TALLINN UNIVERSITY OF TECHNOLOGY

SCHOOL OF ENGINEERING

Department of Materials and Environmental Technology

OXIDATION OF ACID ORANGE 7 AND INDIGOTETRASULFONATE TEXTILE DYES WITH PULSED CORONA DISCHARGE: IMPACT OF TREATMENT CONDITIONS

TEKSTIILVÄRVIDE HAPPEORANŽ 7 NING INDIGOTETRASULFONAADI OKSÜDEERIMINE IMPULSS-KOROONA ELEKTRILAHENDUSEGA: TÖÖTLEMISE TINGIMUSTE MÕJU

MASTER THESIS

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Tallinn, 2020

AUTHOR’S DECLARATION

Hereby I declare, that I have written this thesis independently.

No academic degree has been applied for based on this material. All works, major viewpoints and data of the other authors used in this thesis have been referenced.

“26” May 2020

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Accepted for defence

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THESIS TASK

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Study programme, KAYM, Materials and Process of Sustainable Energetics

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Thesis topic:

(in English) Oxidation of acid orange 7 and indigotetrasulfonate textile dyes with pulsed corona discharge: impact of treatment conditions.

(in Estonian) Tekstiilvärvide happeoranž 7 ning indigotetrasulfonaadi oksüdeerimine impulss-koroona elektrilahendusega: töötlemise tingimuste mõju.

Thesis objective:

Establishing impacts of operation conditions of pulsed corona discharge (PCD) treatment on the energy efficiency of oxidation of textile dyes, aqueous acid orange 7 (AO7) and indigotetrasulphonate. Operation conditions include pulse repetition frequency, solution electric conductivity, temperature and admixtures of a surfactant.

Thesis tasks and time schedule:

No	**Task description**	**Deadline**
1.	Acquiring skills in PCD operation, preparation for experiments and techniques of analyses	16.03.2020
2.	Fulfilling the experimental program	30.04.2020
3.	Writing and submitting the thesis	27.05.2020

Language: English **Deadline for submission of thesis:** May 27, 2020

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PREFACE

This research was carried out at the Laboratory of Environmental Technology, Department of Materials and Environmental Technology.

I want to sincerely appreciate my supervisor, Professor Sergei Preis, for all his patience, consistency and thorough guidance from the beginning to the end of this research and thesis writing. I want to also appreciate my co-supervisor Liina Onga, for all her support during the experimental procedure and continuous kindness and sharing of knowledge as it greatly helped me through to complete the experiments smoothly.

I also want to thank Associate Professor Sergei Bereznev for always sharing up to date information about thesis procedures and guidelines.

In addition, I would also like to thank Juri Bolobajev for sharing knowledge about laboratory safety and ethics before the commencement of my experimental procedures and the entire staff under the Laboratory of Environmental Technology for their kindness and tolerance.

List of abbreviations and symbols

O_3	Ozone
PCD	Pulse Corona Discharge
AOP	Advanced Oxidation Process
OH-	Hydroxyl Radicals
ē	Electron
O (^{1}D)	One-dimensional Oxygen Molecule
ECAP	European Clothing Action Plan
PLC	Public Limited Company
COD	Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
ETDA	Ecological and Toxicological Association of Dyestuff
LD_{50}	Lethal Dose for 50%
NF DK	Nano Filter Membrane Designation
Da	Dalton
PACl	Polyaluminium Chloride
PAFCl	Polyaluminium Ferric Chloride
PFS	Polyferrous Sulphate
PFCl	Polyferric Chloride
Ti/Pt – Ir	Titanium/Platinum-Iridium
NADH-DCIP	Nicotinamide Adenine Dinucleotide – Dichlorophenol Indophenols
PCBs	Polychlorinated Biphenyls
LiP	Lignin Peroxidase
MnP	Manganese Dependent Peroxidase
H_2O_2	Hydrogen Peroxide
SSF	Spontaneous Saccharification and Fermentation
MAC	Mesoporous Activated Carbon
TOC	Total Organic Carbon
UV	Ultraviolet

ROS	Reactive Oxygen Species
DBD	Dielectric Barrier Discharge
PPS	Pulse Per Second
SDS	Sodium dodecyl Sulphate surfactant
CPE	Cloud Point Extraction

INTRODUCTION

The continuous industrialization of the world and the impact of its waste disposal methods have continually increased the need for sustainable and efficient methods of removal of toxic wastes from the environment. One of the major raw materials of industrialization is water. As abundant as this resource seems, it has been predicted to become scarce in the nearest future with its continuous use by industrial and human activities and inappropriate disposal back to the water bodies.

The textile industry generates a large amount of wastewater containing dyes, dying and sizing agents, and fixatives. Reactive azo dyes, popular in the textile industry, are seen to be an environmental hazard as these dyes are resistant to natural degradation processes and are toxic, carcinogenic and mutagenic when living organisms are exposed to those. In aquatic bodies, these dyes hinder light interference obstructing natural photosynthesis [1]. Dying using reactive dyes with concentrations at about 1.5 g/L requires a large amount of salts, at about 5 – 6% of sodium chloride and sodium sulphate in alkaline solutions.

There are conventional methods applied to the treatment and removal of organic waste and toxic chemicals from aqueous solutions including chemical, biological and physical processes. These methods have been proven to be effective but still have their limitations and disadvantages. One of the chemical oxidation methods involving the use of ozone as the major oxidant has been proven effective but expensive, consuming large amounts of energy for its synthesis and mixing with water at its poor aqueous solubility.

Advanced oxidation processes (AOPs), mostly in the form of ozonation, are making their way to the market in the water treatment industry. Ozonation is a human-friendly and powerful approach with its drawback being its high energy consumption and cost. Energy efficiencies for AOPs were calculated in a study by Krichevskaya et al. [2], according to which the energy cost used at electricity is 0.0343 EUR/kWh, 0.7163 EUR/kg is the cost of ferrous sulphate and 0.8217 EUR/kg - H_2O_2 as oxidizing agent. Ozone synthesis requires approximately 15 kWh/kg O_3 using oxygen, which doubles when using air [3].

The application of gas-phase pulsed corona discharge (PCD) for wastewater treatment has been reported to be the most efficient AOP according to Ajo et al. [4]. Electrical discharges in PCD are applied as ultra-short pulses with duration of about 100 ns of corona discharges between electrodes of uneven geometry, plates and wires, for example. Previous studies have shown the formation of short-living reactive oxygen species (ROS) at the interface of the gas-phase side during the reaction [5].

The need to replace ozone, the most commercially available ROS yet expensive, with a still effective, eco-friendly and cost-effective method brought about this research. The treatment of contaminated aqueous media using PCD plasma forming $\bullet OH$-radicals at the air-water interface, consumes energy two to six times smaller than the ozonation method destroying organic contaminants and microorganisms with a high efficiency. The generation of oxidants proceeds as described in Eqs. (1) to (3) [6]:

$\bar{e} + H_2O = \bar{e} + \cdot H + \cdot OH$ (1)

$O\,(^1D) + H_2O = 2\cdot OH$ (2)

$\bar{e} + 3O_2 \rightarrow \bar{e} + 2O_3$ (3)

Wastewater treatment using gas-phase plasma starts to attract interest in science [7]. The ROS in PCD treatment are generated by the impact of electrons dissociating molecules in an avalanche process with subsequent reactions of dissociated species with surrounding media including each other [8]. The discharge provides free OH-radicals playing an important role in degradation of pollutants. The high reactivity of oxidizing agents in PCD treatment makes the radicals not to diffuse deeply beyond the gas-liquid interface boundary as described by Anderson et al. [9,10] explaining the surface character of oxidation. The above is important to note as it is seen that the efficiency of PCD treatment depends on the design of the reactor and the area of contact of the solution to be treated. The mass transfer rate of the ROS from plasma to the solution to be treated also depends on the design of the reactor and hydraulic conditions.

The objective of the research is focused on the treatment of textile wastewater with application of the PCD method and its optimizing by noting the effect of operation parameters on the energy efficiency for the process upscaling. Operation parameters studied in the research include pulse repetition frequency, temperature and electric conductivity of treated solution.[1] Textile dyes selected for this study were the azo dye, Acid Orange 7 (AO7) also known as 2-naphthol orange, and the reactive dye, potassium indigotetrasulphonate dye also called indigo blue.

The use of radical scavengers is also becoming a regular practice in radical reaction studies where hydroterephthalic acids, sodium tetraborate, primary alcohols in liquidsterephthalic, carbon monoxide in gas phase [11, 3]and others are used to study the formation and behaviour of OH-radicals. The present research also applied this method using a surfactant radical scavenger to observe the effect of surface reactions as described earlier [6]. Special attention was paid to the circumstance observed by Onga et al. [12], who observed the role of a surfactant enhancing oxidation of reactive textile dyes RB4 and RB19.

This study structure includes chapter 1 containing general overview of the textile industry with its pollutions of the environment together with the existing methods for textile dyes abatement from wastewaters, chapter 2 describing the experimental details, chapter 3 presenting the experimental results and their discussion and conclusions.

1. RESEARCH BACKGROUND

1.1 Textile industry status

Textile industry is diverse covering a wide span of technologies. These include processing raw fibre to yarns, then to fabric and, finally, a wide range of finished goods - beddings, wool, geo-textiles, clothing, synthetic yarns using high-tech machinery. Textile manufacturing can be traced to the Stone Age before 8,700 B.C.: spun fibres, yarn and woven materials were found in Middle East. Ever since, processes with the manufacturing of textile have continuously evolved, and the way in which they were made available has greatly influenced how people carried their belongings, dressed themselves and decorated the environment.

A pronounced drawback in the growth of the textile manufacturing process is the quantity of wastewater it generates aside from other smaller issues which could be its solid waste, water resource and energy management. A large amount of synthetic dyes goes into the textile manufacturing methods, since retention of dye most times on target fabric is considered weak, enormous amount of dye polluted water is the result of dyeing. When it comes to pollution and consumption of water resources by industrial processes, textile industry ranks as one of the largest polluters. Large quantity of wastewater generated by textile manufacturing in countries like Pakistan and India is released directly into water bodies with no form of treatment and still highly concentrated on pollutants such as dyes, detergents, desizing agents, heavy metals, degradable organics and stabilizing agents. These pollutants find its way into surface- and groundwater becoming a hazard to the socioeconomic life, health and wellbeing of humans and living organisms. [13]

According to Khalid et al. [14], 390 million tons of wastewater is produced in China, 51% of which is generated by industry sector increasing by 1% annually. The textile industry has a larger share producing approximately 70 million tons yearly of wastewater. In countries with high risk of water scarcity, where it is necessary to use large amount of fresh water for agricultural purposes, the need to recycle water for reuse is expedient and since wastewater cannot be reused due to its heavy contamination, it is an urgent issue to begin to seek fast, and cost-effective ways to promote the reuse and recycling of waste water released from industrial processes [15]. Processes during textile manufacturing which includes desizing, singeing, bleaching, scouring, mercerizing, printing, dyeing and finishing, require a lot of water for completion (Figure 1.1) and at every end of each process, pollutants are released into water used during production which is almost always, considered non-reusable and discharged into the environment inappropriately [16].

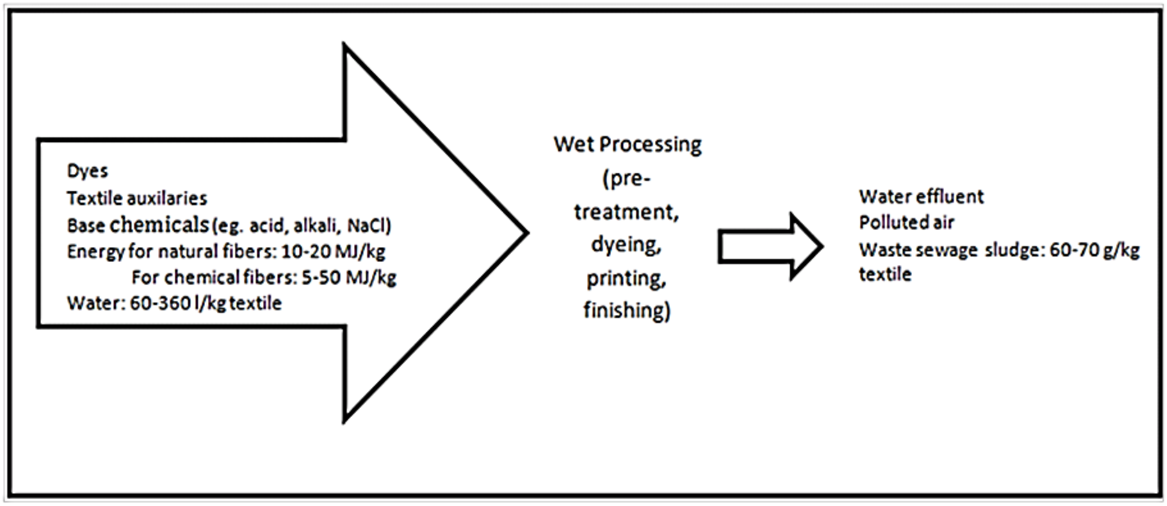

Figure 1.1. Quantity of waste produced from finishing processes in textile production [17]

Textile manufacturing industries has seen a noticeable increase within the past few years as described below on its economic impact and financial value. As fashion trends change and increasing number of people become more material conscious, the need for products made from textile continues to increase. In 2016, a report for the European commission's executive agency for small and medium-sized enterprises by Delden & Aucouturier, showed that between 2010 and 2014 global consumption of technical textiles (sewing thread, medical sutures, etc.) grew by over 6% yearly. The global market size was worth an estimate of 133.3 billion EUR. The industry in 2006 have provided employment to more than 2.5 million people with an average turnover of 190 billion EUR per year and accounted for about 3% of the total manufacturing value added in Europe. During 2007, the industry generated an estimate of 243.3 billion EUR in gross revenue and employed 2.3 million workers with 220,000 companies showing the reliable growth consistency [18].

In more recent times, the textile manufacturing sector has been reported by European Clothing Action Plan (ECAP), to have been responsible for providing over 1.7 billion employments in the European Union. It holds 6% of the whole employment in the entire variety of manufacturing industries in Europe. The sector majorly contains small business and factories of less than 50 workers. The sector yields a turnover of more than 166 billion EUR and investment of 4.8 billion. The textile industry's performance in the preceding decade has been steady since 2009 till date. After Asia, Europe is seen to be the second biggest textile producer, majorly manufacturing synthetic staple fibre since 2014. The textile industry in the EU is additionally looking forward to increasing their market added value by making doing business more digital as this would be key to specify and build the future of the industry in the European region. The textile industry in the EU occupies an important position in the manufacturing sector as it is one of the top contributors to EU's economy. It is also noteworthy to know that EU has a high market for textiles and fashion due to its high rate of consumption per capita compared to other continents. Figure 1.2 shows some EU countries and their respective expenses on clothes. European countries are important exporters of clothing and textiles; especially Germany, Italy, Spain, UK and France. They export up to 30% of throughput either as direct production or by adding value to imported textile products before re-exporting according to EURATEX's annual report 2015. The textile industry is important to the industrialization of the European Union and is predicted to see a growth in the nearest future. Textile industry is majorly focused with producing, distributing and designing of cloth, yarn and clothing. Raw materials can be obtained from nature or by synthetic processes with chemicals from the various chemical industries.

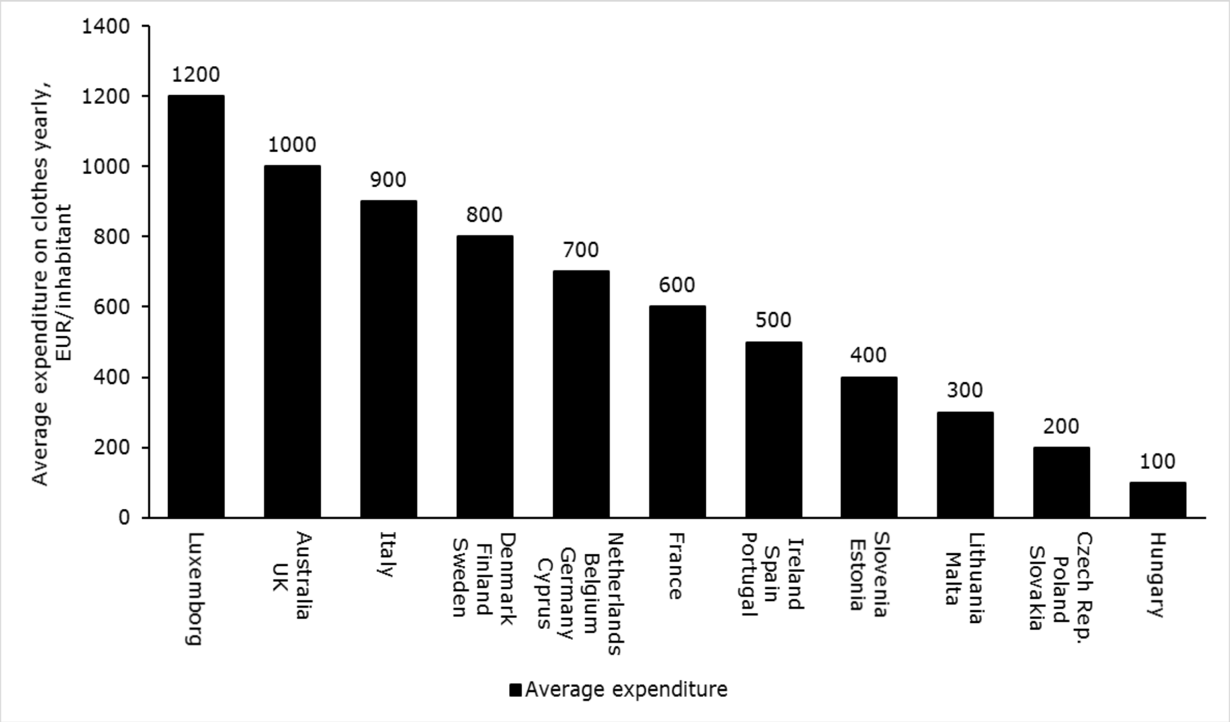

Figure 1.2. Average expenditure on clothes per year. Ranking by the EU member states, EUR/inhabitant [19]

China, being top textile exporter in the world, with over 40% of the world's textile and clothing exportation, holds the biggest textile manufacturing and production industry worldwide and the textile industry, itself, is the biggest manufacturing industry in China with around 24,000 establishments. The Chinese textile sector has a number of sub-manufacturing including synthetic fibre, wool, knitted and woven product industries, printing, silk textile, linen, dyeing and finishing industries, finished textile product manufacturing sectors. This shows that the textile industry is a key player of important in China's economy as it is the world's biggest textile producer and exporter, responsible for over half of the entire world's textile production. In 2015, textile manufacturing accounted for 7% of China's GDP. Textile plays a significant role in China's foreign trade as an export product providing employment opportunities because of its labour-intensive character.

The conference of China National Textile and Apparel Council (CNTAC) held in 2017 stated that the country's textile industry has shown a steady growth rate through the years, stable domestic demand growth, recovering overseas market demand, active investment in the East and steady improvement in performance. The statistic gathered for the conference shows that during the first 11 months in 2017, China's industrial added value growth rate was 6.6%, manufacturing growth rate was 7.7% and textile industry growth was 4.9%. EU reported 105.26 billion EUR worth of textile and apparel imported from China. Despite rising labour costs, appreciation and low demand from export markets, China's textile industry is continuously growing at a steady and positive pace and has been predicted to dominate the international apparel and textile sector both as a manufacturer and a consumer for many years to come [20].

An estimate of 700,000 tons of dye is produced worldwide and majority go into textile industry production processes. Different combinations of these dyes are used to create certain colour combinations which technically increase the number of the type of dyes used for processing in the industry as each combination make a new set of dye [21]. A hand full of these dyes degrades naturally while others need treatment procedures to be degraded. Nitro-, azo-, phthalocyanine, xanthene dyes etc. are the groups in which dyes come. These dyes are chemically different from each other and would react differently to different degradation methods. A study by Maas and Chaudhari [22], suggested that one million tons of dyes are manufactured yearly of which 28%, i.e. about 0.28 million tons, are not used up in industrial processes and, hence, end up being discharged as wastewater into the environment.

In Nigeria, sadly, the growth rate seen in world leading countries cannot be said to be similar in the country as the textile industry has faced a continuous decline since the time of the colonization till date. Figure 1.3 and 1.4 shows the growth and decline rates of the Textile industry in Nigeria as it relates to its performance and employment capacity. Nevertheless, continuous efforts are being made towards the resuscitation of the industry which means in the nearest future the industry would experience a bounce back. The textile industry in Nigeria was once the third largest in Africa after Egypt and South Africa with over 250 factories operating above 50% capacity. It was also the single largest employer of labour after the government providing direct employment to 350,000 people and more with millions of indirect jobs. During the 1990s, the Nigerian government profits as much as 5.6 million USD per annum from textile related taxes and levies. Therefore, the fall of the textile industry during the late 90’s, was a serious challenge to the Nigerian economy. The government, in this light has continuously been taking intentional steps to making sure the textile industry is back and running. In the early 2000, the government placed a ban on the importation of textile products into the country to encourage the local trades and farmers of cotton.

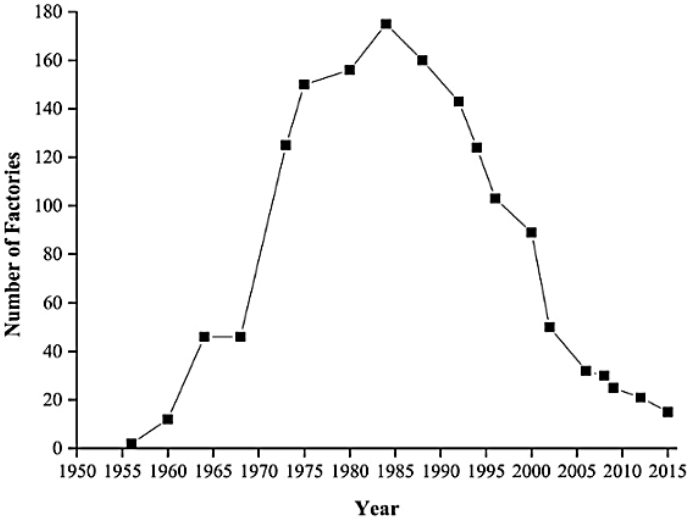

Figure 1.3. Number of textile factories in Nigeria [23]

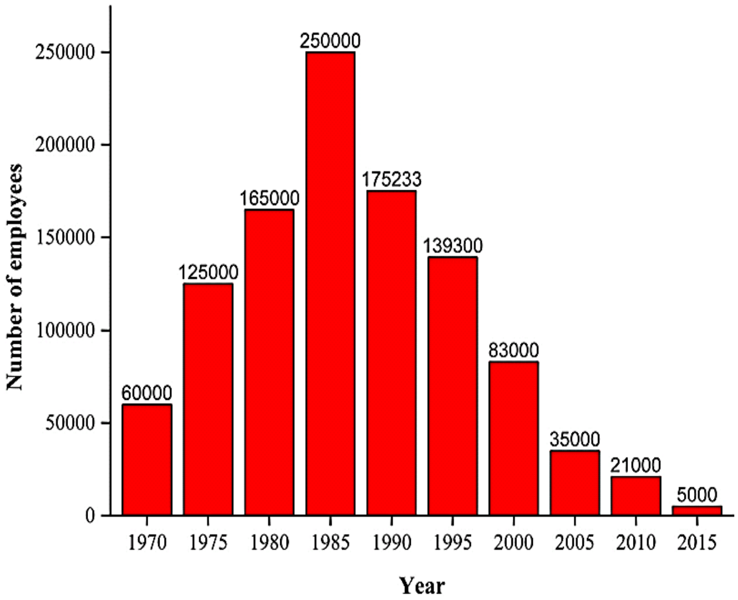

Figure 1.4. Employment statistics of the Nigerian textile industry [23]

Further in 2010, an intervention fund of an estimate USD 194.44 million was pushed into the textile industry. 71% went directly to textile and garment while 29% went to cotton growers. All these were done because of the understanding of how important the industry is and its relevance to economic growth and development. In same 2010, Nigerian Textile PLC which suspended operation in 2007 resumed operation with a work force of 900 employees. The United Nigerian Textile PLC was also reopened [23].

Other African countries have seen a remarkable increase in their textile industry as it has been predicted by Berg et al., in a survey done in 2015 [24]. It shows that searching for textile raw materials and apparels is shifting to east Africa, mainly Ethiopia and Kenya. Ethiopia started its textile manufacturing industry in 1939 when its first clothing factory was created. In recent times, the sector has increased at a rate of 51% per year and over 65 international textile investment projects have been licenced for foreign investors. In the past 2 years, some European textile companies, H&M, Primark and Tesco started sourcing some of their garments from Ethiopia

The Ethiopian government has also invested a sum of 250 million USD to establish the state-run Hawassa Industrial Park entirely dedicated to textile and garment producing industries which is a 1.3 million square meters land mass, making it Africa’s largest manufacturing park [25].

The South African market has always been an important market for the textile and clothing industry. Sales of produced textiles were reported by business wire to be 1.57 bn

EUR and 0.88 bn EUR for finished textile manufactured products in 2017. The country has seen additional improvement in balance of textile trade during the past few years and has seen a steady growth. The textile industry in South African contains a significantly high number of micro and small enterprises as well as operations seen to be informal. There are only around 20 huge companies employing over 150 people in its operation. The industry is still labour intensive and gives employment to more than 31,000 people which included a high number of women [26].

In Turkey, the textile and apparel industry play an important role in its development and industrialization process as it is also seen to be one of the top industrial sectors of its economy and makes up to 22% of its export revenues. The sector has approximately 2 million employees, which also invariably makes it the largest employment group in the country according to Toprak and Anis [17].

The current world population exceeds 7.1 billion expectedly growing to 9.5 billion in 2050. The increase in population would happen mostly in developing countries. As the economic situation in these countries improve, population would have more consumption potential, making textile and clothing materials bound to be on the rise. Population and economic growth are bound to stimulate a rapid increase in textile production.

1.2 Environmental problems with textile dyes

The increase of modern textile manufacturing together with inadequate treatment of effluents has resulted in the release of toxic, harmful, carcinogenic pollutants which included dyes, odorants, heavy metals, volatile organic compounds contributing to high amount of biochemical and chemical oxygen demand, COD and BOD, contents of nitrogen and phosphorus nutrients. This has continuously pushed for developing cost effective and efficient treatment and control methods to deal with the contaminants associated with the textile processing and manufacturing.

One of the environmental challenges caused by textile industry comes from materials usage and production. As the textile manufacturing sector around the world continues to grow, its share in pollution is of a big concern. The disaster of dye pollution has continued to grow due to the high rate of consuming these chemical dyes in large quantities by textile industries. Over 10,000 types of dyes and pigments are consumed daily with an annual production of $7 \cdot 10^5$ tons.

It is hard to evaluate which of the total chemicals used during textile manufacturing would be allowed or termed as eco-friendly. The major problem is the multiplicity of the number of dyestuffs used during textile dying processes. The Colour Index International, a reference database jointly managed by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists, reportedly lists 27,000 products placed under 13,000 colour index generic names [27]. Wastewater discharged from production of textiles could contain high contents of COD, BOD_5, total suspended solids (TSS), phosphates, sulphates, sulphides, fats, grease, and salts of heavy metals [28].

A few reports have established the fact that disperse dyes, non-ionic compounds at low solubility in water, are used more frequently for dying polyester yarns of fabric in the textile factories. It has been reported that an estimate of 10-15% of these dyes used during tanning processes in the textile, biomedical, cosmetics, food, paper, plastic and other dye inclusive industries are lost in the effluents during dying operation [29, 30].

The low rate of the removal of these dyes from textile effluent during primary and secondary wastewater treatment as seen in wastewater treatment plants (WWTPs) is caused by the dyes recalcitrant character towards microbial aerobic conditions caused by the difficulty in breaking down compounds with aromatic structures. These toxic substances also present a threat to the drinking water supply being able to pass by the potable water treatment facilities. Due to synthetic intermediates and by-products of degrading dyes, they reportedly generate aromatic compounds that are highly toxic with mutagenic and carcinogenic properties. At low concentrations, dyes cause an intense colouring to clear water making it aesthetically unattractive. This colour reduces the solubility of oxygen and the water transparency, causing an ecological instability in the growth and development of waterborne life and the development of species [31, 32].

In Europe, the greatest environmental impact caused by contamination in the textile industry comes from material usage and production. Agricultural land is seen to be affected mostly due to its dependency on water consumption. Textile dyes toxifying agricultural lands may cause the deterioration of crops, reducing fertility of soils and shortening food production as the source of revenue. Aquatic lives in the fresh water in need of oxygen to reproduce and breed, suffer due to the low oxygen content caused by light screening, oxygen depletion and toxicity. Due to the constant awareness and understanding of social cognizance concerning the environment, the textile industry has been forced into producing affordable environmentally friendly products. Along with technological and innovative development in recent years, textile industries would continue to play an important role in the environmental problem if effective solutions will not be found. The textile industry is also responsible for other pollution like solid waste, air pollution, energy consumption, odour formation, but, due to the nature of this review, the pollution associated with aqueous textile dyes would remain the key focus.

Textile manufacturing processes uses a large quantity of chemicals and water generating waste during and after processing, making this sector the world's biggest pollution generating industry with 2,000 various chemicals used which includes dyes, transfer agents and more. It is reported that 25% of the sum of the entire world's chemical products, manufactured are used in the textile industry. World Bank provided a rough estimate which concludes dyeing and finishing processes, accounts for 17 – 20% of the industrial processing water pollution and, so far, only 72 of the toxic compounds in wastewater have been detected, out of which only 30 of them are cleaned by existing treatment methods. The population with allergic reactions to most of the chemical waste produce of textile dyes is predicted to increase to 60% by 2020 [33]. This alone has raised concerns for the quick and immediate resolution to the status of wastewater treatment for the removal of textile dyes to avoid physical and internal contact with human.

Wastewater generation is the major environmental impediment for the growth of the textile industry. The coloured textile wastewater affects photosynthesis in plants and affects the aquatic life by reducing the light penetration and oxygen circulation in the water bodies. Therefore, this wastewater must be treated before discharge to the environment. Generally, in humans, excessive and frequent exposure to coloured effluents can cause a broad spectrum of immune suppression, respiratory, circulatory, neurobehavioral disorders or allergies, central nervous breakdown, autoimmune disease, leukaemia, multiple myeloma, vomiting, hyperventilation, cyanosis, insomnia, profuse diarrhoea, salivation, eye or skin infections, tissue necrosis, jaundice, quadriplegia, and irritation to lung oedema [34, 35].

Every stage involving the production of textiles, leads to a new form of wastewater and environmental pollution. Processes from the sorting to the wet processing and drying with packaging produce toxic wastes raising environmental concerns to reduce the waste as the industry cannot be made redundant due to its established importance in the economic development of the world at large. It is inevitable to have a textile industry without the use of these dyes and chemicals, so the reasonable way out is to look for cost effective and economical solutions for the treatment of chemical wastes.

A lot of the organic constituents of textile dye pollutants are resistant to biodegradation thus remaining intact for a long amount of time finding its way into the food chain of humans and animals. Bioaccumulation thus takes place influencing public and animal health.

Many structural varieties if textile dyes fall into the cationic, non-ionic or anionic type. The class of anionic dyes include direct, acid and reactive dyes [36]. Brightly coloured and water soluble reactive and acidic dyes are found to be the most problematic remaining unaffected with conventional treatment processes.

Table 1.1. Popular chemicals and dyes materials used in synthetic textile factories [33]

Chemical	**Quantity kg/month**
Acetic acid	1611
Ammonium sulphate	858
Polyvinyl Acetate	954
Wetting agent	125
Caustic soda	6212
Softener	856
Organic solvent	247
Organic resin	5115
Formic acid	1227
Soap	154
Hydrosulphites	6563
Hydrochloric acid	309
Hydrogen peroxide	1038
Leveling and dispersing agent	547
Solvent 1425	321
Oxalic acid	471
Polyethylene emulsion	1174
Sulphuric acid	678
Disperse dyes (polyester)	1500
Vat dyes (Viscose)	900
Sulphur dyes	300
Reactive dyes	45

Table 1.2. Characteristics of dyeing and printing unit effluent of a textile mill [33]

Process	**Alkalinity, mg $CaCO_3$/L**	**Total solids, mg/L**	**Total dissolved solids, mg/L**	**Suspended solids, mg/L**	**BOD_5 mg O_2/L**	**COD, mg O_2/L**
Dyeing	9.2 - 11	1250 - 3160	3,600 – 6,540	3,230 – 6,180	360 – 370	130-820
Printing	6.7 – 8.2	500 – 1,080	2,110-2,750	1870 - 236	250 – 290	135-1380

Table 1.1 shows an estimate of amount of chemicals used per month in a synthetic dye factory. Dye related chemicals collectively amount to the highest quantity used in the production process. Table 1.2 also shows the characteristics of the wastewater discharged from Dyeing and printing processes, where most of the chemical dyes are introduced.

1.3 Conventional methods of textile dyes abatement

Due to the challenges coming with the textile industry, environmental protection agencies, governments and humanitarian bodies around the world began to legislate and propose laws to curtail the release and dumping of the toxic chemicals with textile industry’s wastewater. These laws limit the amount and kind of wastewater that may be released to the environment. These rules and regulations have given birth to effluent treatment plants using different methods and approaches to remove toxic chemicals from water, and initiating research targeting the cost-effective ways of abatement. Textile companies can save 20 – 50% expenses on water and effluent treatment cost by decreasing the quantity of water used in production. However, before the textile companies reinvent their techniques to reuse water, the problem of excess water pollution will remain, and immediate solutions should be provided.

The formation of the Ecological and Toxicological Association of Dyestuff Manufacturing Industry (ETAD) in 1974 was aimed at minimising the environmental damage, protecting customers, and working with the government and the public over the toxicology impact of their products [37]. The ability for a substance to cause damage to living tissues, impair the nervous system, or cause severe illness when ingested, cause damage when absorbed by the skin or inhaled, makes it toxic. The ETAD has a toxicity data which shows proof of the negative effect of natural manufactured dyes to the health of humans. The

LD_{50} is the most specific figure for toxicity rating of any substance measured in mg/kg of the body's weight. It explains the lethal dose for 50% of the test animals as stated by Ashiskumar and Konar [36].

Over 90% of 4,000 dyes tested in an ETAD survey had LD_{50} values greater than $2 \cdot 10^3$ mg/kg with the highest values found for basic and diazo direct dyes [38]. More government legislations are becoming stricter, mostly in the developed countries, concerning the removal of dyes from textile industrial effluents. Environmental policies in the UK established since September 1997 that synthetic chemicals should not be released into the marine environment, thus making sure that textile industries treat their dye effluents to the necessary standards. The European community (EC) regulations are also becoming strict holding textile industries responsible for textile wastewater released untreated to the environment [39].

There are conventional methods in full-scale use for the cleaning of textile wastewaters effluent. These methods generally fall under three main groups, physical, chemical and biological methods. Usually, methods from separate groups are used in combinations for a more productive result since single methods have proven to be insufficient for removing colour and other pollutants. Some dyes are hard to biodegrade; hydrolysed reactive and certain acidic dyes are not easily adsorbed by active sludge passing the treatment without being altered. Combinations of various effluent treatment procedures have shown higher efficiencies removing over 85% of pollutants from the wastewaters.

1.3.1 Physical and physico-chemical methods

Physical and physico-chemical methods in textile wastewater treatment include coagulation-flocculation, adsorption, sedimentation, flotation, reverse osmosis and nano-filtration, and other methods that would not be discussed. These processes are mainly useful for the colour removal of wastewater which contains disperse dyes. Their decolourising efficiency for wastewaters that contains reactive and vat dyes is low. The physical techniques also limit their use due to poor decolourization and generation of sludge and concentrated liquid wastes.

Adsorption

Organic dyes cannot be easily degraded due to their lengthy carbon chains, making them resistant towards regular biotic conditions. Treating these dyes requires methods that are abiotic. Adsorption is one of the methods popular in the textile. During adsorption, the dye is collected into a spongy, usually granulated material. The wastewater is passed through a sieve bed made up of granular material where dissolved dye molecules are retained. Adsorption has attracted at attention due to its high decolourization efficiency in treating textile wastewater containing various types of dyes. To select an adsorbent for colour removal, it is important to consider the affinity level, capability for the substances and the regeneration of the adsorbent [40]. Activated carbon is a very popular adsorbents for the adsorption of wide ranges of dyes from textile wastewater effluent being, however, expensive, which is a limiting factor for its application.

Certain properties should be considered when using conventional low-cost adsorbents for dye degradation, which have high adsorption capacity, high tolerance to wastewater parameters, efficient in removing a range of dyes (wide ranges of dyes are used during textile production) and high selectivity. Low-cost materials include peat, bentonite clay, fly ash and polymeric resins. Biomaterials include wheat straw and husks, treated ginger peels, charcoal made of groundnut shell, Date seed (*Phoenix Dactylifera*) and potato waste. The problems involving most of these adsorption methods involve its regeneration or disposal, and sludge formation. High-quality adsorbents are of high cost. Adsorption thus should be applied to low concentration of pollutants at accessible cost-effective adsorbent according to Holkar et al. [13]

Alkan et al. [41] carried out an experiment using natural diatomite from Caldiran-van, Turkey, to remove natural red and basic blue from aqueous solutions. Using an adsorbent dose of 20 mg/L with initial concentration of dyes at 20-140 mg/L and temperature between 25 and 45 °C, they observed maximum adsorption of natural red in 150 minutes at 40 to 100 mg/g, whereas basic blue adsorbed in amounts from 20 to 140 mg/g, dependent on the experimental conditions.

Adsorption, however, presents a method of textile dye transfer from aqueous phase to the solid one, which requires further handling of often hazardous solid waste contributing substantially to the cost of treatment.

Membrane filtration

Filtration through membranes dependent on the pore size includes ultrafiltration, nano-filtration, and reverse osmosis. This method is used in water recycling. Membrane permeability is important when temperature and composition of textile dye wastewater are the important factors. Reports indicate using membrane filtration in the textile industries for wastewater treatment brought good results with a potential for the recycling of wastewater containing hydrolysed reactive dyes and auxiliaries, reducing BOD, COD and colour [42]. Membrane filtration methods also have significant disadvantages in the investment cost, fouling of membranes and generation of wastes containing water insoluble dyes, e.g. indigo dye and starch resulting in needs in their further handling [43].

A series of experiments was performed by Khouni et al. [44], with a laboratory wastewater specimen combining two reactive dyes, blue Bezaktive S-GLD 150 and Black Novacron R with auxiliary chemicals using crossflow nano-filtration. An NF DK 2540F standard membrane was used with a total surface area of 2.5 m^2, length 1.05 m, a cut-off of 200 Da and a permeability of 8 $L\ h^{-1}\ m^2\ bar^{-1}$. The experiments were conducted with a fixed dye concentration of 40 $mg\ L^{-1}$, effluent flowrate of 80 $L\ h^{-1}m^{-2}$ and temperature of 25°C. The results showed that temperature has no effect on the dye retention at the colour removal of about 99%. The obtained permeate appeared reusable in the dyeing process.

Membrane filtration has been increasingly used during the treatment of textile wastewaters and for recovering useful compounds from the wastewater effluent and to make water reusable. Nano-filtration experiments on dye bath wastewater treatment have been done to process removal of colour and COD reduction with water and salts recovery. The basic problems of membrane filtration include production of concentrate, declined flux and fouling of the membrane surface. To overcome those, the combination of various separation techniques is being adopted to achieve a high quality of separation [45].

Coagulation-flocculation

A review made on pre-hydrolysed coagulants, polyaluminium chloride (PACl), polyaluminium ferric chloride (PAFCl), polyferrous sulphate (PFS) and polyferric chloride (PFCl) appeared to be more effective than traditional alum or ferric chloride. They suggested these coagulants for decolourization of the textile wastewaters, mainly the disperse ones. In the experiments, an optimized dose of 100 mg/L potassium ferrite used as a coagulant aided with polyamine-based polymer treated a textile wastewater contaminated with disperse dye at 6.5-8.5 pH with a 95% colour removal. The dose of PACl of 10 mg/L removed the disperse dye contaminated water at pH 7.2 with 99.9% colour removal. Alum coagulant dose as high as of 200 mg/L aided with polyacrylamide at a pH of 5.3 removed the disperse dye from textile wastewater to a lesser extent, for 78.9%. For reactive dyes and acids, alum dose of 20 mg/L only at a neutral pH aided with commercial cationic flocculant, Colfloc-RDeCiba, showed the efficiency of 98% for colour removal. At the same time, ferric chloride at a dose as high as 293 mg/L was used to treat a textile wastewater containing reactive and disperse dyes at a pH 6.0 to yield the efficiency of only 71% for colour removal. Magnesium chloride used as a coagulant with a dose of 400 mg/L aided with polyelectrolyte Koaret PA 3230 removed reactive dyes from textile wastewater at pH 11 for 85%. Within pH range from 4 to 12.9, reactive, disperse, direct and acid dyes were degraded with the efficiency ranging from 58% to 99.9%. Polyaluminium chloride appeared to be the most efficient coagulant [46].

The drawbacks of coagulation include the inevitable sludge production, which may present a toxic residue requiring further handling as a hazardous waste. Possible coagulant regeneration or disposal may add to the coagulant cost.

1.3.2 Chemical methods

Chemical methods involve the change in chemical composition, properties and phases of substances through chemical reactions.

Electrochemical Processes

Electrochemical oxidation is a destructive process. It is a relatively new technique developed in the middle of the 1990s. The advantage of this method used during dye removal is the reduced consumption of chemicals and no sludge build up. The broken-down metabolites or the end products of this process are generally not harmful making the treated water safe to be released to the environment. It removes dyes at a high rate and degrades recalcitrant pollutants. Due to the high flow rates, there is a direct decrease in the dye removal, and the cost of electricity used is comparable to the cost of the chemicals which may be on the high side [47].

In electrochemical process, pollutants are removed by indirect or direct oxidation processes. The indirect process involves strong oxidants such as hypochlorite or chlorine, hydrogen peroxide, ozone generated electrochemically, with which pollutants are destroyed in the bulk solution by oxidation reaction with the generated oxidants [48]. The direct anodic oxidation involves the initial adsorption of the pollutants on the surface of anode followed by electron transfer reaction from the anode. The oxidants are usually generated and used immediately [49]. The electrochemical generation of hypochlorite/chlorine in chloride solution can be described with the following reaction:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1.1)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (1.2)$$

$$HOCl \rightarrow H^+ + OCl^- \quad (1.3)$$

Studies of textile dye treatment done by Vlyssides and Israilides [50], using electrochemical degradation of the wastewater with Ti/Pt anode show that at the end of 40 min of electrolysis, 92.2% of BOD, 92% of COD and 94% of colour removal was achieved with a total energy consumption of 44 kWh/kg of COD removal. Another experiment made by Szpyrkowicz et al., using different electrodes for the breaking down of disperse dyes showed the best results with a chloride-rich medium under acidic pH with a Ti/Pt – Ir anode. Another report by Naumczyk et al., showed the formation of organochlorine compounds during the treatment of textile dyeing wastewater.

Application of the electrochemical method for the treatment of textile water has been successful so far but the formation of chlorinated organic compounds measured as AOX (adsorbable organic halides) during the electrochemical degradation of resorcinol and cresol containing wastewater have been reported. Therefore, these require polishing treatment using activated carbon to remove the chlorinated organic compound before the discharge of the treated water.

1.3.3 Biological Methods

Biological process involves mostly the degrading of textile wastewater dissolved matter and presents transformation of organic compounds to the bacteria cells construction material easily removed from the treated wastewater by sedimentation. The efficiency of this process is usually controlled by the ratio of substrate-to-biomass load, dissolved oxygen concentration and the temperature. Biological methods can also be classified with reference to its bacteria oxygen requirement to aerobic, anaerobic and facultative. These classes can be combined for the efficiency improvement. In aerobic method, microbes are used for oxidation of pollutants in presence of oxygen, while the microbes in the anaerobic method digest organic matter in anoxic conditions.

Biological process of breaking down dye chemicals can be seen as a cost-effective method in comparison to physiochemical and photochemical processes. A wide range of possibilities for biological methods of dye degradation have been widely studied and are currently applied at industrial and small scales for dye degradation using different combination of microorganisms [51]. The study showed that a single microorganism strain (bacteria or fungi), if found effective for degrading a certain type of dye, would most likely not degrade any other type of dye making it challenging to use biological treatment methods in a commercial scale [52]. In a pond experiment, a colonized algae and duckweed plant occurring naturally, were reported by Işık and Sponza, to be very effective in the degradation of textile dyes. There are three generally practiced biological methods of degradation: aerobic, anaerobic and facultative processes. Anaerobic and aerobic processes have been reported to both give better results when it comes to the degradation of organic pollutants from textile wastewater. It was also reported that aerobic processes do not produce good results when it comes to colour removal from textile wastewater [53]. A technology which involves textile wastewater treatment called a sludge blanket reactor has been said to give good results in treatment of xenobiotic compounds and resistant dye compounds [54].

Aerobic Biodegradation

This process simply means chemical processes occurring in the presence of oxygen. These processes occur naturally in aquatic habitats and can also be triggered artificially using specific bacteria with oxygen present. The determining factor of how degradable a compound is depending on specific data set: BOD_5, COD, evolution of carbon dioxide and dissolved oxygen (DO) [55]. Cruz and Buitron [56] mentioned in their study that if a compound is tested to be biodegradable under favourable conditions, the compound would most likely also be biodegradable in a natural environment just as it would be in a biological wastewater treatment plant.

Anaerobic Biodegradation

This is the breaking down of target compounds in the absence or very low quantity of oxygen, and it occurs in the lower sections of natural aqueous environments due to its poor oxygen content. This is usually made possible by the presence of anaerobic microorganisms which digests the waste as food. Sewage waste is also degraded by this method showing that compounds which possess low solubility in water and adsorb on solids, can be degraded by anaerobic processes.

Combining of anaerobic and aerobic processes for wastewater treatment has been in real life practice over a long time and it is implemented by using the anaerobic process to reduce COD, followed by using the aerobic treatment method to polish the result. Anaerobic digestion produces methane-containing biogas. The textile wastewater is treated anaerobically with an economy benefit having BOD_5 higher than 3.0 g O_2/L provided by high content of biodegradable organic compounds [57].

The process of biological treatment can be explained thus: microorganisms adapt themselves to the target textile dye being treated in the wastewater, forming new resilient strains growing naturally to aid their survival requirements. During this process, the dyes are converted into less hazardous forms. The biodegradation process for recalcitrant dyes is usually dependent on the stroke of the enzymes which could be a lignin peroxidase, tyrosinase, aminopyrine N-demathylase, laccase, NADH-DCIP reductase and hexane oxidase. The advantages of biological degradation processes include it being [58]:

a. An eco-friendly method
b. Cost competitive
c. It produces non-hazardous metabolites or fully mineralized pollutants

The effectiveness of the biological method used for breaking down textile dyes in wastewater depends on the capacity of the microbes used to adapt and its enzyme activity. Many enzymes and microorganisms exist which were isolated and tried for the degradation of dyes. Microorganisms such as bacteria, fungi and algae have been seen to degrade a variety of dyes present in textile wastewater.

The most common and widely studied white-rot fungi regarding xenobiotic degradation used for textile wastewater treatment are the *Phanerochaete Chrysosporium*. Generally, white-rot fungi degrade lignin, the structural polymer found in woody plants. The fungi degrade a wide range of toxins including polychlorinated biphenyls (PCBs), dioxins and other chlorinated organic compounds. The fungi have also shown potential to decolorize textile effluent by up to 99% within 7 days of treatment. The fungi utilize the use of enzymes such as lignin peroxidase (LiP), manganese dependent peroxidase (MnP) for the treatment of textile dye wastewater. Other enzymes used include H_2O_2-producing enzymes, such as glucose-1-oxidase and glucose-2-oxidase, laccase, and a phenol oxidase enzyme. Although white-rot fungi have been shown to decolorize a wide range of textile dyes during liquid fermentations processes, the production of these enzymes has also shown to be unreliable. This is because of the unfamiliar environment of liquid fermentations. The ability to utilize these fungi in their natural environment means that they are more likely to be more effective in SSF (Spontaneous Saccharification and Fermentation). The white-rot fungus *Pleurotu Eryngii* was used to degrade naphthalene in a wastewater resulted in its degradation producing a metabolized 1,4-naphtha quinone, benzoic acid and catechol [59].

White-rot fungus *Coriolopsis sp.* (1c3) extracted from compost was used to degrade triphenylmethane (TMP) dyes - crystal violet (CV), methyl violet (MV), cotton blue (CB) and malachite green (MG) with 94%, 97% and 91% decolorization degree observed for CV (100 mg/L), MV (100 mg/L) and CB (50 mg/l), respectively. Decolorization of MG (100 mg/L) was observed for 52% in 9 days. Laccase, lignin peroxidase and NADH – DCIP reductase were responsible for degradation of the TMP dyes [60].

Aspergillus Niger fungi were used for the treatment of remazol brilliant blue R (RBBR) and acid red 299 with a result of 40 – 60% for RBBR removal and 30% discoloration for acid red 299 within 200 min [61]. *Lichen Permelia perlata* fungi were used to treat wastewater containing disperse dye solvent red 24 with laccase and manganese peroxidase responsible for biotransformation: 100% discoloration was observed within 24 h under pH 8 and temperature of 50°C. The metabolites obtained after biotransformation were naphthalene 1 yldiazene, naphthalene, 1-(2-methylphenyl)-2-phenyldiazene and diphenyldiazene [62].

The challenges facing the use of biological treatment include the extensive use of electric energy necessary for long aeration. Aerobic digestion also produces large amounts of bio-solids known as excess sludge requiring proper disposal. Inadequate disposal of the nutrient-rich sludge may result in algae growth and eutrophication killing aquatic life. Both problems may be alleviated by treating the wastewater in combination with preliminary anaerobic digestion. Even though the biological treatment of textile wastewater is efficient in removing organic contaminants, some studies indicate that certain toxic chemicals may remain after the treatment. Besides, although the anaerobic digestion leaves little carbon footprints, it is considered to be slow.

1.4 Advanced oxidation processes (AOPs) in textile dyes abatement

The existing dye removal methods, as described above, separate dyes from wastewaters having the major disadvantage in the sludge or other waste generation requiring further handling. Advanced oxidation processes (AOPs), according to Glaze et al. [63] is defined as oxidation processes involving the generation of powerful oxidizing agent such as hydroxyl radicals (-OH) in enough concentration to effectively decontaminate and treat wastewater.

With AOPs, complex dye compounds may undergo degradation until the ultimate oxidation called mineralization. The end products of this process include water, carbon dioxide and various inorganic ions. AOPs received attention in recent years due to their efficiency in removing textile dyes from wastewater. The process is based on production of highly reactive hydroxyl radical mostly amongst others, which has a high oxidizing potential of 2.8 V (Table 1.5), reacting at a rate constant in the order of 10^7 – 10^{10} L/mol/s. OH-radicals are also non-selective oxidizing agents and react with organic compounds by electrophilic attack, adding OH-radical groups during the reaction process by hydrogen atom abstraction [64]. The AOPs currently in practice for oxidation of textile dye wastes are reviewed below pointing out their advantages, drawbacks, attributes and efficiencies.

Table 1.4. Some types of AOP processes

Non-photochemical	**Photochemical**
O_3/OH- (Ozonation in alkaline media)	H_2O_2/UV
O_3/H_2O_2	O_3/UV
O_3/Ultrasound (US)	O_3/H_2O_2/UV
O_3/AC (activated carbon)	H_2O_2/Fe^{2+}/UV (photo-Fenton)
H_2O_2/Fe_2+ (Fenton system)	UV/TiO_2
Electro-Fenton	H_2O_2/TiO_2/UV
Pulsed plasma	O_2/TiO_2/UV
H_2O_2/US	Vacuum UV (VUV)
O_3/Catalyst	
Wet Air Oxidation	

Table 1.5. Oxidants and their oxidation potentials

Oxidant	**Oxidation potential (V)**
$h^+(TiO_2)$	3.5
Fluorine	3.03
Hydroxyl radical	2.8
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78

Dulov [64] carried out a study to show the potential of different AOP methods by treating industrial wastewater from textile industry, industrial park and synthetic aqueous solution containing propoxycarbazone-sodium, picric acid and nonylphenol. Using ozonation to treat the industrial wastewater, the study reported a COD removal of 28 and 32% for textile and industrial water respectively. The study also showed that Fenton-based AOP treatment showed to be dependent of pH values of the wastewater samples. The lower the pH the more effective the treatment process is. Treatment with ozonation using O_3 as oxygen source during the treatment of industrial wastewater cost an estimate of 3.24 EUR/m^3.

A typical textile industry wastewater composition has been reported by Oller et al. [65] to have a COD range from 150 to 12,000 mg O_2/L, total suspended solids between 2,900 and 3,100 mg/L, total nitrogen from 70 to 80 mg N/L, and BOD_5 range from 80 to 6,000 mg O_2/L leading to a BOD_5/COD ratio of around 0.25, which shows a large content of non-biodegradable organic matter. Application of chemical oxidation improving the textile wastewaters biodegradability thus presents a viable trend.

1.4.1 Homogeneous and Heterogeneous Fenton Process

Homogeneous Fenton process involves reactions of hydrogen peroxide with ferrous iron as a catalyst for oxidation of contaminants while heterogeneous oxidation includes the use of mesoporous activated carbon (MAC) or any other porous material with iron impregnated to the support crystal lattice as a heterogeneous catalyst. A study compared homogeneous and heterogeneous Fenton methods pointing out that the use of homogeneous Fenton reagent results in an amount of sludge. Their study was targeting two elementary processes to provide oxidation and to avoid sludge formation:

- providing a sink to abstract an electron from hydroxyl ion to generate hydroxyl radical;
- providing a second matrix phase to prevent ferric ion from combining with hydroxyl ion.

Both processes are endothermic, but the activation energy of reaction was reduced from 38.18 to 19.22 KJ/mol when the heterogeneous catalyst was used. At an optimum treatment time of 4 h and pH 3.5, the COD removal increased from 50% to 90%, BOD_5 from 61% to 88% and TOC from 64.1% to 90%. The drawbacks include the cost of MAC catalyst [66].

1.4.2 Ozone Related Oxidation Methods

Oxidation methods are commonly used for the decolourization of industrial textile dye wastewaters due to simplicity in application. The oxidant usually requires activation, for example with ultraviolet (UV) radiation. The chemical oxidation removes dyes by aromatic ring cleavage of the dye molecules [67].

Ozonation related oxidation processes are specified as follows.

- **Ozone/UV**

This involves the treatment of textile wastewater by using ozone for oxidation and the UV rays of 254 nm wavelength for activation of ozone decomposition in treated water producing OH-radicals. According to Al-Kdasi et al., regular ozonation of organic compounds does not completely oxidize them to CO_2 and H_2O [68].
Ledakowicz and Gonera, reported a degradation of COD of 30 – 47% and 90% colour removal using ozone/UV treatment method [69].

- **Ozone/UV/H_2O_2**

The mechanism of ozone and H_2O_2 interaction involves decomposition of H_2O_2 producing OH-radicals, i.e. hydrogen peroxide also participates in production of OH-radicals. This combination also accelerates ozone decomposition. This method has been reported to be a more efficient AOP method due to the high rate of oxidation compared to conventional ozonation. Azbar *et al*. (2004) documented 99% COD removal from acetate and polyester fibre dying process effluent in batch mode operation using combination of O_3/H_2O_2/UV in 90 min [70].

- **Ozonation and photochemical oxidation**

These include combinations such as ozone/TiO_2/electron–beam radiation, ozone/electron-beam radiation and ozone/ultrasonic treatment [71]. Just like using UV rays for further oxidation of toxic intermediates formed by ozone, the radiation is used to improve ozonation by increasing the OH-radical yield.

The drawback of the ozonation process is the cost involved in generating ozone. A tabular report of the cost of using some AOP for textile water treatment made by Holkar et al. [13], shows that ozonation was the most expensive costing about 4.94 – 5.02 USD/m^3 when used for the colour and COD removal from biologically pre-treated textile wastewater in a textile factory in Turkey. This is followed closely by the Fenton oxidation varying from 0.4 to 3.5 USD/m^3 excluding the sludge disposal and labour costs, which may be substantial in Fenton application.

The AOPs are often combined with biological and/or other processes to obtain a high percentage of COD, BOD$_5$ and TOC degradation showing a promising result.

1.5 Reviews on electric discharge methods for textile dyes abatement

Since AOPs based on the generation of strong ROS, primarily hydroxyl radicals, can abate various organic pollutants, their implementation was under the scope, and new ways to generate the OH-radicals were found. Ozone is generated naturally by electrical discharges in air or oxygen while hydroxyl-radicals are normally produced in electric discharges in humid air or at the gas-water interface. Given these facts, methods to generate discharges in liquid, above water and in contacts with liquids to produce ROS, were studied [72].

High voltage discharge method of treating waste waters is a hybrid gas-liquid electrical discharge type AOP with, sometimes, the inclusion of chemical oxidation, photochemical oxidation, high energy electron radiation, etc. This method of treatment has the capacity to non-selectively oxidize organic compounds effectively. Usually, high pressure, temperature or external light sources are not required, which has made this method gaining attention in studies [73]. OH-radicals are not produced in the liquid phase during oxidation process but on the gas side of its interface. A gaseous atomic hydrogen scavenger is required for the OH-radicals to cross the gas-liquid interface boundary in order for a reactive affinity with the dissolved components. The scavenger as oxygen is an asset advantage to increase the oxidation potential of OH-radicals but not necessarily required. OH-radicals are also strongly dependant on temperature when it comes to its oxidation efficiency in liquid phase reactions [74].

The removal of textile dyes from effluents by oxidizing the dissolved organic pollutants with the reaction paths are the major research subjects for the electric discharge applications. Kozakova et al. [74], carried out an experiment for the treatment of reactive yellow 125 (RY125) and direct red 79 (DR79) dyes using dielectric barrier discharge (DBD) plasma in a falling film reactor made of Pyrex glass tube having inner diameter 27 mm and length 600 mm with outer electrode made of aluminium foil glued on the outer side of the glass tube. The tube of 20 mm diameter covered with silver coating on the inside surface served as an inner electrode. In the reactor, water passed through the annulus at a laminar flowrate of 70 mL min^{-1} with the falling film thickness less than 0.3 mm in direct contact with plasma. The discharge was generated within a gap of about 3.0 mm between the inner tube glass surface and the water film at the inner surface of the outer tube by applying an amplifying voltage of 17 kV at a 200 Hz frequency. The mean input power was about 150 W. The solution was recirculated 10 times in the system with the applied energy accumulating. The flowrate was increased subsequently to 210 mL min^{-1} with inclusion of three identical discharge reactors connected in parallel. The result of their experiment focused on the maximal absorption wavelength of each dye, 390 nm for RY125 and 508 nm for DR79, showed the highest discoloration obtained for 90% for both dye solutions at energy doses of 270 and 450 kJ L^{-1} (75 and 125 kWh m^{-3}) and retentions time of 13.95 and 12.89 min for RY125 and DR79, respectively. Calculated energy efficiency for this experiment gives for 60 mg/L of initial concentration 0.72 and 0.43 g/kWh, respectively.

During a study to understand the relationship between electrode distance from the applied voltage to sustain plasma generation, electrical diagnostic through the variation of time during the forming of plasma in the form of voltage and current waveform and the evolution of plasma channelling, Kasih [73] studied the use of non-thermal plasma (NTP) for the removal of aqueous methyl orange dye using point-to-point geometry with electrodes of 2 mm in diameter, 66 V applied voltage which sustained the plasma channels through delivering a current of 2.4 A into the solution. The report shows a complete mineralization of the organic contents of methyl orange including azo groups into harmless species. With the above stated condition, 150 mL of methyl orange solution was completely decolorized into a clear transparent one in 30 min. Mineralization occurred during oxidation using this plasma treatment to breakdown functional groups in the organic dye used which were harmful into harmless species while simultaneously decolorizing the orange colour of the dye into a clear transparent solution (water) in about 30 min which gives an oxidation energy efficiency of 0.038 g/kWh.

Bingyan and Huazhu [74], reported a plasma discharge procedure made using a pulse generator whose discharge reactor was designed as a gas-liquid discharge wire-to-plate model with positive pulsed polarity of pulse width < 500 ns and pulse rise time < 100 ns. The pulse repetition frequency could be adjusted between 0 – 200 Hz. The reactor vessel was made from Plexiglas cylinder. A wired-plate pulsed discharge reactor which uses high voltage wire electrodes immersed in the aqueous phase and connected with plate ground electrode suspended in the gas phase above the water surface was established. This was used to treat rhodamine B in an aqueous solution by using a hybrid gas–liquid pulsed discharge. The influence of pulsed voltage, pulsed frequency, wire-to-plate spacing, wire-to-wire spacing and rate of bubbling of the reactor on discoloration efficiency was checked. 99.43% of the rhodamine B effluent was decolorized and the TOC was decreased to 26.9 mg C/L from 70 mg C/L under the optimal conditions of pulsed voltage being 35 kV, pulsed frequency 60 Hz, wire to plate spacing 8 cm, wire to wire spacing 5 mm, rate of bubbling 15 L/h and treatment time 50 min.

A study to understand the effect of surfactant and non-surfactant radical scavengers induced in aqueous reactions with PCD equipment was made by Wang et al. [6], where phenol, oxalic and humic acids were oxidized. The study showed a reduction in pulse repetition frequency from 800 to 200 pps increasing the oxidation efficiency of phenol to about 18% from 39 to 46 g/kWh. Oxalate acid showed a 50% increase in oxidation efficiency of 20 to 30 g/kWh at 200 and 800pps, respectively, while humic acid was less dependent on the frequency of pulse repetition, with only a 4% difference in oxidation efficiency of 5.3 to 5.5 g/kWh at pulse frequency of 800 and 200pps, respectively. The increase in efficiency with decreased pulse frequency was due to the longer time exposure of the long living ROS since the reduced frequency requires longer time for an equal delivery of pulsed energy for solution to be treated. With surfactants, phenol showed a dual mechanism of its oxidation as it was oxidized via radical mechanism in the bulk of the treated solution. Oxalate showed a dependence on the presence of surfactant as its oxidation efficiency was reduced to two fold smaller extent. Humic acid showed a complex reaction as which was not particularly sensitive to the presence of surfactant or non-surfactant radical scavenger. The surfactant showed small but visible reducing rate of oxidation effect which was consistent to its concentrations.

PCD was used to degrade a drug micro-pollutant, carbamazepine (CBZ), from a synthetic solution and spiked wastewater form a municipal wastewater treatment facility in a study done by Ajo et al. [75]. Concentration of 5 μg/L, which is the concentration commonly found in wastewater treatment plants, was treated and a 97% reduction of CBZ concentration was achieved with the application of only about 0.3 kWh/m^3 of energy consumption and a removal of over 99.9% was removed at 1.0 kWh/m^3. This showed PCD easily and more efficiently oxidizing CBZ and its parent substance compared to CBZ ozonation data in literature.

Reactive blue RB4 and RB19 were oxidized using PCD to understand surface reaction and its enhancement in a study carried out by Onga et al. [12], where dye removal efficiency of up to 340 – 360 g/kWh in the presence of a surfactant was reported. The reduction of RB's oxidation efficiency was also observed in the presence of sodium sulphate and chloride with respect to electric conductivity and no observation of electrolysis. Temperature was also reported to have a negative effect on the entire oxidation process.

1.6 Objectives of Study

Textile manufacturing and its industry in general would continue to see growth in the future as established in the preceding chapters. The industry has been shown to be a key to the generation of employment, capital and the general increase of Nation's wealth and GDP. It is therefore, an important segment of industrialization which has come to stay as long as mankind remains.

Dye and other related chemicals would also continue to be in use and as predicted in a paper by O'Neill et al. [27], the demand of dye products is going to see an increase. This simply means, dye manufacturing would invariably bring about the rise in wastewaters that are heavily contaminated by dye products.

Dye chemicals still remains anti-eco-friendly as it does not degrade on its own and requires additional methods by factories to treat its wastewater before being discharged. This adds additional cost and strain to Textile production as industries are mandated by EPA, Environmental Protection Agencies to treat wastewater to an acceptable level of reduced toxicity before being discharged into the environment or water bodies.
In Nigeria, due to some of the cost of mandatory treatment of wastewater discharge implemented by EPA's and other cost of production, the industry tends to increase cost of

products in an unstable economy which leads to boycotting of internally produced materials by domestic consumers and a general slow rate in ROI (Return of investment) which can render some of these factories bankrupt.

Cost effective solutions that can be easily operated with easy to understand technical know-how, has become necessary to match the continuous increase in the use of dyes in the textile production industries. Solutions that would treat dye contaminated waste water effectively would not only reduce the cost of production for Textile Manufacturing companies, but would also increase the possibility of resource reuse, which is Water in this case. Treated wastewater could also have the possibility of being reused instead of being flushed out. As fresh water continues to go scarce, it is expedient that technologies begin to focus on ways to redeem water to avoid the future treat of foreseen scarcity.
This study is important as it explores the possibility of an emerging technology in AOP using pulsed corona discharge (PCD), for the abatement of dye contaminated wastewater which is shown to be more cost effective to the widely used and industrialized ozonation method in a study by Ajo et al. [4].

The objective of this study is to further explore the PCD method which has been studied in previous work done by Onga et al., to understand underlying conditions that would be favourable for the use of PCD methods for Textile dye abatement. The preliminary study done by Onga et al. [12], showed an unpredicted effect of a surfactant (SDS), which was supposed to slow down oxidation, noticed to enhance oxidation and degrade a Reactive Blue dye faster. This observation triggered this study to further observe the effect of SDS and other Treatment conditions in respect to textile dyes of the nature different from RBs used. Acid Orange 7 (AO7) and Indigotetrasulfonate Textile dyes would be studied during this experiment. Results of this study is predicted to further guide the understanding and possible future scaling of the use of PCD methods for the treatment of textile dye contaminated water.

2 EXPERIMENTAL METHODS

2.1 Experimental apparatus

The equipment for experiments includes a high-voltage pulse generator with a laboratory scale reactor (FlowRox Oy, Finland). The non-thermal plasma (NTP) reactor and a power supply producing high voltage pulses of 18 kV are connected using a high voltage cable. Power is supplied to the pulse generator from the three-phase mains. The pulse repetition range is adjusted at 50 to 880 pulses per second (pps).

The connection of the pulse generator to the main body of the reactor is presented in Fig 2.1. The NTP reactor is made of stainless steel as shown in Fig 2.2. A stainless-steel tank with a 40 L capacity of recycled solution is installed below the reactor. The electrode system consists of multiple string high-voltage electrodes positioned horizontally, between grounded vertical parallel plates. The whole length of the wire electrode is 20 m and the distance between a wire electrode and the grounded plates is 18 mm at each side. Diameter of a single electrode wire is 0.55 mm.

Maximum output power of the device is adjusted by the pulse repetition frequency from 50 to 880 pps within the range from 9 to 123 W. The pulse duration is about 100 ns at the pulse energy from 0.14 to 0.18 J decreasing linearly with increased frequency. The device is turned off and on using a circuit breaker at the pulse generator.

Dye-contaminated water to be treated is filled in the tank 2 of the reactor and, using a pump, the water containing dye to be treated is ran through the water feed above the electrodes and sprinkled through the perforated plate with 51 perforations of 1 mm diameter over the high-voltage string electrodes in a continuous circle.

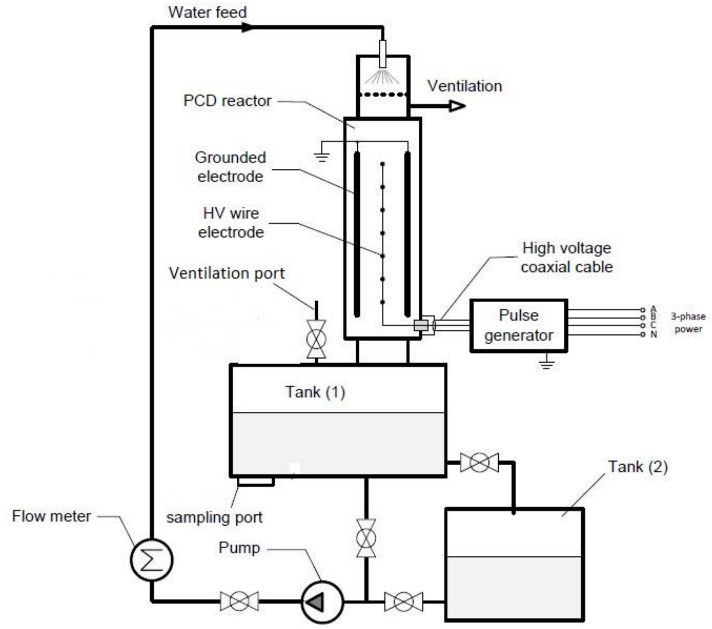

Figure 2.1. PCD water treatment device

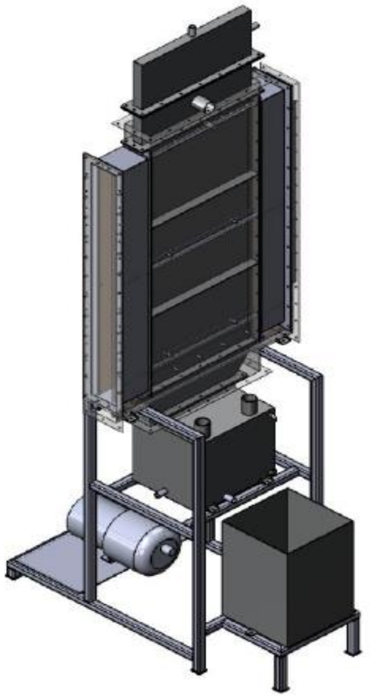

Figure 2.2. 3D View of the PCD reactor

2.1.1 Chemicals

The azo dye, Acid Orange 7 (2-naphthol orange) (Fig. 2.3), and the reactive dye, potassium indigo tetrasulphonate (Fig. 2.4), both analytical grade of 98% purity, in powdered form, were purchased from Sigma Aldrich. Aqueous solutions were made by dissolving measured dye samples in distilled water to be treated during the experiments.

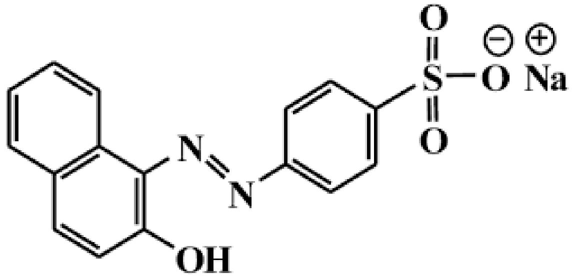

Figure 2.3: Acid Orange 7

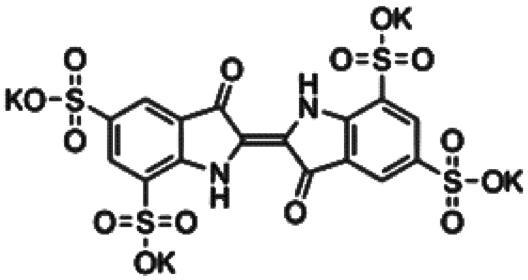

Figure 2.4: Indigo tetrasulphonate

A sodium dodecyl sulphate surfactant ($CH_3(CH_2)_{11}SO_4Na$, SDS) was purchased from Lach-ner, Czech Republic. Analytical grade sodium chloride and sodium sulphate with 99% purity, purchased from Lach-ner, were both used as inorganic salts during the experiment. These salts were used to increase the conductivity of the solution to quantify the effect of conductivity and observe for the presence and effect of chloride electrolysis during treatment of the laboratory prepared textile wastewater. Distilled water was used to prepare all solutions.

2.1.2 Experimental methods

Measurements and preparations

Indigo blue dye and AO7 were prepared and treated separately. Mass of each dye was measured using a microgram scale. The absorption wavelength, calibration curve and dye absorbance, was determined using a Helios-beta spectrophotometer manufactured by Thermo Electron Corporation, USA. To calibrate the spectrophotometer for concentration profile creation for both dyes, solutions of 50 mg/L of indigo blue and 75 mg/L of AO7 were made, diluted to smaller concentrations and measured to generate a calibration curve. Absorbance was measured and plotted against concentration to give a straight-line graph described with Eqs. (2.1) and (2.2) for AO7 and indigo blue dyes, respectively:

$$\text{Absorbance} = 0.4625C + 0.03344 \tag{2.1}$$

$$\text{Absorbance} = 0.02582C + 0.09782 \tag{2.2}$$

Where C is concentration in mg/L.

10 mg of AO7 and 46 mg of indigo dye were dissolved in 10 L of water and treated separately at room temperature, 22 °C. AO7 was treated at a 200 and 880 pps whereas indigo dye - at 50 pps for substantially higher reactivity of this dye. Table 2.1 summarizes experimental conditions for both dyes studied.

Table 2.1: Constant Data used during Experiment.

	AO7		**Indigo blue**
Pulse frequency, pps	200	880	50
Flow rate v, L/min	15.8	15.8	15.8
Initial concentration, mg/La	10	10	50
Spray Density, m/s	0.3	0.3	0.3
Delivered power, W	32	123.2	9

Dye solutions was sprayed into the reactor at a flow rate of 15.8 L/m with a spray density of 0.3 m/s. Spray density was calculated using the equation (2.3) below:

$$q = \frac{v}{S} \tag{2.3}$$

where v is flowrate of dye solution in m/s and S is cross sectional arear of the horizontal plasma zone [76].

Fig 2.5. PCD reactor setup

Dye concentrations where measured in the calibrated spectrophotometer at specific time intervals after a round of treatment in the PCD reactor to monitor the amount of dye degraded per time interval. The time interval of treatment for specific dye mixture in the reactor was determined by an estimated time range determined by how much dye was degraded from the first round of treatment. Time intervals used for treatment varied from 30 s to 2 min depending on how slow the dye degradation was.

Conductivity

Inorganic salts were used to determine the effect of conductivity during the treatment. Salts were used to increase the conductivity of solutions from about 50-60 µS/cm to 10 and 20 mS/cm. Such conductivity numbers were achieved with concentrations of 5.6 and 11.2 g/L of NaCl and 8.4 and 16.8 g/L of Na_2SO_4.Corresponding mass of salts was dissolved in distilled water, which was introduced to the tank of the reactor along with the dye solutions. The solution is allowed to circulate for about 5 mins before treatment started. Conductivity was measured using a HQ430dD laboratory conductivity/TDS meter package.

pH

pH values were recorded to monitor the changes in pH of every sample collected from the PCD reactor. The pH of the solutions was measured using A7 compact pH meter S220 manufactured by Mettler Toledo.

Temperature

The effect of temperature on the degradation of both dyes was determined by heating up dye solutions to specific temperatures, from room temperature of 22 to 35˚C and 45 ˚C using heating elements. Temperature was measured at intervals of treatment using a glass thermometer. Experiments on how temperature affects the process during degradation in the presence of inorganic salts and surfactants were also carried out.

Measurement of Energy Efficiencies

Oxidation efficiency i.e. dye degradation per kWh of energy delivered to the reactor was calculated using Eqs. (2.4) and (2.5):

$$\text{Energy Efficiency} = \frac{\Delta C \times V}{\Delta t \times P} \tag{2.4}$$

$$\text{Delivered Energy} = \frac{P \times \Delta t}{V} \tag{2.5}$$

where, ΔC is change in concentration, g/m^3;

V - volume, m^3;

Δt - change in time, h;

P – power, kW.

3 RESULTS AND DISCUSSION

3.1 Effect of pulse repetition frequency: AO7 and Indigo blue reactivity

In the degradation process of AO7, two sets of data were collected, at 200 (32 W) and 880 (123 W) pps. Running the reactor under 200 pps, AO7 degradation was completed in about 3.5 min at average delivered energy of 106.5 Wh/m^3 and dye degraded from 10 mg/L to zero, which makes 69 g/kWh (Fig 3.1 and 3.2). Treating the solution with pulse frequency of 880 pps degraded the dye in about 1 min for 90% at the average delivered energy dose of 93.2 Wh/m^3 and dye degradation efficiency 62.43g/kWh.

Indigo blue dye treatment showed a faster degradation rate. Treatment with 50 pps (9 W) of the solution containing 46 mg/L of the dye at 100% colour removal in 3.5 min resulted in delivered energy of 52.5 Wh/m^3 and energy efficiency of 859 g/kWh (Fig. 3.1). Such high oxidation rate did not allow accurate experimenting at higher frequencies; the substance, most probably, does not benefit from lower frequencies for the high rate of oxidants' consumption.

One can see moderate difference in AO7 degradations at various frequencies (Figs 3.1 and 3.2). Taking into account relatively high oxidation rate comparable with phenol, indifference towards frequency may be explained by AO7 yielding to oxidation only with OH-radicals and smaller role of ozone in oxidation as earlier studied by Wang et al. [6]

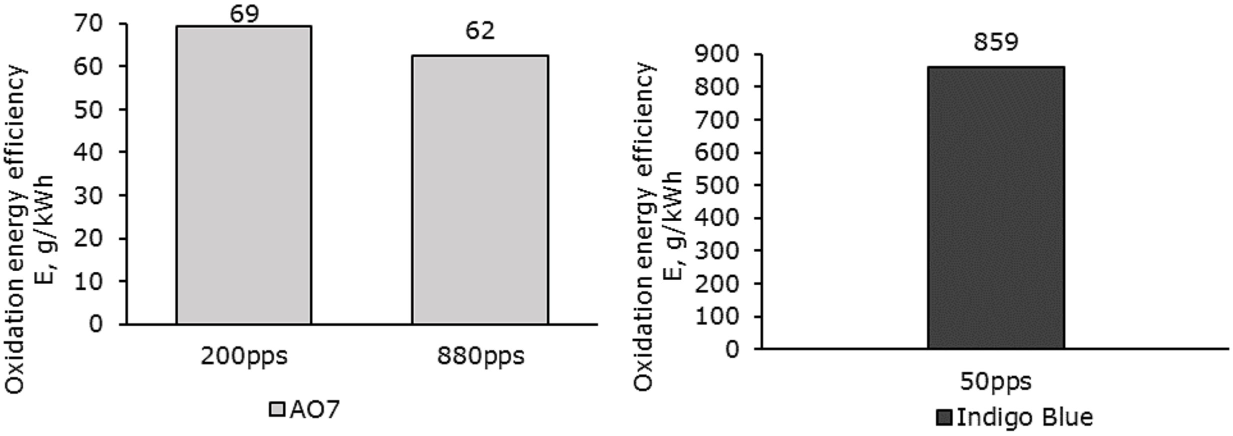

Figure 3.1. Effect of pulse repetition frequency on oxidation efficiencies of AO7 (left) and indigo blue (right) dyes: initial concentration of 10 and 46 mg/L respectively, pulse repetition frequency, pps (power delivered to reactor) of 200 (32 W) and 880 (123 W) for AO7 and 50 (9 W) for Indigo Blue, oxidation efficiency calculated for 90% degradation.

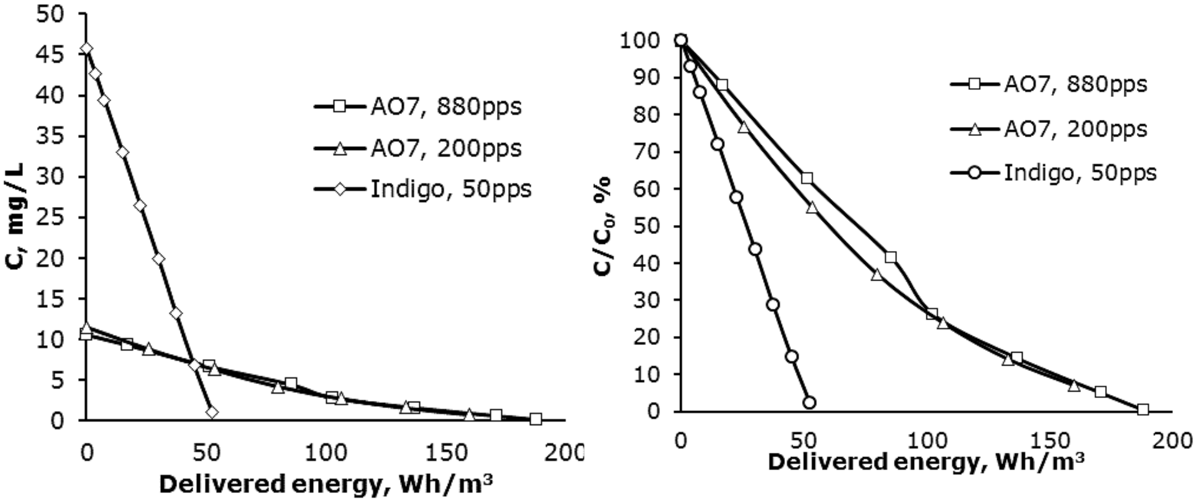

Figure 3.2. Dependency of absolut (left) and relative (right) concentrations of acid orange 7 (AO7) and indigo blue on pulsed energy delivered to the reactor at various pulse repetition frequencies: pH 7, reactor atmosphere air, temperature 22°C

High reactivity of indigo blue in comparison with AO7 may be explained by the number of sulphonic groups highly reactive with OH-radicals in the structure of indigo blue thus eliminating steric effects potentially attributed to the AO7 lower reactivity.

3.2 Effect of conductivity

Conductivity effect was determined using sodium chloride and sulphate. Figure 3.3 shows for AO7 dye (left), a decrease in oxidation efficiency from addition of both salts although the increase of conductivity to 20 mS/cm showed no significant difference from increasing conductivity to 10mS/cm. indigo blue dye showed a more visible decrease in oxidation energy efficiency as a drop was seen from 858.7 to 674.9 and 626.3 g/kWh for the use of sodium chloride and sodium sulphate, respectively. No significant difference was observed during the use of different salts thus excluding the possibility for electrolysis of chloride with evolution of free chlorine: curves of the colour degradation dependent on the delivered energy practically coincided for both chloride and sulphate (Fig. 3.4). Increased conductivity responsible for ohmic losses [77] resulted in decreased efficiency of dyes oxidation, no other effects were seen.

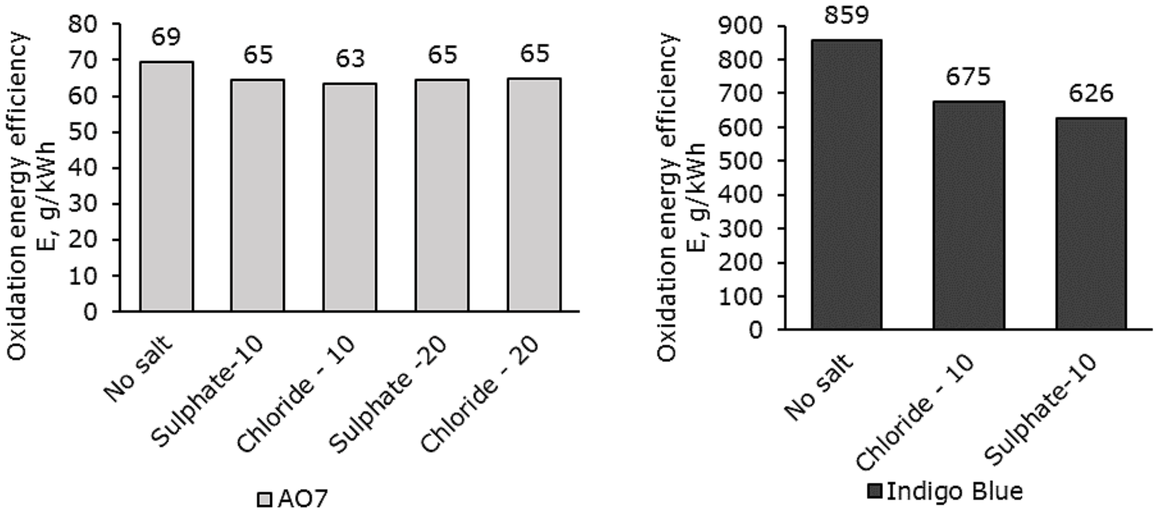

Figure 3.3. Effect of increased conductivity at 10 and 20 mS/cm on oxidation energy efficiency of AO7 (left), and indigo blue (right) dyes, initial concentration of 10 mg/L and 46 mg/L respectively, oxidation efficiency for 90% colour removal, pulse repetition frequency of 200 pps (32W) and 50pps (9W) for AO7 and indido blue dye, respectively at 22˚C

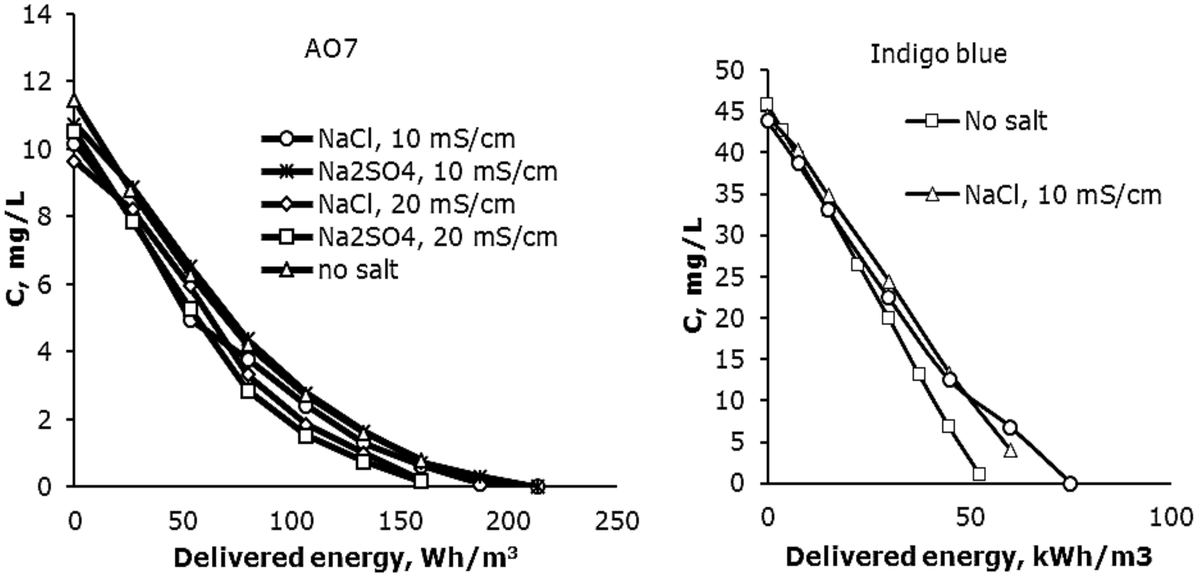

Figure 3.4. Colour degraded dependent on delivered energy at increased conductivity for AO7 (left) and indigo blue right (right), initial concentration of 10 mg/L and 46 mg/L respectively, oxidation efficiency for 90% colour removal, pulse repetition frequency of 200 pps (32W) and 50pps (9W) for AO7 and indido blue dye respectively at 22˚C

3.3 Effect of surfactants

Textile production wastewater used for the dying of fabrics and cleaning of excess dye contains detergents. This has made the investigation of the effect of surfactants in textile dye wastewater of importance for the surface character of reactions in PCD treatment. Besides, previous research, Onga et al. [12], showed the SDS surfactant dramatically enhancing PCD oxidation of reactive blue dyes RB4 and RB19. This work was carried out for expanding the knowledge in respect of different type of textile dyes.

The introduction of surfactant showed a significant increase in the oxidation rate of the AO7 and a decrease for indigo blue dyes on the other hand. Figure 3.5 shows the dependence of oxidation energy efficiency on the content of SDS in treated samples.

Oxidation of AO7 at 200 pps using 75, 100 and 150 mg/L concentrations of SDS degraded the dye showing 61, 76 and 111 g/kWh efficiencies, respectively, as compared to the one without SDS comprising 69 g/kWh at 200pps, i.e. the increase of energy efficiency from treatment without SDS to treating with 100 to 150mg/L SDS, comprises 10.1 and 60.9% respectively. Acceleration of oxidation of AO7 may be explained by the molecular interaction of SDS with AO7 which brings the dye molecules closer to the gas-liquid interface, the place of the radical species formation. SDS and AO7 are the anionic molecules of organosulphate class with similar hydrophilic sulphate functional groups and incomparable organic residues. The author does not have a reliable explanation for this phenomenon. However, a method called cloud point extraction (CPE), used for removal of textile dye from wastewater by floatation was reported by Kartal and Akbas, 2005 [78]: dye molecules are enclosed in surfactant micelles formed in the solution due to steric restriction of hydrophobic alkyl chains. This may explain the increased rate of degradation with surfactant, although SDS concentrations applied in the present research are much lower than those required for the micelles formation. Nevertheless, the established fact of molecular interaction between surfactants and textile dyes offers a reasonable explanation.

Oxidation of indigo blue dye in presence of SDS, on the other hand, was not promoted with SDS addition. The surfactant acted as a radical scavenger, screening off oxidants and thus reducing the oxidation efficiency consistently with the SDS concentration (Fig. 3.5). A steady decrease by 3.1, 4.5 and 9.7% in energy efficiency for 100, 150 and 200 mg/L respectively.

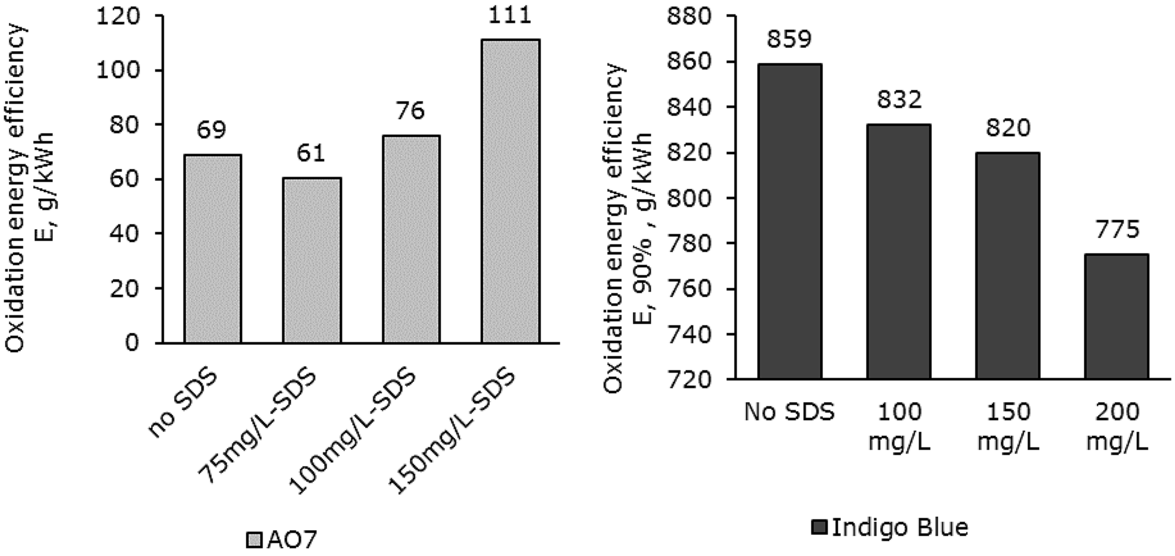

Figure 3.5. Dependence of AO7 (left) and indigo blue (right) oxidation efficiency on SDS concentration: pulse repetition frequency 200 and 50 pps respectively, reactor atmosphere air, temperature 22°C, spray density 0.3 m/s, no salts added.

3.4 Effect of temperature

Negative effect of increased temperature to the dyes oxidation rate is shown in Figure 3.6. In experiments with AO7 at 200 pps, temperature increased from 22 to 40 and 50 °C resulted in decreased oxidation efficiency from 69 to 42 and 28 g/kWh, respectively, i.e. the decrease in efficiency comprised 41% and 60%.

Oxidation of indigo blue also showed a decrease in efficiency with increased temperature: the raise from 22 to 45°C resulted in the efficiency decreased from 859 to 379 g/kWh, i.e. for 56%, with increased temperature.

Temperature effect was also studied in experiments at 200 pps with surfactant and inorganic salt added to the AO7 solutions. The results of AO7 PCD oxidation at SDS concentration of 150 mg/L are shown in Figure 3.7: with the temperature increased from 22 to 40°C and 45°C, the efficiencies of 44 and 31 g/kWh were achieved, which is dramatically lower than the number of 104 g/kWh observed at 200 mg/L of SDS (see 3.3. Effect of surfactants). A 62.2%, from 63.8 (Figure 3.3 above) to 24 g/kWh (Figure 3.7), reduction of oxidation efficiency also occurred with the increase of temperature from 22 to 50°C during the treatment of AO7 with an increased conductivity of 10 mS/cm.

Reduced oxidation efficiency at higher temperatures may be explained by scavenging side-reactions of OH-radicals described earlier by Ajo et al. [5]

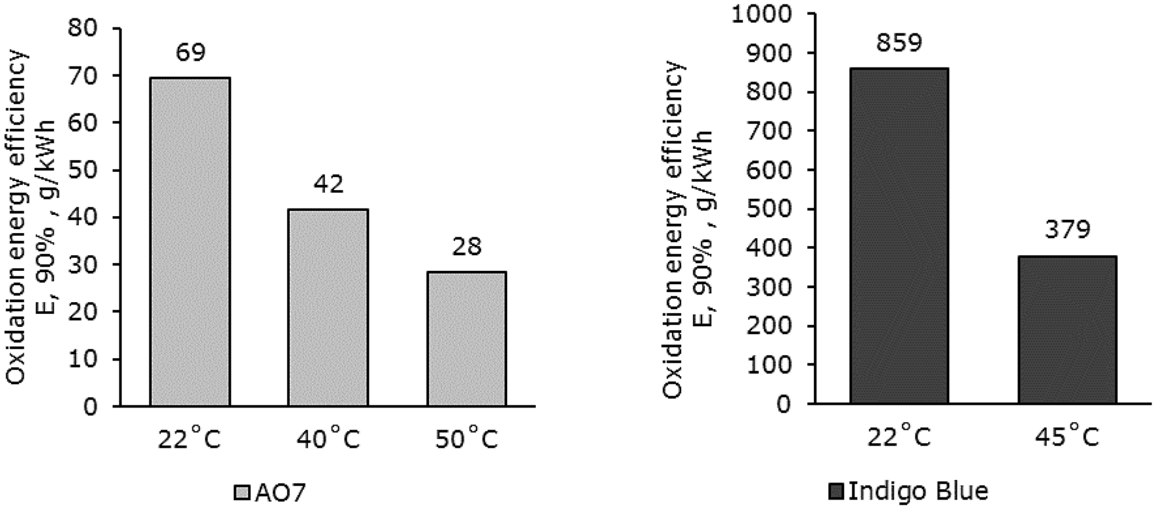

Figure 3.6. Effect of temperature on oxidation energy efficiencies of degrading AO7 (left) and indigo blue (right): pulse repetition frequency 200 and 50 pps respectively, oxidation efficiency for 90% colour removal considered.

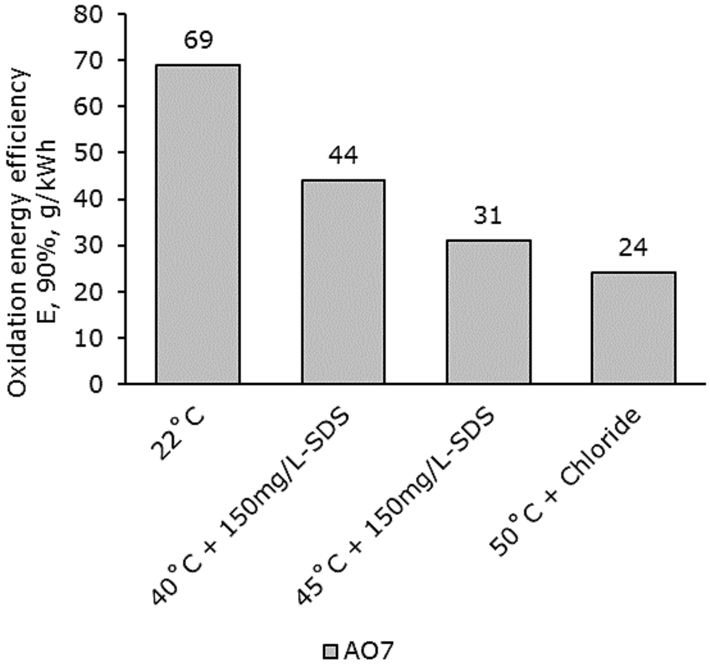

Figure 3.7. Effect of temperature on oxidation energy efficiencies of degrading AO7 in the presence of SDS, 150mg/L and single experiment showing effect with conductivity (10mS/cm): initial concentration of AO7 as 10mg/L, 200pps (32W).

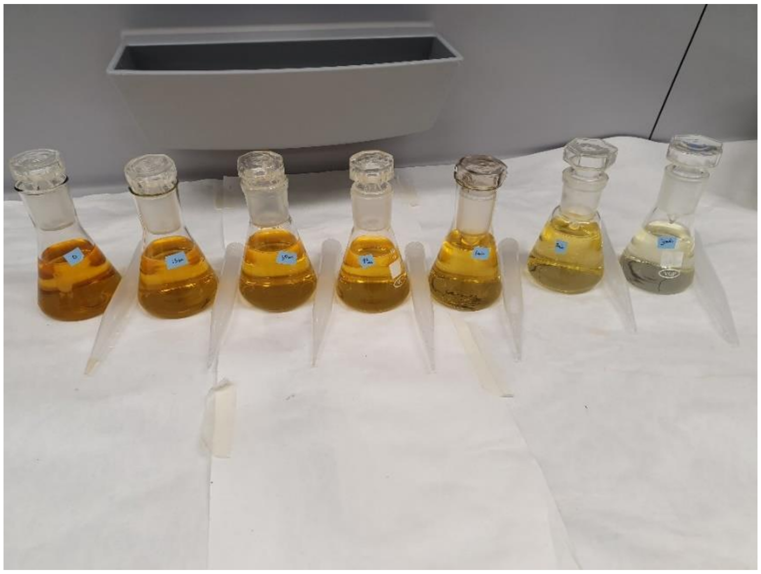

Figure 3.8. AO7 dye collected samples at different time intervals from initial state of decolouration to final state: initial concentration, 10 mg/L

Figure 3.9. Indigo blue dye collected samples at different time intervals from initial state of decolouration to final state: initial concentration, 46mg/L

Figure 3.8 and 3.9 shows dye solution samples from start of degradation process to final state of AO7 and indigo blue dye respectively.

4. CONCLUSIONS

Pulsed corona discharge has shown in this study to be effective in the degradation of textile dyes, acid orange AO7 and indigo blue. Experiments were targeted at the effect of external parameters including pulse repetition frequency, presence of surfactant, conductivity and temperature.

Oxidation efficiencies as high as 859 g/kWh for indigo blue at 50 pps, and 62.4 and 69.5 g/kWh for AO7 at 200 and 880 pps, respectively, were achieved at 90% degradation extent. Wu et al., during an ozonation experiment to enhance hydroxyl radical generation using carbon nanotubes, degraded AO7 dye at a 100 mg/L initial concentration in a 500-mL reactor where 95% of dye was degraded in 10 min, with a calculated energy efficiency of 34.0 g/kWh [79]. This efficiency is lower than the energy efficiency achieved degrading same dye using PCD method.

The moderate effect of the pulse repetition frequency in AO7 oxidation efficiency points to the predominantly radical mechanism of oxidation with minor role of ozone. Indigo blue, being utmost reactive substance, is most probably indifferent towards pulse repetition frequency for its ability to rapidly react with all available oxidants. Both textile dyes under consideration thus benefit in oxidation from high power, i.e. high pulse repetition rate. Such high reactivity of indigo blue is explained by the molecular structure containing four symmetrically positioned sulphonate groups, whereas AO7 molecule contains only one providing steric effect for the OH-radical attack.

Application of PCD in presence of surfactant showed a significant increase in the oxidation efficiency of AO7, while indigo blue dye showed a decrease in oxidation efficiency consistent with growing surfactant concentration. Such difference, although not precisely understood, may be explained by the difference in molecular structures: symmetrically positioned four hydrophilic sulphonate groups in the indigo blue molecule do not provide a possibility of interaction between hydrophobic moieties of SDS and the dye as with AO7 and reactive blue dyes as also reported by Onga et al. [14] The question requires additional studies for systematic approach with explicit answer to the question, why a molecule does benefit in oxidation from a surfactant presence, whereas another does not.

Conductivity increased by adding sodium chloride and sulphate to 10 and 20 mS/cm resulted in decreased oxidation efficiency of both dyes explained by ohmic losses in PCD reactor. Both salts behaved identically in dyes discoloration thus confirming the absence of electrolysis theoretically capable of free chlorine formation.

Effect of temperature elevated up to 50 °C in respect to dyes oxidation efficiency was consistently negative explained by increased water vapour concentration screening part of electronic beams from the treated water surface and increased rate of radical scavenging. The effect was consistent with reported earlier with other substances and seems to have a universal character. The effect of conductivity is summing with the one of temperature.

PCD method has shown to be promising in the treatment of textile dye contaminated water, given its energy-efficient character. The effects of detergent, temperature and conductivity disclosed in the present work quantify limiting factors considered in practice. Further study is recommended in the role of surfactants in removal of specific dyes. Offering a systematic approach to the observed phenomenon may be an asset.

SUMMARY

Dye pollution in textile manufacturing effluent brings a major environmental concern as these effluents contaminate water bodies by blocking sunlight penetration for the photosynthesis processes carried out by freshwater species and general production of sea water oxygen. As industrial textile activities across the world continue, the need for cost effective methods for dye degradation from textile wastewater and purification methods is becoming important.

In this study, a non-thermal plasma AOP method, pulsed corona discharge (PCD), was used to degrade acid orange 7 (AO7) and indigotetrasulfonate textile dyes. The effect of surfactant, conductivity, temperature, and pulse repetition frequency on the energy efficiency was evaluated and reported.

A laboratory-scale PCD reactor made by FlowRox Oy was used. Power supply to the reactor provided high-voltage pulses at the voltage peak of 18 kV, current peak 380 A, pulse duration 100 ns and pulse repetition rate of 50, 200 and 880pps, which correspond to 9, 32, and 123 W. The electrode system of the reactor consists of multiple strings, 20 m of total length and 0.55 mm in diameter. The strings are horizontally placed between two ground plates which are parallel to each other; the distance between the strings and the plates is 18 mm.

Results showed indigo dye reacting fast with oxidants at the oxidation energy efficiency of 859 g/kWh. Oxidation energy efficiency during the degradation of AO7 is also seen to increase with lesser delivered energy as 200 and 800 pps degraded at 69 and 62 g/kWh energy efficiencies respectively, considering 90% dye degradation.

Conductivity and temperature were noticed to have a negative effect on oxidation efficiency. The effect of electrolysis was neglected as the two inorganic salts used, sodium sulphate and sodium chloride, showed no practical difference in results. Sodium dodecyl sulphate (SDS) increased the degradation rate of AO7 by 57.7% at 200 mg/L of SDS and acted as a scavenger during the degradation of indigo blue dye reducing its oxidation efficiency by 9.7% at similar concentration.

In summary, the PCD method appears to be promising being effective with less energy consumption. Recommended further study would be to understand the role of surfactants in PCD oxidation of specific dyes and possible use of the effect of surfactant in practice.

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