. Absorbance at different contact time was taken to monitor the extent of dye removal. The procedure was repeated using the stainless-steel electrodes. The efficiency of the removal of both the electrodes was determined.

3.5 Calculation of operating cost of the system

The operating cost of the system was estimated after optimization of the operation parameters according to Geraldino *et al*., (2015). The cost included; electrode material, electrical energy costs, labour, maintenance, sludge dewatering and disposal. The energy and electrode material costs are major cost items in the calculation of the operating cost (Ghosh *et al*., 2008);

$$\text{Operating cost} = \mathbf{a}\, C_{\text{energy}} + \mathbf{b}\, C_{\text{electrode}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(3.3)}$$

where: C_{energy} (KWh/m^3 of dye solution) and $C_{\text{electrode}}$ (kg Al/ m^3 of dye solution) are consumption quantities for the dye removal, which are obtained experimentally. "**a**" and **"b"** given for Kenya market in October 2017, are as follows: "**a**" electrical energy price 21.00 Kenya Shillings/ kWh; "**b"** electrode material price 100 Kenya Shillings /kg for SS and 150 Kenya Shillings/kg for Aluminium. Cost due to electrical energy (KWh/m^3 dye solution) is calculated as;

Specific Energy Consumption

$$= \frac{VIt}{\text{volume}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(3.4)}$$

Where;

V= is the average voltage of the EC system (V)
I= electrical current intensity (A)
t= reaction time (h)

The theoretical faradaic amount of the dissolved aluminium/Iron was calculated using the formula: -

$$\textit{Mass of Al} = \frac{I\,t\,M}{z\,F} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(3.5)}$$

Where, I = current intensity (A), t = time (s), M = Molecular weight.
z = number of electrons transferred in the chemical reaction 5 noted earlier.
F= Faraday's constant (96500 C/mol).

3.6 Physico-chemical Analysis

Raw and treated wastewater was analysed for pH, colour, conductivity, turbidity and COD. The Physico-chemical characteristics of wastewater were analysed by methods described by APHA (2005).

3.6.1 Determination of chemical oxygen demand (COD)

Determination of chemical oxygen demand (COD) was determined according to standard methods described by APHA, (2005). 50 mL of the dye sample was added into a 500 mL refluxing flask. 1g HgSO4, about 50g glass beads, and 5 mL sulphuric acid reagent were mixed and cooled. 25 mL of 0.0417M $K_2Cr_2O_7$ solution was added. The flask was then connected to the condenser and cooling water turned on. Additional 70 mL of sulphuric acid reagent was added through an open end of the condenser. The contents were refluxed for 2 hours and allowed to cool. The condenser was washed with distilled water to double the volume of the contents. Ferroin indicator (2 drops) was added and the solution titrated with Ferrous Ammonium sulphate (FAS) until the colour changed from bluish green to reddish brown. As a control, a blank of distilled water with reagents was refluxed and titrated.

The Standards of 0.00417M $K_2Cr_2O_7$ and 0.025M FAS were used when analysing very low COD samples. The technique and reagents were evaluated by conducting the test on potassium hydrogen phthalate solution. Chemical oxygen demand was then calculated using the following equation: -

$$\text{COD (mg/l)} = \frac{(A-B) \times M \times 8000}{\text{Ml sample}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (3.6)$$

Where:

A = Ferrous ammonium sulphate used for blank, mL

B = Ferrous ammonium sulphate used for sample, mL

MI = Molarity of Ferrous ammonium sulphate

Calculation of percentage removal of COD was done using the formula: -

$$\%\ \text{COD removal} = \frac{C1-C}{C1} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (3.7)$$

Where: $C_{1=}$ COD before electro-coagulation

C =COD after electro-coagulation

3.6.2 pH

The pH meter was calibrated using standard pH buffers of pH 4, pH 7 and pH 9. A sample of 80mL was placed in 100mL beaker and the electrode meter dipped in. The readings were taken directly from the meter and recordings made. Measurements were taken in triplicate

3.6.3 Conductivity

80 ml of sample was placed in 100mL beaker and the conductivity meter electrode was dipped in. Reading was taken directly from the metre and recorded. Readings were made in triplicate

3.6.4 Turbidity

Standards were used to calibrate turbidity meter; 80 mL of sample was placed in 100mL beaker and the turbidity meter electrode was dipped in. Reading was taken directly from the metre and recorded. Readings were taken for each sample.

3.7 Data analysis

The data was transformed and subjected to analysis of variance (ANOVA) and the means compared using the Student–Newman–Kuels (SNK) test (IBM, SPSS software version 22). The results were presented in various forms of tables, line graphs and bar graphs

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Effect of initial dye concentration on colour and COD removal

The effect of initial dye concentration on colour and COD removal was investigated. Colour and COD removal decreased with the increase of initial dye concentration. Dye removal in disperse blue with SS electrodes decreased from 90.67% to 54.23% and COD decreased from 70.21% to 30.03% when initial dye concentration was increased from 0.1 g/L to 0.4 g/L. The highest percentage colour removal recorded was 99.99% at 0.1g/L concentration of disperse black with SS. (Figure 4.1. and 4.2)

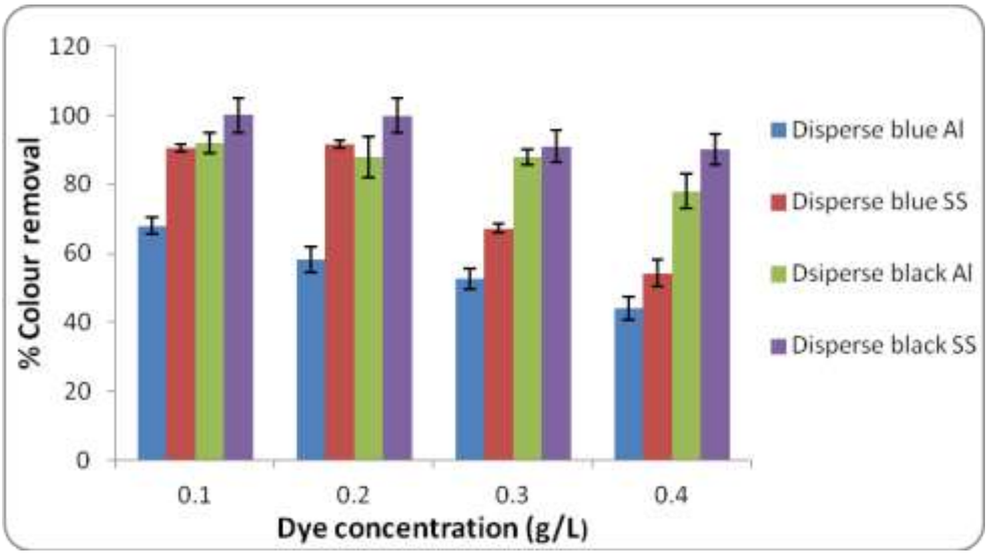


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Figure 4.1: Effect of dye concentration on colour removal

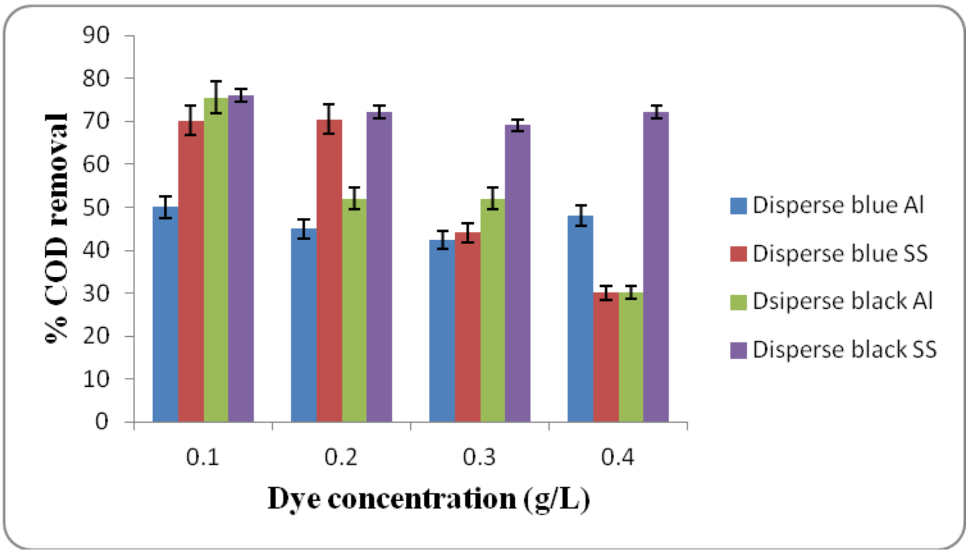


Figure 4.2: Effect of dye concentration on COD removal

The results were comparable to those obtained by Deb and Majumdar, (2013) in which aluminium electrodes were used in studying the removal of a Novacron Red C4B \ reactive dye in laboratory batch reactor at optimum conditions (Voltage: 15V, inter-electrode distance: 1cm, Contact time: 30 min.). The results showed that the decrease in initial concentration from 0.05 g/L to 0.3 g/L led to the percentage removal of dye and COD to rise from 63.4 to 98.9% and 50.3 to 84.7% respectively. This trend was attributed to the fact that during electrolysis at constant time and current, the amount of ions that dissolve from the anodic reaction is fixed according to the Faradays law.

It was also confirmed by one way-ANOVA that the percentage colour removal decreased significantly with the increase in dye concentration for all the runs ($p<0.05$), except disperse black with aluminium electrodes ($p=0.206$, $\alpha=0.05$). The COD removal did not differ significantly with the increase of dye concentration in disperse blue with Al electrodes ($p=0.526$, $\alpha=0.05$) and in disperse black with SS electrodes (p=0.183, α =0.05). However, there was a significant decrease in disperse black with Al electrodes, one way-ANOVA, (p=0.001, α =0.05). (Appendix 4).

The decrease in removal was because at a constant time of 20 minutes and current density of 47 A/m^2 same amount of Aluminium and Iron hydroxide complexes are formed which leads to the generation of the same quantity of flocs, Hence, the same percentage of dye removal. Consequently, at high dye concentration, the flocs produced are inadequate to absorb all the molecules of the dye in solution. In explaining a similar trend, Deb and Majumdar, (2013) affirms that when the dye concentration is low, the iron hydroxide and aluminium hydroxide complexes were higher than the dye molecules. This results in 100% dye removal in a short time.

4.2 Effect of pH on Colour removal and Specific Energy Consumption(SEC)

Determination of the effect of pH on the removal efficiency was done and the results presented as in the figure 4.3. The highest removal efficiency of colour was recorded at pH of 4 with an exception of disperse blue with SS at pH 7. From the results, increase in pH from 2 to 4 led to increase of colour removal efficiency. For disperse black with SS colour removal increased from 70.1% to 90.3% while in disperse blue with Al removal increased from 61.2 to 69.2 %. When the initial pH was above 4, colour removal was constant and beyond pH 7 there was slight decrease.

The results are comparable to what was obtained by Bazrafshan *et al.*, (2014) working with aluminium electrodes to remove BR-18 dye. When the pH was increased from 3-7, removal of increased from 84.6% to 98.4% at a reaction time of

60 minutes. Further increase in pH to 9 and 11 led to reduction of dye removal to 97.38 and 87.91%, respectively.

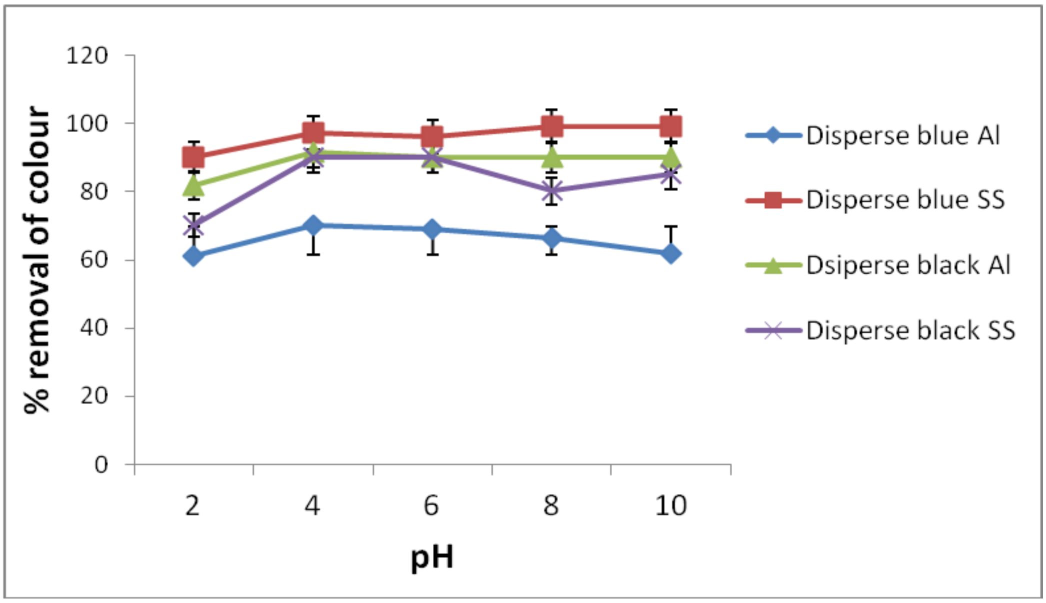


Figure 4.3: Effect of pH on colour removal

The effect of pH on specific energy consumption was also determined and results are reported as in figure 4.4. At a pH of 4, there was a low in specific energy consumption. The pH of 4 was then adopted as optimum because the best results were recorded in terms of colour removal and power consumption. From the study, it was further noted that at very low pH of 2, SEC is higher for both the electrodes for the two dyes. Increasing the pH beyond 7 led to increase in SEC. Increasing the pH to 9 and 10 resulted in higher SEC and hence reduction in dye removal efficiency (Figure 4.4 and 4.5). Similar trends of pH were observed by Nandi and Patel, (2017), working on the removal of organic dye (brilliant green) by EC using Fe electrodes. The pH of the medium increased in the reactive phase and stabilized at a pH range close to 6.5 – 10.5.

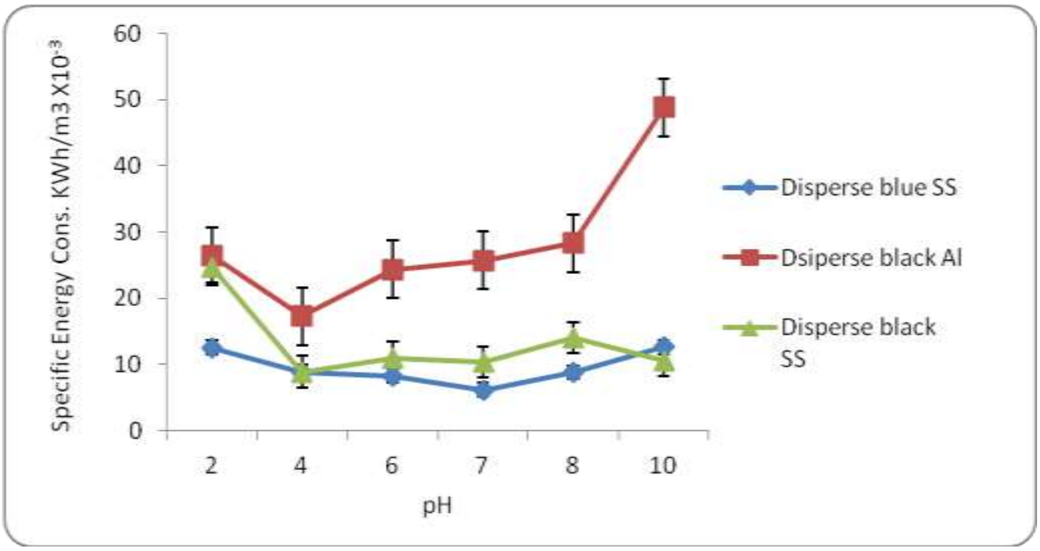


Figure 4.4: Effect of pH on SEC

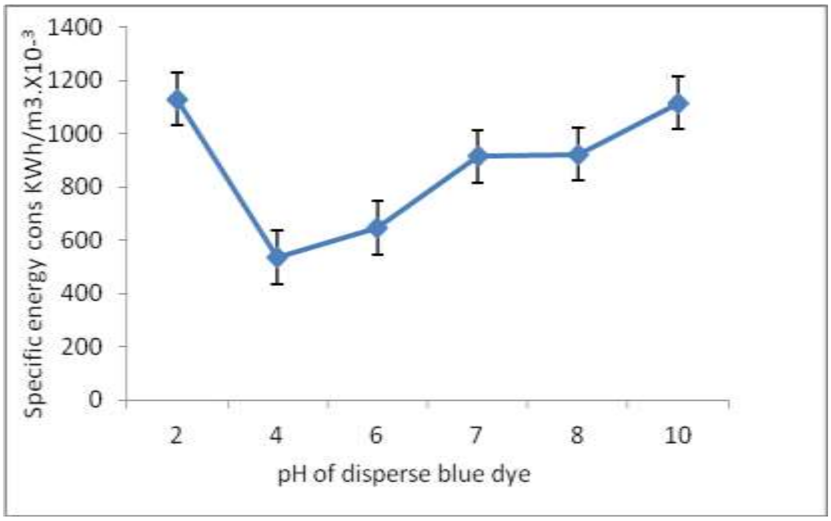


Figure 4.5: Effect of pH on SEC

Results are also consistent to what was obtained by Muhammad *et al.*, *(*2013), who attributed this to the fact that the charge on the particles is modified when the pH changes. Hydrolysis generates hydroxy-aluminium ions i.e $Al(H_2O)_6^{3+}$. The $Al(H_2O)_6^{3+}$ aqueous complex is dominant at pH< 4 and products $Al(OH)^{2+}$ and $Al(OH)_2^{+}$ are formed between pH 5 and 6. The ion that is prevalent from pH 5.2 and pH 8.8 is $Al(OH)_3$ and at pH of 9, $Al(OH)_4^{-}$ is predominant (Sharma, 2014). The large surface area of $Al(OH)_3$ is helpful in quick adsorption of the organic soluble compound and the colloidal particles are entrapped (Sharma, 2014). As a result, increase in colour removal and COD when the pH increased up to 7. Increasing the pH above 7 leads to a reduction of colour and COD removal as $Al(OH)_4^-$ which is produced is not involved in colour removal and COD reduction (Sharma 2014).

4.3 Effect of Inter-Electrode Distance (IED) on colour removal efficiency and Specific Energy Consumption(SEC)

The effect of inter-electrode distance (IED) on SEC and removal efficiency was determined, and the results are presented figure 4.6 and appendix 2.

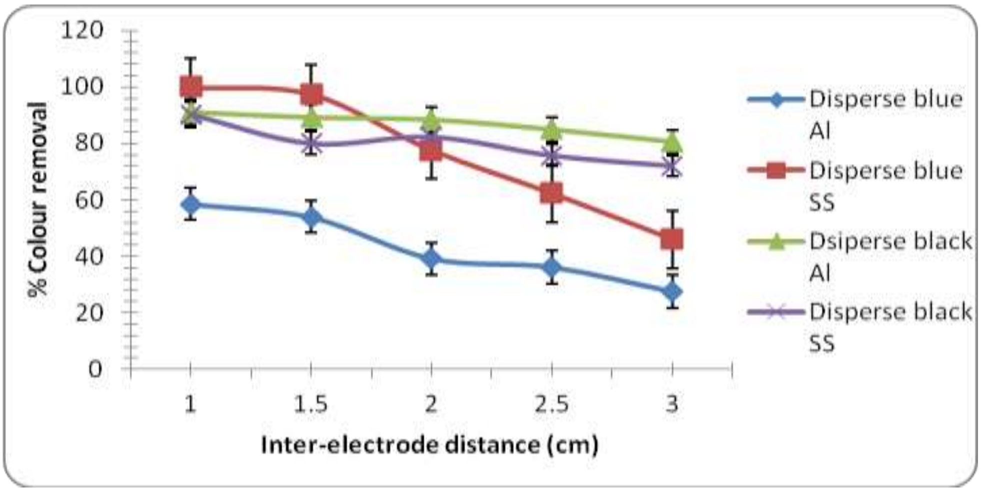


Figure 4.6: Effect of inter-electrode distance on colour removal efficiency

Increase of IED from 1-3cm led to decrease in colour removal efficiency of Al electrode disperse blue from 58.6% to 27.54% while SS electrode disperse blue decreased from 99.97 to 45.94%. The inter-electrode distance of 1cm produced the highest colour removal for all the runs. It was clear from the results that the greater the inter-electrode distances the lower the removal efficiency. Electrical resistance increased with the increase of inter-electrode distance leading to the low flow of current and less production of hydroxide ions resulting to decrease in colour removal. Consequently, high energy consumption as the electrocoagulation takes longer time (Figure 4.7).

The results are comparable to what was obtained by Deb and Majumdar, (2013) using aluminium electrodes to treat aqueous solution of Novacron Red C4B. When the IED was increased from 0.5 to 2cm dye removal decreased from 98.59 to 90.43% after 30 minutes contact time. The percentage COD and colour removal differed significantly with IED ($p<0.05$). However, SS disperse black electrodes did not differ significantly ($p=0.299$, $\alpha=0.05$). The SEC differed significantly with IED ($p<0.001$) except in disperse blue using SS electrodes which did not differ significantly ($p=0.472$) (Appendix 2). The 1cm IED gave the highest percentage colour removal in all the runs with the highest reduction recorded at 99.97±0.03% by SS disperse blue electrodes.

The electric resistance is directly proportional to distance, the shorter the distance the lower the resistance and consequently lowers specific energy consumption and cost of wastewater treatment. At a constant anodic surface area and conductivity of the solution, voltage drop increases with the increase of the IED. This is explained by variation in a voltage drop (ηIR) according to the equation (Sharma and Chopra 2017);

$$\eta IR = I.\frac{d}{s \times k} \quad \ldots\ldots (4.1)$$

Where,

I = current (A),

R= Resistance

d = distance between two electrodes (m),

S = active anode surface (m^2),

k = specific conductivity (10^3 mS/m).

The constant conductivity and anodic surface area increase inter-electrode distance resulting in an increase in a voltage drop (Equation 19). Furthermore, when the inter-electrode distance is increased leads to higher resistance of the current hence increasing specific energy consumption. The increase in electrode distance reduces ion interaction with hydroxide polymers (Nandi and Patel, 2017).

4.4 Effect of current density on SEC, Colour and COD removal

The effect of current density on removal efficiency was determined. The increase of current density from 15 to 47 A/m^2 increased the colour removal efficiency of SS disperse blue from 71.47 to 99.39% and Al disperse blue electrode from 58.73 to 69.39%. (Figure 4.8, Appendix 6)

In similar study Nandi and Patel 2017, using iron electrodes in removal of brilliant green dye from aqueous solution at optimum conditions of (0.1g/L initial dye concentration,0.2g/L NaCl support electrolyte, and IED 1cm) when the current density was varied from 13.9-34.7A/m^2 dye removal increased from76–96%. The present study gave a higher percentage removal of colour with the Stainless-Steel electrodes.

The efficiency of ion production at the anode and cathode increased with increase in current density, leading to an increase in flocs production. This conformed with Faraday’s law that current density increase causes an increase in the production of aluminium ions at the anode leading to increased efficiency of colour removal. High current density increases the number of oxidised metal ions, thus increasing the hydroxide flocs and pollutant removal (Krishna and Omprakash, 2013). The current increase led to density increase of the bubbles, making them smaller in size resulting to high removal of pollutants.

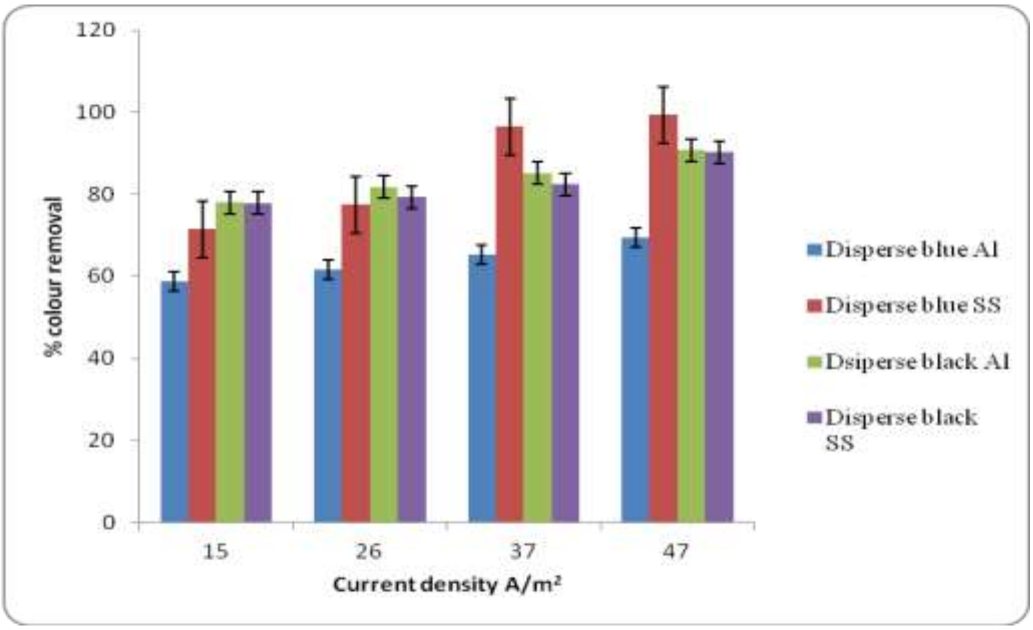


Figure 4.7: Effect of current density on colour removal

The SEC differed significantly with the current density (*p*<0.001) (Table 4.1). SEC increased with an increase in current density. COD and colour removal differed significantly with current density but disperse blue with aluminium electrode did not differ significantly (*p*=0.186). The current density of 47.22 A/m^2 produced the highest removal efficiencies. Thus was taken as the optimum current density. A supporting electrolyte of NaCl was added to regulate specific energy consumption at higher current densities.

Table 4.1: Effect of current density on SEC, colour and COD removal

Dye and Type of Electrode	Curr. density A/ m^2	%Colour Rem. Mean±SE	%COD Rem. Mean±SE	SEC, kWh/m^{-3}x 10^{-3} Mean±SE
Disperse	15.28	58.73±4.35	52.66±6.25	17.33±6.33
blue	26.25	61.72±3.27	62.83±1.88	62.83±1.88
Al	36.67	65.31±2.59	68.85±1.88	68.85±1.88
	47.22	69.39±0.45	78.75±2.04	78.75±2.04
p-value		**0.153**	**0.009**	**0.016**
Disperse	15.28	71.47±4.80^{a}	79.60±0.98	11.33±0.33
blue	26.25	77.49±1.86^{a}	80.97±1.43	19.60±0.70
SS	36.67	96.54±0.52^{b}	82.10±0.57	27.07±0.67
	47.22	99.39±0.42^{b}	84.40±2.17	34.23±0.23
P-Value		***0***	***0.186***	***<0.00***
	15.28	77.95±3.81	60.82±5.36a	11.00±0.58
Disperse	26.25	81.80±2.51	70.56±2.94ab	19.30±0.35
black	36.67	85.23±3.81	76.30±2.77b	27.40±0.58
Al	47.22	90.80±1.21	79.63±1.10b	34.33±0.88
p-value		***0.084***	***0.02***	***<0.00***
	15.28	77.93±0.14^{a}	62.38±1.78	11.33±9.89^{a}
Disperse	26.25	79.36±0.83^{a}	72.90±0.68	21.93±8.88^{b}
black	36.67	82.37±0.61^{b}	78.53±0.48	26.80±0.40^{b}
SS	47.22	90.21±0.18^{c}	86.57±0.43	34.53±0.53^{c}
p-value		***<0.00***	***<0.00***	***<0.00***

Mean value followed by same small letter (a,b) within the same column do not differ significantly from one another (One-way Anova, SNK test, α =0.05)

The current density is the most important parameter in controlling the reaction rate (Nasrullah *et al.*, 2014). Increasing current density increases the removal efficiency of COD, BOD, and suspended solids. Increasing the electrical power leads to immediate decay of electrodes thus reducing their lifespan. The Current drawn is directly proportional to the voltage input. A current density of 47 A/m^2 was adopted as an optimum during the EC processes in this research work due to its low specific energy consumption.

4.5 Effect of contact time on Colour and COD removal

The effect of contact time was investigated at a current density of 47A/m^2, 1cm IED, 0.2g/L sodium chloride support electrode and 0.1 g/L dye concentration. The COD and colour removal increased with the increase of contact time up to 25 minutes, above which it remained constant (Figure 4.9). When the contact time was changed from 5 to 30 min. the colour removal of disperse blue with aluminium electrodes increased from 25.1% to 62.34% which was the lowest recorded. With the same change of contact time, disperse blue with SS electrodes colour removal increased from 75.16% to 99.83% which was higher in terms of colour removal. In terms of COD removal disperse blue with SS increased from 26 to 78% when contact time increased from 5 to 30 minutes (Figure 4.10). The 25 mins electrolysis time produced maximum colour removal for all runs. This was taken as the optimum operating contact time.

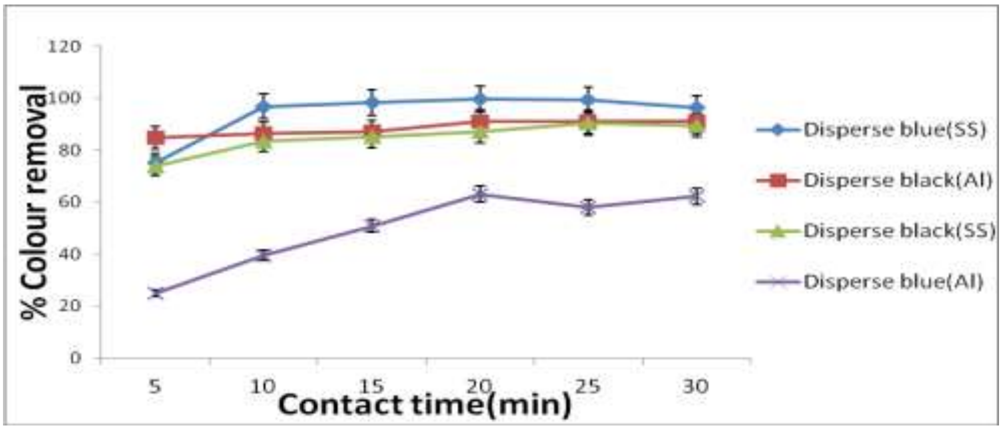


Figure 4.8: Effect of contact time on colour removal efficiency

The results are in line with the study carried out on the impact of current density, operating time and pH on textile wastewater treatment by electrocoagulation process by Hossain *et al*., (2013). They observed that changing the contact time from 10 to 50 min the removal efficiency of turbidity and COD increases from 45.21% to 96.88%, and 23.97% to 79.86% respectively. In explaining the observation, they stated that EC is a two-stage process involving destabilization and aggregation.

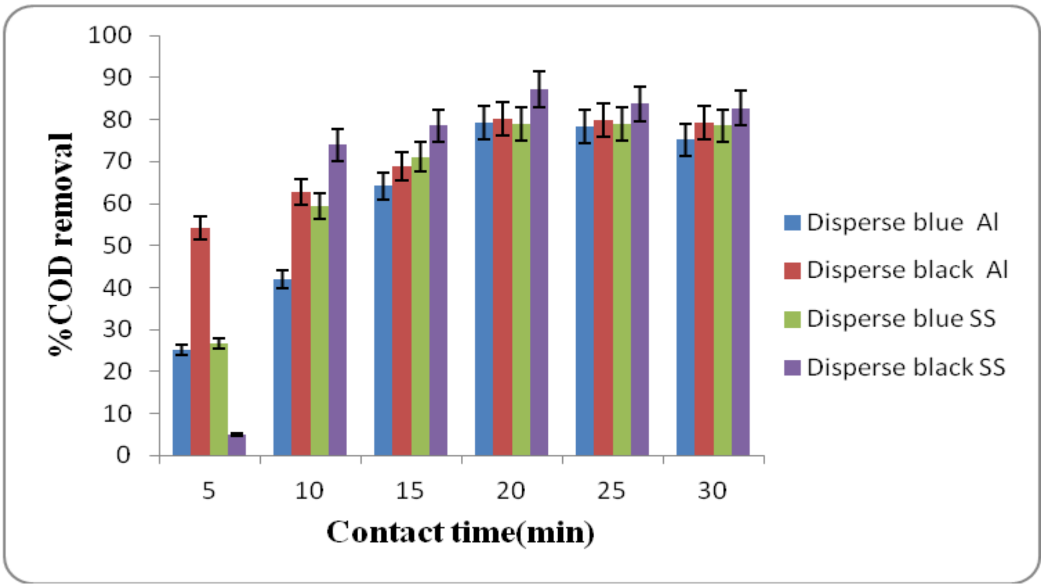


Figure 4.9: Effect of contact time on COD removal

The destabilization stage takes a shorter time whereas the aggregation stage takes longer time. Electrochemical reactions at the anode produce metallic ions which are agents of destabilization. Therefore, if contact time is shortened there will be slow charge loading. This results to low metal ions which are insufficient for the destabilization process of colloidal particles. The maximum removal was obtained at 20 minutes contact time beyond which no significant effect on colour removal efficiency. The specific energy consumption, percentage colour and COD removal differed significantly with contact time (p<0.001) (Appendix 3).

4.6 Effect of support electrolyte (SE) concentration on Electrocoagulation

Sodium chloride was added at different levels and its effect on colour removal investigated. The results obtained shows that increasing the amount of SE from 0.1 to 0.4g/L increased the colour removal efficiency of disperse blue with SS from 42.79% to 90.38%. Specific energy consumption (SEC) decreased from 41.97x10^{-3} to 8.72 x10^{-3} kWh/m^{-3} when SE was increased from 0.1 to 0.4g/L (Figure 4.12, figure 4.13).

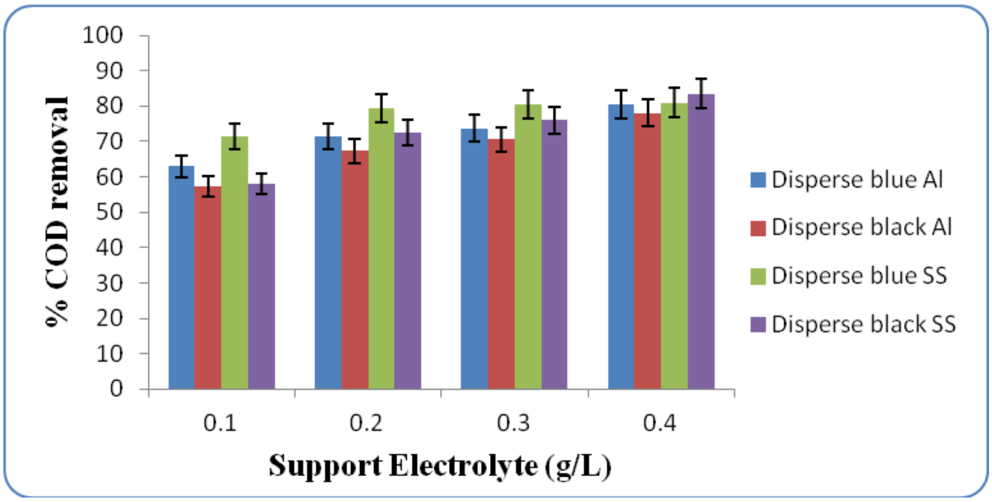


Figure 4.10: Effect of support electrolyte on COD removal

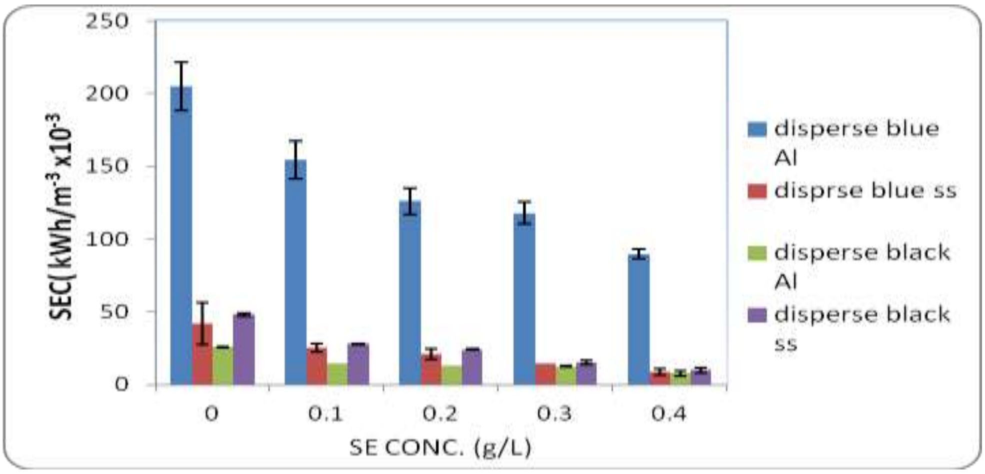


Figure 4.11: Effect of supporting electrolyte (SE) on specific energy consumption (SEC)

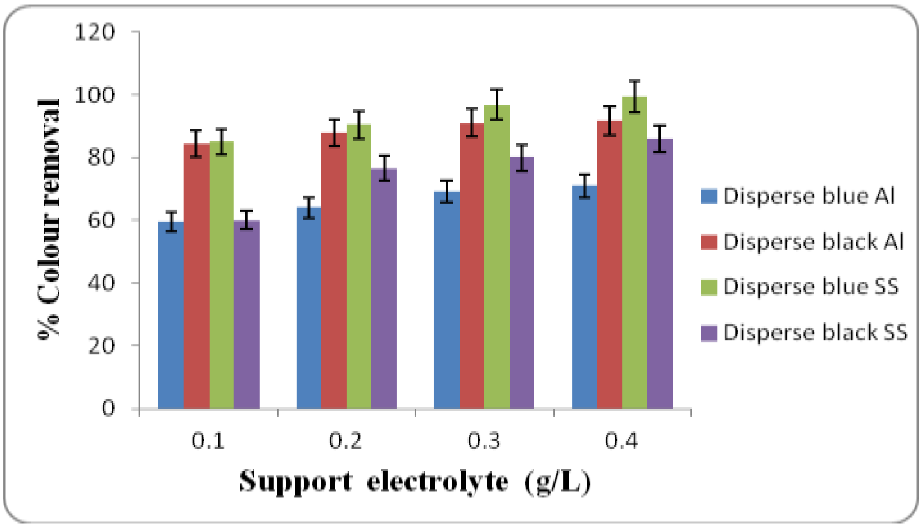


Figure 4.12: Effect of support electrolyte on colour removal

The addition of NaCl increased the conductivity of wastewater from 969µS/cm to 3999µS/cm (Appendix 5) and decreases the resistance between the anode and the cathode. This then leads to decrease of both voltage and specific energy consumption. These results were in agreement with the experimental findings of Nandi and Patel (2017) that involved the determination of energy consumption and dye removal from wastewater. The results indicated that there was a drastic improvement of conductivity of solution from 0.38 to 1.94mS when the NaCl concentration was increased from 0.1g/L to 1 g/L. Eventually, this led to reduction of cell voltage from 21.5 to 3.9 V and decrease in specific electrical energy consumption from 17.15 to 3.11 kW h/kg Fe. They also noted that percentage of dye removal at the contact time of 30min. increased slightly.

The presence of Sodium chloride; in the solution was explained by Maghanga *et al*., (2017) that leads to formation of hypochlorite ion at the anode as shown in equations

$2Cl^- (aq) \rightarrow Cl_2 (g) + 2e$………………………………………………… (4.2)

$Cl_2 (g) + H_2O (l) \rightarrow HOCl (aq) + H^+ (aq) + Cl^-(aq)$……………………….. (4.3)

$HOCl (aq) \rightarrow H^+ (aq) + OCl^-(aq)$………………………………………….. (4.4)

The hypochlorite ion increases dye removal by oxidation of the dye molecules as shown in equations 5 and 6. The electrochemical oxygen transfer reaction between an organic compound R and the hydroxyl radicals takes place close to the anode's surface (Maghanga *et al*., 2017):

$R+M (OH) n/_2(aq) \rightarrow M+CO_2 (g) +n/2H+ (aq) +n/2e-$ ……………….. (4.5)

$M (OH) (aq) \rightarrow M+1/2 O_2 (g) + H^+ (aq) + e$……………………............... (4.6)

From one-way ANOVA (Appendix 5) the percentage colour removal and COD differed significantly with the support electrolyte ($p<0.05$). Increasing the concentration of the supporting electrolyte (NaCl) above 0.2g/L led to a slight decrease in percentage colour removal. SEC decreased significantly with an increase of SE. 0.2 g/L concentration of SE, this was taken as the optimum level for the process operation.

4.7 Effect electrode type on colour and COD removal

To investigate the performance of the electrode 10 tests in each category were selected at random and their mean and standard deviation of percentage colour removal compared (Figure.4.9).

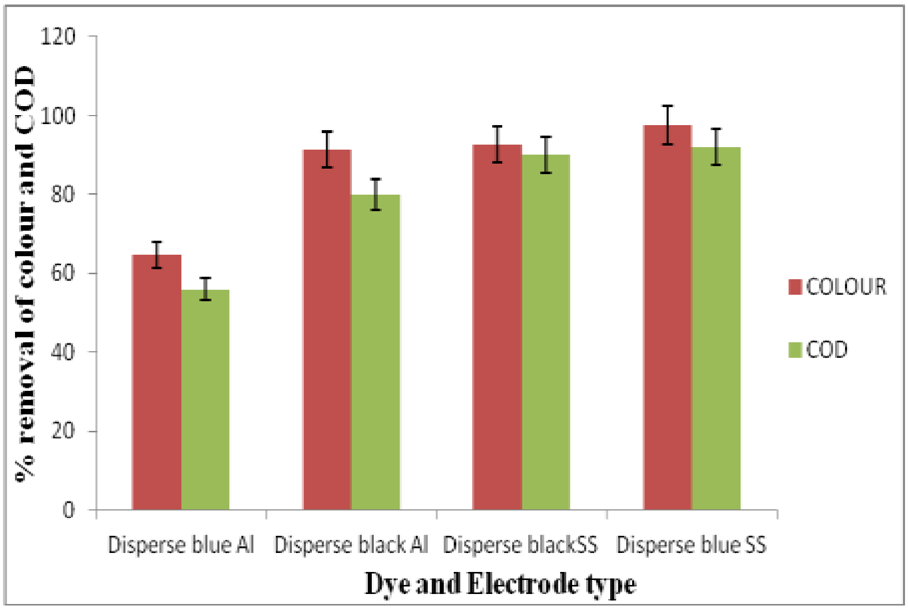


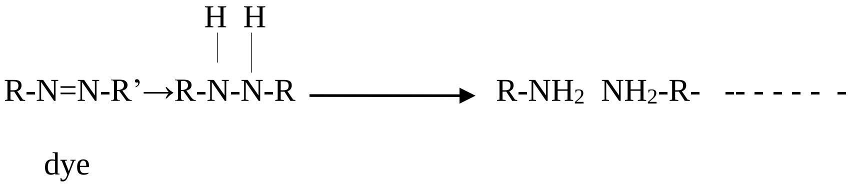
Figure 4.13: Effect electrode type on colour and COD removal

From the results, SS disperse blue electrodes produced highest percentage colour removal of 97.46% at optimum conditions. Disperse black with SS electrodes and disperse black with Al electrodes produced 92.7 and 91.24% colour removal respectively. Disperse blue with Al had the least performance in terms of colour removal of 64.80%. From these findings, it is evident that the choice of the electrode plays a great role in colour removal. The SS electrode was found to be a better electrode than Al electrodes.

Stainless steel was found to be more effective than Al for the dye wastewater treatment. SS is an alloy of chromium, silicon, molybdenum, aluminium, nickel and carbon, with iron, carbon and Chromium being the main components (Nasrullah *et al.*, 2014).

It was observed that using SS electrodes, the colourless solution turned green after 10 minutes of electrolysis and on further electrolysis. The green colour was as a result of Fe^{2+} ions which was then oxidised to Fe^{3+} (brown colour) on further electrocoagulation. However, this did not affect much on the outcome since it happened towards the end of the process. The low performance of Al electrodes with disperse blue dye was contributed by a thick white sludge which formed at above 15 minutes contact time. This was due to fact that aluminium electrode was eroded and formed a trivalent aluminium ($Al^{3+)}$. The (Al^{3+}) formed an ionic pair with the pollutant (dye) of wastewater. There was of a strong coagulant formed. An excellent flocculation and coagulation was observed. (Ismael *et.al.*, 2019)

Process of degradation and removal according to



$$\underset{\text{dye}}{R\text{-}N{=}N\text{-}R'} \rightarrow R\text{-}\overset{H}{\underset{}{N}}\text{-}\overset{H}{N}\text{-}R \longrightarrow R\text{-}NH_2\ \ NH_2\text{-}R\text{-}\ \text{------ -}\ (4.7)$$

The Fe(OH)n(s) remains in the aqueous phase as a gelatinous suspension, which can remove the pollutants from the wastewater by either complexation or by electrostatic attraction followed by coagulation. In the surface complexation mode, the pollutant acts as a ligand (L) to chemically bind hydrous iron (Kabdasli *et.al.,*2012)

$L\text{-}H_{(aq)} + (OH)OFe_{(S)} \rightarrow L\text{-}OFe(s) + H_2O_{(l)}$----------------------------(4.8)

L represents the dye being removed from the solution.

4.8 Operating cost

After optimization of the conditions (current density 47.22A/m^2, IED 1cm, SE 0.2g/L, 0.1 g/L dye concentration and 20 minutes of contact time) the operation cost was determined. Disperse blue SS electrodes were found to be better than Al electrodes which produced the highest colour removal of 99.83% while the Al electrodes had a lower colour removal at 64.80%.

The electrical energy was calculated using the equation: -

$$\text{Electrical Energy} = \frac{\text{V I t}}{\text{volume}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4.9)}$$

$(12\text{V}\times 0.06\text{A}\times 0.333\text{h})/0.1 = 2.3976\text{Kwh/m}^3$

Calculation of the electrode wears equation 15

$$\text{Mass of SS} = \frac{\text{I t M}}{\text{z F}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4.10)}$$

$$\frac{0.06\text{x}1200\text{x}56}{2\text{x}96500\text{x}0.01} = 2.089\text{g}$$

2.089/1000=0.002089Kg

Operating cost= **a** C_{energy} + **b** $C_{\text{electrode}}$ …………………………………………… (4.11)

a and **b** are the cost of electricity (kWh/m^3) and cost of electrode per Kg respectively according to the market price as at October 2017.

Operating cost for SS = 21.00 x 2.3976 + 100x0.002089 = 50.56KES/m^3

For aluminium operating cost= 21 x2.3976+150 x 0.000671= 50.55KES/m^3.

4.9 Physico- chemical parameters

The following selected physico-chemical parameters were determined for both raw and electrochemically treated dye water (Table 4.5).

Table 4.2: Physico-chemical parameters (±SE) of raw and electrochemically treated dye water

Parameter	**Raw disperse blue n=10**	**EC Treated disperse blue n=10**	**Raw disperse black n=10**	**EC Treated disperse black n=10**	**NEMA Standards discharge**	**% removal**
COD (mg/L)	480.00 ±20.00	180.00± 2.00	420.00±15.00	90.00± 7.22	50.00	81.25
pH	6.81± 2.00	8.76± 0.80	7.95±2.21	8.56± 2.00	6.5-9.0	*
Conductivity (µS/cm)	141.40 ±10.10	82.00±12.0	26.80±8.11	15.00± 2.50	*	89.36
Turbidity (FNU)	6.81± 4.12	2.00± 0.50	6.12±2.20	0.8±0.25	8-10	88.25

From table 4.2 the highest COD level for the raw sample was observed to be 480.00 mg/L and the lowest at 420.00 mg/L. After treatment, the values of the COD were decreased to 180.00 mg/L and 90.00 mg/L for disperse blue and disperse black respectively. This is within the permissible limits of NEMA of 50 mg/L COD. The pH, conductivity and turbidity were also reduced to disposable level (Mundial, 2007). COD was reduced by 81%, conductivity by 89% and turbidity by 88%.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusion were drawn from the results

i. Increasing current density and contact time significantly increased the removal of colour and COD. Increase in current density increased both COD and colour removal. When current density was increased from 15 to 47 A/m^2 the colour removal increased from71 to 99 % for the case of disperse blue with SS. Increase in contact time 5- 20min. caused increase in colour and COD removal from below 50 to 98 and 78 % respectively for disperse blue with SS.

ii. When inter-electrode distance and dye concentration was increased the colour and COD removal declined significantly. As the IED decreased from 3-1cm the percentage removal of colour increased from 45 % to 99% for the case of disperse blue with SS.

iii. Addition of sodium chloride enhanced the electrocoagulation process. Addition of NaCl from 0.0 - 0.4g enhanced colour removal from 15 to 80% for disperses black with SS.

iv. Under optimum operating conditions (current density 47.2 A/m^2, Inter-electrode distance 1cm, SE 0.2 g/L, 0.1 g/L dye concentration and 25 minutes contact time) the performance of stainless steel on removal of colour recorded the highest removal at 97% compared to that of aluminium of 90 %.

v. On physio-chemical parameters where reduced to NEMA disposable levels making it possible for treated water fit for re-use. COD was reduced by 81%, conductivity by 89% and turbidity by 88%.

vi. Operating cost was evaluated by adding cost of electrode per Kg at the market price and the cost of electricity per (kWh/m^3) for SS= 50.56 KES/m^3 and Al =50.55 KES/$m^{3.}$ This confirms the viability and a cost-effective process.

5.2 Recommendations

The following are recommended from this research and for further research:

i. Electrocoagulation as an alternative technology is unable to remove infinitely soluble matter this method can be combined with filtration.

ii. After electrocoagulation by Aluminium and stainless electrode and a support electrolyte residual aluminium and iron and also chlorinated organic are present. It's therefore important to carry out toxicity assessment on the effluents before re-use.

iii. The system can still be operated by alternative source of power like solar and wind this can drastically reduce the running cost.

However, to improve the performance of EC process, the following further studies are necessary:

i. The study of the effect of geometry and shape of the electrodes, so that can enhance the conductivity of the cell and reduce energy consumptions.

ii. In order to reduce the problem of passivation film rotating electrodes can be used. This will enhance electrolyte homogeneity and increase floc generation

iii. Electrocoagulation mechanism process of chemo-adsorption or physio-adsorption in respect to removal of dye.

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APPENDICES

APPENDIX I: Effect of pH on SEC, COD and colour removal efficiency

Dye and Type of Electrode	**pH**	**%Colour Rem. Mean±SE**	**%COD Rem. Mean±SE**	**kWh/m-3x 10^{-3} Mean±SE**
Disperse	2	61.27 ± 0.50^{a}	60.00 ± 0.11^{a}	1130.61 ± 21.99^{d}
Blue	4	70.12 ± 0.88^{c}	80.46 ± 0.96^{e}	536.18 ± 10.62^{a}
Al	6	69.24 ± 0.45^{c}	75.78 ± 0.35^{d}	647.10 ± 11.81^{b}
	7	66.52 ± 0.41^{b}	73.66 ± 0.26^{c}	916.20 ± 20.57^{c}
	8	66.49 ± 0.78^{b}	70.00 ± 0.63^{b}	922.31 ± 41.10^{c}
	10	61.92 ± 0.53^{a}	60.46 ± 0.67^{a}	1116.78 ± 12.57^{d}
p- value		***<0.00***	***<0.00***	***<0.00***
Disperse	2	90.00 ± 0.08^{a}	77.00±.079	12.58 ± 0.00^{c}
Blue	4	97.22 ± 1.04^{c}	79.00±0.93	8.89 ± 0.26^{b}
SS	6	96.29 ± 0.24^{b}	77.53±1.17	8.33 ± 1.03^{b}
	7	99.92 ± 0.07^{d}	80.85±0.35	6.14 ± 0.30^{a}
	8	99.29 ± 0.48^{d}	80.00±1.67	8.82 ± 0.60^{b}
	10	99.12 ± 0.02^{d}	82.00±1.09	12.62 ± 0.15^{c}
p –Value		***<0.00***	***0.045***	***<0.00***
Disperse	2	81.93 ± 1.06^{a}	75.58 ± 1.65^{b}	26.41 ± 0.34^{c}
Black	4	91.77 ± 0.54^{b}	77.70 ± 1.32^{b}	17.31 ± 0.17^{a}
Al	6	90.00 ± 0.28^{b}	78.00 ± 0.63^{b}	24.38 ± 0.67^{b}
	7	90.39 ± 0.45^{b}	74.13 ± 1.53^{ab}	25.73 ± 0.19^{bc}
	8	90.10 ± 0.73^{b}	77.50 ± 1.59^{b}	28.32 ± 0.20^{d}
	10	90.01 ± 0.23^{b}	70.20 ± 1.11^{a}	48.83 ± 1.03^{e}
p- value		***<0.00***	***0.011***	***<0.00***
Disperse	2	70.14 ± 0.62^{a}	60.55 ± 0.66^{a}	24.70 ± 0.53^{d}
Black	4	90.30 ± 1.07^{d}	72.52 ± 1.46^{b}	8.90 ± 0.20^{a}
SS	6	90.14 ± 0.65^{d}	71.02 ± 1.67^{b}	11.01 ± 0.15^{b}
	7	90.17 ± 0.59^{d}	68.57 ± 0.56^{b}	10.39 ± 0.14^{b}
	8	80.22 ± 0.47^{b}	71.01 ± 1.88^{b}	14.03 ± 0.18^{c}
	10	85.20 ± 0.62^{c}	68.22 ± 1.39^{b}	10.56 ± 0.11^{b}
p- value		***<0.00***	***0.001***	***<0.00***

Mean value followed by same small letter (a, b) within the same column do not differ significantly from one another (One-way ANOVA, SNK test, α =0.05)

APPENDIX II: Effect of inter-electrode distance on SEC, COD and colour removal efficiency

Dye and Type of Electrode	IED (cm)	%Colour Rem. Mean±SE	%COD Rem. Mean±SE	kWh/m-3x 10^{-3} Mean±SE
Disperse	1	58.60 ± 4.02^{c}	63.45±6.52	64.14 ± 3.66^{a}
Blue	1.5	53.97 ± 3.07^{c}	57.21±6..72	81.03 ± 10.19^{a}
Al	2	39.23 ± 3.22^{b}	47.80±1.06	188.00 ± 21.71^{a}
	2.5	36.19 ± 2.48^{ab}	46.93±0.64	280.00 ± 40.00^{a}
	3	27.54 ± 0.35^{a}	44.43±0.23	1200.00 ± 200.00^{b}
p-value		***0***	***0.045***	***0***
Disperse	1	99.97±0.03	77.58±6.19	10.16±0.66
blue	1.5	97.46±0.39	70.54±10.14	10.12±0.52
SS	2	77.58±0.48	80.31±0.50	10.87±0.03
	2.5	62.27±0.39	80.31±2.51	39.78±29.41
	3	45.94±0.28	56.83±1.97	12.77±0.26
P-Value		***0***	***0.061***	***0.472***
	1	91.06 ± 0.55^{c}	81.20 ± 1.52^{c}	8.50 ± 0.00^{a}
Disperse	1.5	89.21 ± 0.42^{bc}	80.11 ± 0.12^{c}	9.24 ± 0.76^{a}
black	2	88.47 ± 1.86^{bc}	78.45 ± 0.37^{c}	11.66 ± 0.83^{b}
Al	2.5	84.98 ± 1.89^{ab}	75.50 ± 0.54^{b}	11.66 ± 0.83^{b}
	3	80.62 ± 1.43^{a}	70.22 ± 1.13^{a}	14.13 ± 0.34^{b}
p-value		***0.002***	***0***	***0.001***
	1	90.29±0.10	86.77±0.49	107.47±1.35
Disperse	1.5	80.04±4.90	82.13±0.66	234.81±20.73
black	2	82.41±0.58	81.42±0.33	276.10±3.38
SS	2.5	75.74±3.10	74.18±0.48	349.74±13.83
	3	72.03±5.92	71.52±0.48	396.64±7.31
p-value		***0.049***	***0.299***	***0***

APPENDIX III: Effect of contact time on SEC, colour and COD removal

Dye and Type of Electrode	Contact time Min	%Colour Rem. Mean±SE	%COD Rem. Mean±SE	kWh/m-3x 10^{-3} Mean±SE
Disperse	5	25.10± 2.41^{a}	25.25±2.90a	8.75±0.20
blue	10	39.49±4.42^{b}	41.99±5.90b	18.13±0.77
Al	15	50.89±3.11^{c}	64.14±5.01c	26.56±0.67
	20	63.19±0.181^{c}	79.13±0.97c	32.86±1.99
	25	58.19±4.08^{c}	78.41±1.71c	37.10±0.35
	30	62.34±0.32^{c}	75.18±5.0c	40.17±0.42
p-value		<0.00	<0.00	<0.00
Disperse	5	75.16±1.22^{a}	26.68±3.43^{a}	8.47± 0.12^{a}
blue	10	96.78±0.56b^{c}	59.39±1.96^{b}	15.73±1.27^{b}
SS	15	98.49±0.10b^{cd}	71.06±0.18^{c}	21.73±1.22^{c}
	20	99.82±0.24^{d}	78.89±0.42^{d}	31.16±2.83^{d}
	25	99.33±0.38c^{d}	78.89±0.65^{d}	36.63±0.07^{e}
	30	96.28±0.94^{bc}	78.52±1.63^{d}	37.93±0.18^{e}
P-Value		<0.00	<0.00	<0.00
	5	84.81±0.76^{a}	54.18±1.37^{a}	8.76±0.18^{a}
Disperse	10	86.37±0.18^{b}	62.80±1.26^{b}	15.33±2.19^{b}
black	15	87.11±0.17^{b}	68.86±0.62^{c}	26.47±0.58^{c}
Al	20	91.08±0.31^{c}	80.22±0.13^{d}	32.13±2.92^{d}
	25	90.96±0.45^{c}	79.92±0.41^{d}	38.47±0.26^{e}
	30	91.03±0.43^{c}	79.37±0.38^{d}	40.67±0.44^{e}
p-value		<0.00	<0.00	<0.00
	5	73.93 ± 6.87	4.96±7.59^{a}	8.54±0.00
Disperse	10	83.64± 2.6	73.93±6.87^{b}	17.80±080
black	15	85.15± 4.98	78.53±48^{bc}	17.80±0.76
SS	20	90.31± 0.06	87.14±0.04^{c}	31.37±1.43
	25	87.19±3.49	83.75±2.78^{c}	34.33±0.33
	30	89.49±0.67	82.77±1.39^{c}	38.00±0.65
p-value		<0.00	<0.00	<0.00

Mean value followed by same small letter (a, b) within the same column do not differ significantly from one another (One-way ANOVA, SNK test, α =0.05).

APPENDIX IV: Effect of dye concentration on %colour removal, % COD removal and SEC

Dye and Type of Electrode	Dye Conc. g/L	%Colour Rem. Mean ± SE	%COD Rem. Mean ± SE	kWh/m^{-3} (x 10^{-3}) Mean ± SE
Disperse	0.1	68.00 ± 2.34^{c}	50.00±4.57	673.27±138.93
Blue	0.2	58.04 ± 3.66^{bc}	45.00±2.98	2.26±44.12
Al	0.3	52.50 ± 3.03^{ab}	42.30±2.99	2.91±73.37
	0.4	54.23 ± 3.44^{a}	48.00±4.26	3.65±73.79
p- value		<0.004	0.526	<0.00
Disperse	0.1	90.67 ± 1.11^{c}	70.21 ± 5.83^{b}	134.81 ± 7.99^{a}
Blue	0.2	91.53 ± 1.12^{c}	70.53 ± 5.61^{b}	168.40 ± 5.67^{b}
SS	0.3	67.24 ± 1.30^{b}	44.10 ± 5.34^{a}	174.49 ± 2.24^{b}
	0.4	54.23 ± 3.99^{a}	30.03 ± 3.56^{a}	206.61 ± 3.08^{c}
p –Value		<0.00	<0.001	<0.00
Disperse	0.1	92.01±2.91	75.55 ± 3.74^{c}	48.00±0.19
Black	0.2	88.00±5.88	52.00 ± 6.77^{b}	52.17±0.19
Al	0.3	88.00±5.12	52.00 ± 4.72^{b}	62.22±0.22
	0.4	78.00±5.12	30.25 ± 2.40^{a}	70.66±0.36
p- value		0.206	0.001	<0.00
Disperse	0.1	99.99 ± 0.00^{b}	76.00±1.76	112.05±3.32
Black	0.2	99.97 ± 0.19^{b}	72.11±1.50	128.73±0.35
SS	0.3	91.00 ± 1.35^{a}	69.10±2.06	138±2.00
	0.4	90.11 ± 2.86^{a}	72.20±2.51	152.84±0.85
p- value		0.003	0.183	<0.00

Mean value followed by same small letter (a, b) within the same column do not differ significantly from one another (One-way ANOVA, SNK test, α =0.05).

APPENDIX V: Effect of supporting electrolyte (SE) concentration on SEC, COD and colour removal efficiency

Dye and Type of Electrode	SE g/L	%Colour Rem. Mean±SE	%COD Rem. Mean±SE	kWh/m^{-3}x 10^{-3} Mean±SE
Disperse	0.1	69.38 ± 0.36^{bc}	62.96 ± 2.02^{ab}	154.51 ± 13.17^{b}
Blue	0.2	71.07 ± 2.00^{c}	73.78 ± 3.67^{bc}	126.07 ± 8.90^{ab}
Al	0.3	64.15 ± 2.66^{abc}	71.54 ± 1.28^{bc}	117.97 ± 7.44^{ab}
	0.4	59.56 ± 2.32^{ab}	80.60 ± 0.52^{c}	89.87 ± 2.96^{ab}
p- value		***0.016***	***0.001***	***<0.00***
Disperse	0.1	84.96 ± 12.39^{b}	71.38 ± 6.05^{b}	25.25 ± 3.03^{ab}
Blue	0.2	96.79 ± 3.21^{b}	81.00 ± 2.72^{b}	21.31 ± 3.52^{ab}
SS	0.3	99.37 ± 0.38^{b}	80.42 ± 1.22^{b}	14.64 ± 0.32^{ab}
	0.4	90.38 ± 5.64^{b}	79.52 ± 4.69^{b}	8.72 ± 2.15^{a}
p -Value		***0.001***	***0.009***	***0.056***
Disperse	0.1	84.53±3.23	57.20 ± 4.59^{ab}	14.79 ± 0.19^{b}
Black	0.2	91.80±0.83	67.37 ± 3.63^{bc}	13.36 ± 0.07^{b}
Al	0.3	87.80±0.83	78.13 ± 0.09^{c}	12.68 ± 0.25^{b}
	0.4	91.10±0.98	70.56 ± 5.93^{bc}	7.90 ± 1.84^{a}
p- value		***0.054***	***0.002***	***<0.00***
Disperse	0.1	60.19 ± 5.75^{b}	58.05 ± 3.95^{b}	28.04 ± 0.63^{d}
Black	0.2	85.95 ± 4.11^{c}	76.09 ± 2.07^{bc}	24.11 ± 0.27^{c}
SS	0.3	76.63 ± 8.92^{bc}	72.59 ± 6.31^{bc}	15.15 ± 1.45^{b}
	0.4	80.04 ± 5.34^{bc}	83.46 ± 3.67^{c}	10.09 ± 1.87^{a}
p- value		***<0.00***	***0.002***	***<0.00***

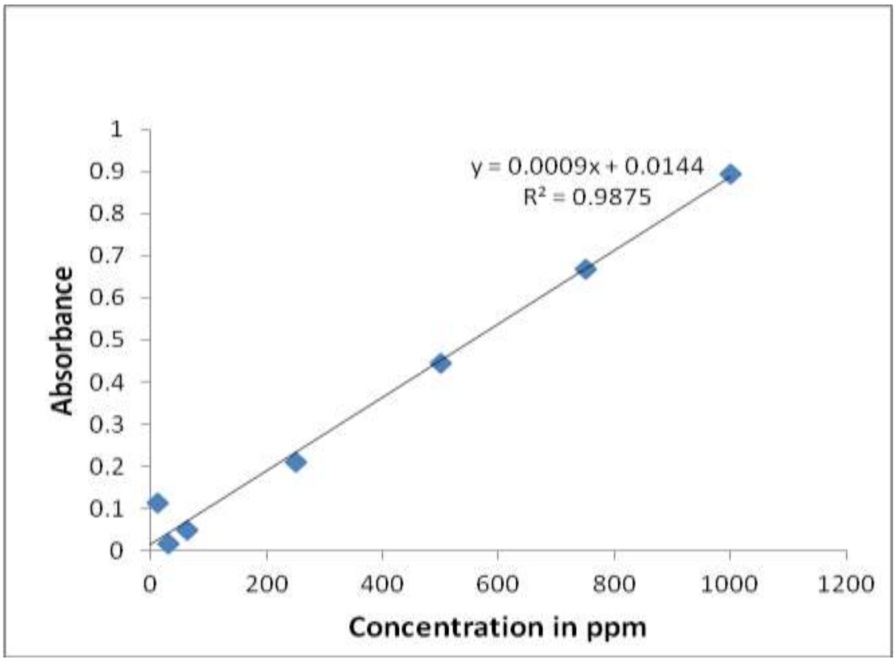
Mean value followed by same small letter within the same column do not differ significantly from one another (One-way ANOVA, SNK test, α =0.05).

APPENDIX VI: Effect of current density on SEC, colour and COD removal

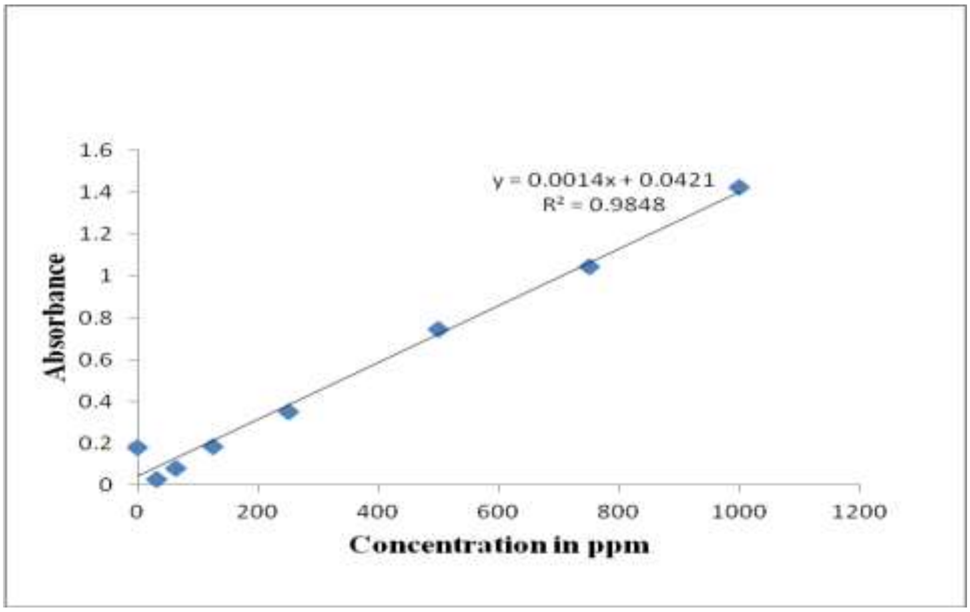
Dye and Type of Electrode	Curr. Density A/ m^{2}	%Colour Rem. Mean±SE	%COD Rem. Mean±SE	SEC, kWh/m-3x 10^{-3} Mean±SE
Disperse	15.28	58.73±4.35	52.66±6.25	17.33±6.33
Blue	26.25	61.72±3.27	62.83±1.88	62.83±1.88
Al	36.67	65.31±2.59	68.85±1.88	68.85±1.88
	47.22	69.39±0.45	78.75±2.04	78.75±2.04
p-value		***0.153***	***0.009***	***0.016***
Disperse	15.28	71.47±4.80^{a}	79.60±0.98	11.33±0.33
Blue	26.25	77.49±1.86^{a}	80.97±1.43	19.60±0.70
SS	36.67	96.54±0.52^{b}	82.10±0.57	27.07±0.67
	47.22	99.39±0.42^{b}	84.40±2.17	34.23±0.23
P-Value		***<0.00***	***0.186***	***<0.00***
	15.28	77.95±3.81	60.82±5.36a	11.00±0.58
Disperse	26.25	81.80±2.51	70.56±2.94ab	19.30±0.35
Black	36.67	85.23±3.81	76.30±2.77b	27.40±0.58
Al	47.22	90.80±1.21	79.63±1.10b	34.33±0.88
p-value		***0.084***	***0.02***	***<0.00***
	15.28	77.93±0.14^{a}	62.38±1.78	11.33±9.89^{a}
Disperse	26.25	79.36±0.83^{a}	72.90±0.68	21.93±8.88^{b}
Black	36.67	82.37±0.61^{b}	78.53±0.48	26.80±0.40^{b}
SS	47.22	90.21±0.18^{c}	86.57±0.43	34.53±0.53^{c}
p-value		***<0.00***	***<0.00***	***<0.00***

Mean value followed by same small letter (a,b) within the same column do not differ significantly from one another (One-way ANOVA, SNK test, α =0.05).

APPENDIX VII: CALIBRATION CURVES

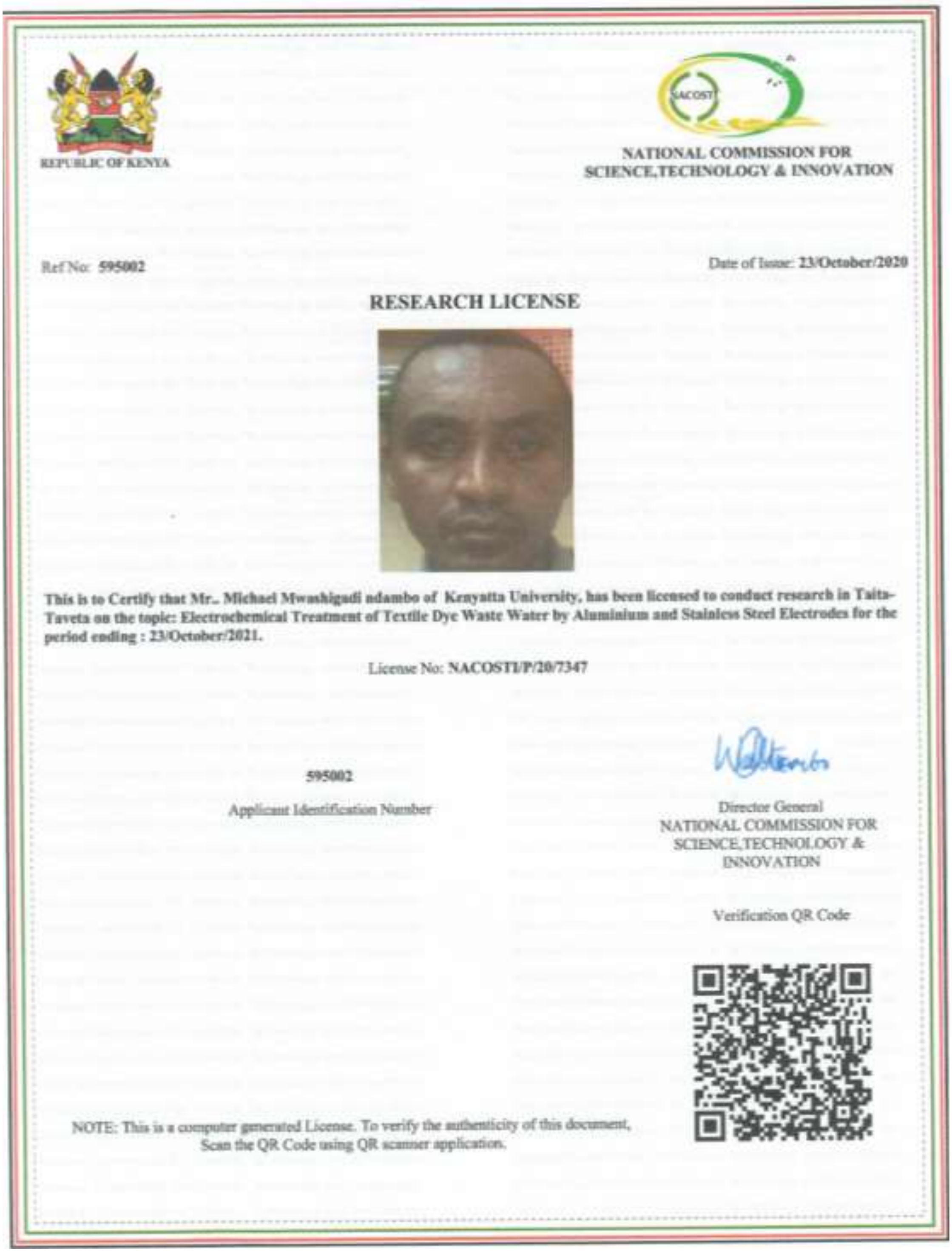


a)Calibration curve of absorbance against the concentration of disperse blue dye



b) Calibration curve of absorbance against the concentration of disperse black dye

APPENDIX VIII: Research Licence



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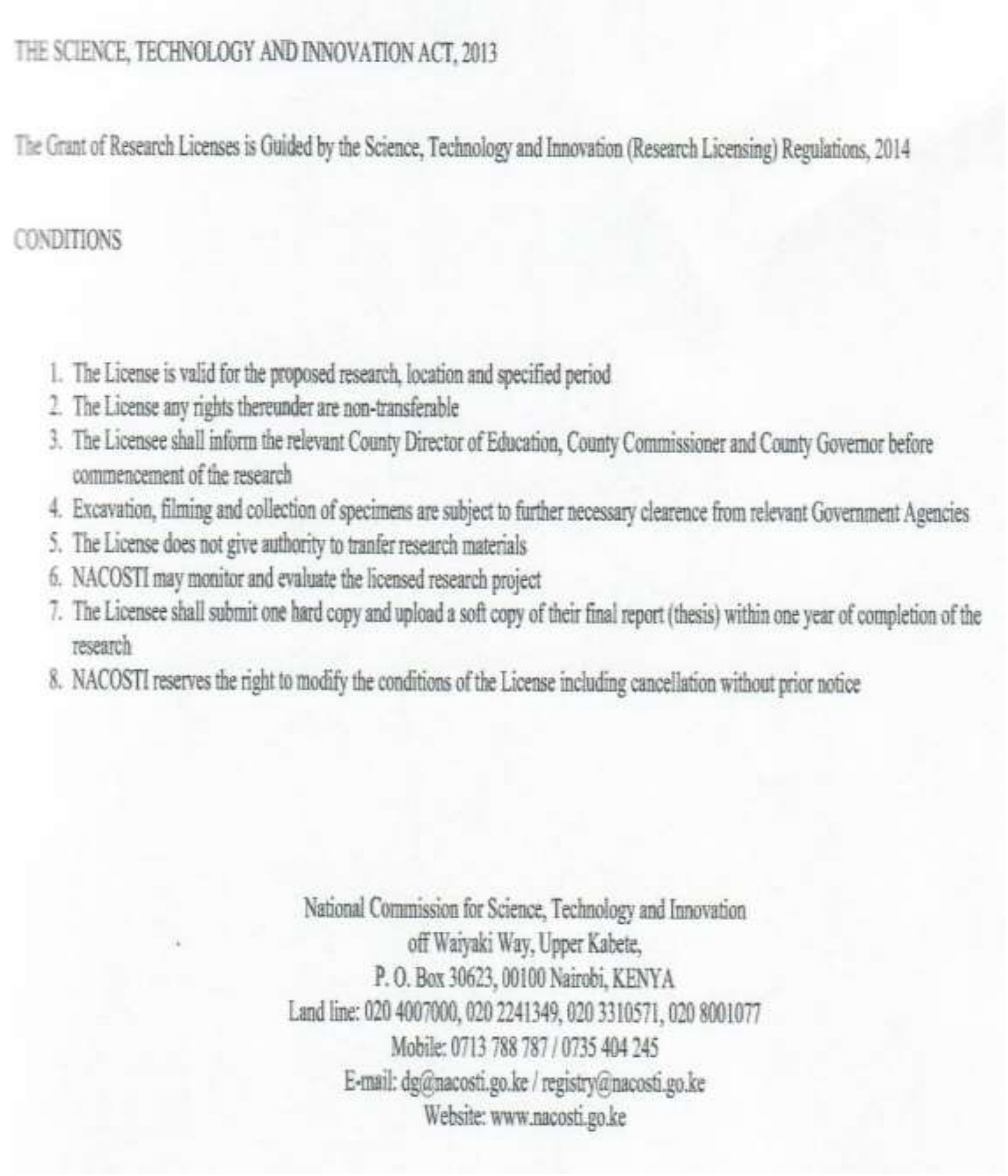

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