Cape Peninsula University of Technology

REUSE OF A TREATED TEXTILE EFFLUENT FROM COBALT OXIDE AND SULPHATE RADICAL-BASED ADVANCED OXIDATION PROCESS

BY

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Abstract

Reactive dye waste effluents are the most difficult to treat, as they are highly polluted due to the structure of the dyestuffs and chemicals used during the dyeing process. Due to the water shortage and environmental pollution, textile industries are encouraged to treat the waste effluent produced during dyeing processes so as to facilitate its reuse, as this will contribute to mitigating environmental pollution and minimise water consumption. However, relatively few of the treatment technologies employed for the treatment of textile wastewater are applicable for water that is intended for reuse. Many treatment technologies exist for the treatment of textile waste effluents, but are either limited in efficiency or high in operating and energy cost. Chemical treatment methods such as the cobalt oxide mediated sulphate radical-based advanced oxidation process (CO-SR-AOP) shows promise but have not yet been evaluated for the reuse of textile wastewater in the dyeing process.

The purpose of this work is to study the reusability of a treated reactive dye effluent obtained from dyeing cotton fabrics using peroxymonosulfate (PMS) activated by a cobalt oxide (Co_3O_4) catalyst and using a laboratory-scale continuous wastewater treatment reactor. In order to achieve this, a cobalt oxide catalyst was hydrothermally synthesised, cotton fabrics were bleached as pre-treatment prior to being dyed using blue reactive dye and tap water to produce the necessary textile waste effluent. The produced waste effluent was treated with Oxone (PMS) and a cobalt oxide catalyst; then reused in the next dyeing process, using an identical dyeing recipe. The pH of the treated effluent was corrected to neutral before its reuse. The waste effluent from the first cycle of dyeing was treated before its next reuse. This process was carried out for a maximum of three cycles. The dyed fabrics obtained using the treated effluent were compared with the ones dyed with tap water in terms of colour fastness. The optimisation of the reusability of a treated effluent from cobalt oxide and sulphate radical-based advanced oxidation process was carried out using Design-Expert software version 11.1.2.0 using a Box-Behnken design taken from response surface methodology. The effects of three factors were studied: Oxone level, dye concentration and reuse cycles at low, high and medium levels in fifteen experimental runs. Colour fastness of the dyed fabrics was studied as the response of the trials.

Based on the preliminary results, the treated effluent can be reused in two successive reuse cycles without altering the fabric's quality. To obtain more or less 80% colour removal, waste effluent with 3% dye concentration must be obtained and treated with a high dosage of Oxone (3.5 g/l). Salt can be recovered by using this process, but with a darker shade of dyed fabric as a result, when compared with

the reference. Varying dilution factors and standing times of the treated effluent were investigated but did not have significant influence on the colour quality of the dyed fabrics.

A useful model was found to predict the colour fastness of dyed fabrics with an effluent treated with the continuous wastewater treatment reactor system using PMS activated by Co_3O_4. The study of the interaction effects of all three parameters led to the finding that to obtain good colour fastness grading of the dyed fabrics, the treated effluent can be reused a maximum of two iterations, with a dye concentration of 5% and an Oxone concentration of 1 g/L. The predicted optimum process conditions for this process were 1.3 g/l of Oxone used to treat a waste effluent with 4.4% dye concentration and reuse in a maximum of three reuse cycles.

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Dedication

To my dearest and loving parents

Andre and Sidonie Mangoua

For their encouragement, loving support, their guidance, advice and financial contribution throughout my studies

To my lovely sisters

Rachelle, Jeanne and Caro

For their support and encouragement

To my family and close friends for their encouragement and support.

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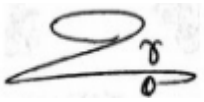
Declaration

I, Flash Colombe Tchono Depgni declare that this dissertation is my own unaided work. It is being submitted for the Master of Engineering Chemical of Engineering Degree at Cape Peninsula University of Technology, Cape Town. It has not been submitted before for any degree or examination in any other University.



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Glossary- Terms and concepts

AOPs: Advanced Oxidation Processes are efficient methods used to remove organics pollutants not degradable by means of biological processes.

Cellulosic fibres: Fibre structures created by dissolving natural materials such as cellulose or wood pulp, which are then regenerated by extrusion and precipitation.

Chemical Oxygen Demand (COD): Defined as the amount of (dissolved) oxygen required to oxidise and stabilise (organic and inorganic content of) the sample solution.

Colour fastness: Refers to the resistance of the colour of textiles to the different agents to which these materials may be exposed during manufacture and subsequent use.

Decolourisation: Removal of colour from a piece of fabric or wastewater.

Dyeing effluents: Polluted water obtained after the dyeing of a material.

Dyeing process: A process in which colour is transferred to finished textile materials to add permanent and long-lasting colour.

Effluent: Wastewater discharged into the environment and serving as a pollutant.

Exhaustion dyeing: The process of dyeing in which the textile takes all the available dyestuff.

Fixation: The step in the dyeing process in which the dye is fixed onto the fabric to avoid poor colour fastness.

Nanoparticles: Any particles less than 100nm are known as nanoparticles.

Reactive dye: A type of dye that completely saturates the fibre for long-lasting colour.

Reuse of textile effluent: The process of using treated textile wastewater for a beneficial purpose.

Synthetics fibres: Any of the various man-made textile fibres including those made from petroleum based resources materials.

Total dissolved solids (TDS): Are the solids dissolved in a water sample, and the value is approximately proportional to the measured conductivity of the water.

List of Abbreviations

ANOVA - Analysis of variance

AOP - Advanced oxidation process

BBD - Box-Behnken designs

COD - Chemical oxygen demand

CO -SR-AOP- Cobalt oxide sulphate radical advanced oxidation process

DF - Degrees of freedom

DoE - Design of experiments

MS - Mean sum of squares

PMS- Peroxymonosulfate

PRB - Permeable reactive barrier

RMS - Response surface methodology

SEM - Scanning electron microscope

SS - Sum of squares

TEM - Transmission electron microscope

WWTW - wastewater treatment works

XRD - X-ray diffraction

List of Symbols

Symbol	Description	Unit
A	Oxone level	g/l
B	Dye concentration	%
C	Reuse cycles	-
p- value	Probability	-
Adj.R^2	Adjusted coefficient of determination	-

Chapter 1: Introduction

1.1 Background

The scarcity of freshwater resources is a concern in many countries. Large cities such as Cape Town, Sao Paolo, Beijing, Istanbul, and Cairo, for example, face pressure to meet water demands for domestic usage and drinking. More than 60% of the world's population (largely in Asia, Africa and Latin America countries) lives with significant imbalances between water requirements and supplies (Thopil & Pouris, 2016). Due to the growing shortage of water, there is an urgent need to implement water reclamation methods such as the treatment, recycling and reuse of wastewater.

The textile industry is a major consumer of water, energy and chemicals, all utilised in dye-related processes. The industry produces large amounts of highly coloured wastewater (Wang, 2006). Over 20 to 40% of the dyes used in textile industries are released to the environment via effluent discharge (Singh, 2014). The generated effluent is therefore highly polluted with contaminants formed by unfixed dyes and other additives, such as cleaning, bleaching and rinsing agents used in the dyeing processes. These generated contaminated effluents present a danger to the environment and human health (Ozturk *et al.*, 2015).

Currently, the systems for treating dye wastewater are based on high operating and energy costs, generation of sludge, production of damaging by-products, the requirement of large amounts of chemicals and energy penalties (Vikrant *et al.*, 2018). Several methods of treatment of dye-house effluents have been proposed and investigated. Chemical or physical methods such as coagulation (Hendaoui *et al.*, 2018), adsorption (Guiza *et al.*, 2004), activated carbon (Wong *et al.*, 2018) and ion-exchange (Üstün *et al.*, 2007) have been used as treatments for dye removal. The difficulty in treatment of dye-house effluents is attributed to their high toxicity and resistance to biodegradation (Hendaoui *et al.*, 2018). Therefore, it is important to find effective treatment methods capable of removing both strong colours and toxic organic compounds from textiles wastewater (Ledakowicz *et al.*, 2001). Chemical oxidation techniques, such as ultraviolet photolysis (Souza *et al.*, 2018), Fenton reagents (Cetinkaya *et al.*, 2018), ozone reagents (Muthukumar *et al.*, 2004) and advanced oxidation processes (AOPs) are promising approaches towards the treatment and reuse of textile wastewater (Feng *et al.*, 2010). AOPs focus on persulfate radicals using cobalt oxide catalysts (Wang *et al.*, 2016; Cruz *et al.*, 2019; Rasheed *et al.*, 2019) and several other procedures have been explored as plausible treatment methods for textile wastewater treatment, and some of them for the reuse of textile wastewater.

Throughout this work, the feasibility of reusing treated dyeing effluent using cobalt oxide and sulphate radical-based advanced oxidation is presented. The effects of different parameters such as the dye concentration in dyeing process, Oxone concentration during the treatment process and the number of reuse cycles in the reuse dyeing process on the treated effluent and dyed fabrics were all evaluated.

1.2 Research problem

Most water treatment processes treat a textile waste effluent to disposable standards for discharge to wastewater treatment works (WWTW) or the environment. However, this does not lead to reduce use of water. Furthermore, advanced oxidation processes (AOP) such as cobalt oxide-mediated sulphate radicals advanced oxidation (CO-SR-AOP) could result in harmful by-products that are toxic to biological systems used in wastewater treatment. By using the treated effluent on site, this risk can be minimised. Treated effluent resulting from CO-SR-AOP has not been evaluated for reuse in the dyeing process.

1.3 Aim and objectives

The aim of this study was to assess whether textile wastewater from reactive dyes in the dyeing of cotton fabric, and treated using the cobalt oxide-mediated sulphate radical-based advanced oxidation process, will be suitable for reuse in dyeing processes in the textile industry. The objectives were to:

Reuse the same treated effluent in the dyeing process for three reuse cycles.

Characterise the treated textile effluent from cobalt oxide-mediated advanced oxidation process.

Characterise the colour fastness of fabrics dyed with domestic tap water and treated wastewater using the advanced oxidation process.

1.4 Significance

This study contributes to a great achievement for textile wastewater treatment processes, as the treated effluent can be reused instead of simply being standard disposed or discharged and therefore minimizing the load on municipal treatment works and most importantly saving water.

1.5 Delineation

In this study, only laboratory-scale work is carried out. Reuse of permeable reactive barriers was not investigated as part of this study. Fresh filters were prepared for each wastewater treatment run. No industrial textile effluent was evaluated, as industrial effluent contains many other additives that are

difficult to identify and contribute to the effect of dye uptake. Once the reuse process is understood with laboratory effluent, further studies will be conducted on more complex textile effluent.

1.6 Thesis structure

Chapter 1: In this chapter the background and the objectives of this study are presented.

Chapter 2: This chapter presents a review of the literature of all the different topics related to the reuse of treated textile effluent.

Chapter 3: In this chapter, the different equipment and research methodology used in this work are discussed.

Chapter 4: This chapter shows all the preliminary studies carried out on the treated effluent and dyed fabrics during this study.

Chapter 5: The effects of process parameters on colour fastness of the dyed fabrics are discussed here.

Chapter 6: In this chapter, the conclusions and recommendations of this study are presented.

Chapter 2: Literature review

2.1 Introduction

This chapter gives an overview of the textile industry, with specific focus on the dyeing of fabric, the characterisations of textile waste effluent and the effect of discharging textile wastewater into the environment. Furthermore, a brief description of the different treatment technologies used to treat textile wastewater is presented. Finally, the reusability of the treated textile wastewater is described.

2.2 Textile industry: An overview

The industrialisation of the world led to the expansion of many industries, among which is the textile industry. The industrialised textile industry was created after the invention of the multi-spindle spinning frame (Spinning Jenny) in the late eighteenth century in Britain. The industry then moved to Japan, Hong Kong, Taiwan and Korea from the 1950s to the 1980s. Next, the yarn and fabric manufacturing industry moved to China, India, Pakistan, Sri-Lanka, Bangladesh, Indonesia, Malaysia, the Philippines and Thailand in 1980 to 1990 (Nimkar, 2018). The textile industry was brought from Eastern Africa to South Africa by the South Asian emigrants in the mid-nineteenth century (Akyeampong *et al.*, 2014). South Asians perceived Eastern Africa not as a captive market, but as a partner for the development of textile production. Over the twentieth century, the textile industry experienced a major revolution, with widescale innovations in machinery, globalisation of businesses and the invention of synthetic fibres (Agarwal *et al.*, 2017).

Although the textile industry is a significant contributor to the economic wellbeing of countries, the industry consumes a large amount of water during their manufacturing processes, specifically during the wet processing operations (Hossain *et al.*, 2018). Their total production per year is estimated at 88.5 million tonnes of textile produtcs (Dey *et al.*, 2017). According to United Nations Environment Programme (UNEP, 2010), every year 400 to 500 million tonnes of deadly chemicals are discharged into the environment. During the manufacturing operations of the textile industry, more than 10,000 different dye colours are used, as well as the fact that their production of synthetic dyes is more than 700,000 tonnes annually, and most of the dyes used are recalcitrant to degradation (Ogugbue & Sawidis, 2011; Dey *et al.*, 2017).

2.2.1 Classification of dye

2.2.1.1 Natural dye

Before the twentieth century, natural dyes were the most widely-used colourants in dyeing processes. Natural dyes origin is mostly from plants; but they can also be extracted from animal, mineral and microbes (Bechtold *et al.*, 2003). The advantages of using natural dyes, among others, are the fact that they are renewable and biodegradable (Vankar, 2017). However, due to their poor properties with respect to colour fastness during washing, and also the fact that there are many varieties of synthetic dye available at low prices, their usage has tapered off (Samanta & Agarwal, 2009). Some examples of natural dyes are indigo, cochineal, madder, cutch, turmeric and ochre (Vankar, 2017).

2.2.1.2 Synthetic dye

A wide range of synthetic dyes found in the market is used in many industries such as textiles, cosmetics, leathers, plastic and paper (Forgacs *et al.*, 2004; Yang *et al.*, 2016). Synthetic dyes present superior colour fastness properties. Such dyes are usually characterised by the presence of chromophores and auxochromes. Chromophores are responsible for colour production, due to their capacity to absorb light in the near-ultraviolet region. Auxochromes help in the fixation of dye to the fibres over stable chemical bonds such as acidic groups ($-OH, -COOH$, -SO_3H) and basic groups $-NH_2, NHR_1$, NHR_2 (Erkurt, 2010).

Synthetic dyes can be categorised into direct dyes, azoic dyes, sulphur dyes, vat dyes, chrome dyes, metal-complex dyes, acid dyes, basic dyes, indigo dyes, pigment dyes, disperse dyes and reactive dyes. They can also be classified in terms of the colour index and chemical structures. Based on their chemical structures, the most important types of dyes are azo dyes, anthraquinone dyes and phthalocyanines (Mahapatra, 2016). Although they are the most used and produced in textile industries, they are also considered a major threat to the environment. Azo dyes are the most popular variety of dyes produced worldwide, since they are the most cost-effective. Their production represents 60 to 70% of all organic dye production (Silveira *et al.*, 2017). Azo dyes are versatile, with wide-ranging colours, are easy to manufacture, and stable at varying pH and high temperatures (Vastag *et al.*, 2018). They present high resistance to degradation due to their aromatic compounds in which one or more chromophoric azo groups are found (-$N = N$) as chromophore linked with aromatic systems connected to other groups such as $-OH, SO_3H, NO_2$ and Cl (Elfarash *et al.*, 2017), as illustrated in Figure 2-1. However, Singh (2014) states that azo dyes with hydroxyl or amino groups were found to be easier to degrade than those with methyl, methoxy, sulpho or nitro groups. Some examples of azo dyes are: acidic, basic, direct, disperse, mordant, reactive and solvent dyes (Vastag *et al.*, 2018).

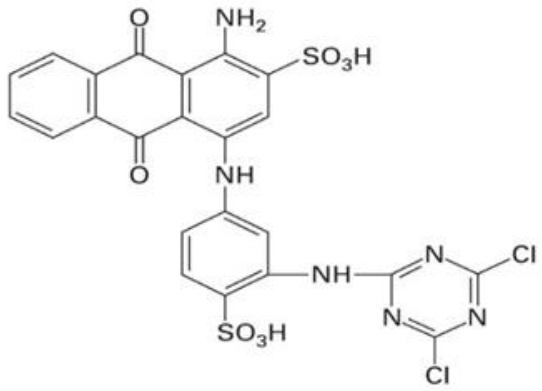


Figure 2-1: Chemical structure of C.I. Reactive Blue 4 (Christie, 2007)

Among azo dyes, reactive dyes are the most used due to their large production. 175000 tonnes (25%) of azo dyes are reactive dyes, and they are usually used with cellulosic fibres at high temperatures and a wide range of pH, as they present high affinity to bond with cellulosic fibres (Petcu *et al.*, 2016; Khemila *et al.*, 2018). Hence, the production of reactive dyes has grown around the world and it is considered to be at four times the level of that of conventional dyes (Karim *et al.*, 2018). Reactive dyes are linked to chromophoric groups responsible for the formation of a covalent bond with the hydroxyl groups of the cellulosic fibres during the dyeing process, while the unfixed dye is hydrolysed and removed in the dye bath effluent (Christie, 2007). Nevertheless, reactive dyes are known to be the most difficult to treat, as their rate of fixation to the fibres is low; with less than 70% to 90% fixation rate (Christie, 2007). The fixation rate of reactive dyes is generally affected by the type of fibres, the chemicals in the dyeing process, the required shade and finally the number of reactive groups present in the dye (Karim *et al.*, 2018). Their low fixation rate is due to their tendency to react with water instead of reacting with the hydroxyl group of the cotton fibres (Christie, 2007). Therefore, dyeing effluents from reactive dyes are one of the principal sources of many environmental pollution problems (Karim *et al.*, 2018).

2.2.2 Textile fabric types

The textile industry produces and uses a diversity of fibres. Textile fibres can be classified into two main types: natural fibres and manmade fibres (Mahapatra, 2016). Natural fibres are derived from the organisms such as plants or animals and they are based on protein and cellulose. Manmade fibres, on the other hand, are mostly derived from petroleum sources (Mahapatra, 2016).

Cellulosic fibres are made from regenerated or derivative fibrous polymers such as wood pulp. Synthetic fibres, on the other hand, are manufactured from non-fibrous materials, often undergoing complex chemical reactions to form the fibre-forming substances (Houck, 2009). Usually, cellulosic fibres such as cotton, linen, rayon and jute fibres are dyed with reactive dyes, as seen in Figure 2-2, due to the fact that their reactive group can easily react chemically with the cellulosic reactive groups of the fibres (Soleimani-Gorgani & Taylor, 2006) On the other hand, synthetic fibres are dyed with disperse dyes, as

they are known to have better stability at various stages during the dyeing process (Markandeya *et al.*, 2018).

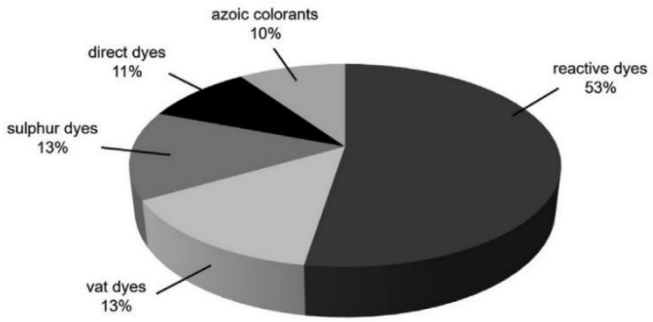


Figure 2-2: Estimated consumption of dyes for cellulosic fibres (Burkinshaw & Salihu, 2017)

The two most important textile fibres used in the textile industry are polyester and cotton. Polyester fibres have difficulties absorbing dyestuff molecules due to their hydrophobic character and tendency to swell to a very small extent in the water bath. Polyester fabrics are only dyed with disperse dyes, due to the fact that they don't have active chemical groups in their molecules (Mohamed, 2010). Reactive dyes are used to dye most cotton fabrics, due to the fact that they produce a full range of shining colours with a high degree of colour fastness when washing (Khatri *et al.*, 2015). Cotton fabrics present many advantages, such as strong fibres, a high degree of comfort for the wearer, are easy to launder and dry-cleaning, have good absorbency and they are good conductors of heat. The ease of cotton fabrics for dyeing or printing processes means that cotton fabrics can be dyed with almost all the classes of dyes beside acid, basic and disperse dyes, due to their lack of affinity with these dyes. However, cotton fabrics have drawbacks, such as their high flammability and tendency to retain water, when compared to nylon and polyester (Souza, 1998).

2.3 Textile wastewater from the textile industry

2.3.1 Dyeing process

The textile industry includes different divisions in its operations, such as de-sizing, printing, dyeing, sieving, scouring, washing, rinsing, bleaching, mercerising, carbonisation, finishing and dyeing processes. The dyeing process is one of the wet processes of the textile industry that produces the most hazardous wastewater, as an average of 60 to 70% of the auxiliary dyebath is consumed during this process (Speel & Schwarz, 2013). The first necessity of any dyeing process is to obtain a stable colour fastness of the dyed fabric, as the main objective of this process is to change the shade of the material (Alam *et al.*, 2008). The dyeing process is divided into many stages in which alkali and inorganic electrolytes are added to the dyebath solution (Siddiqua *et al.*, 2017). Using reactive dyes to dye cellulosic fibres produces strong

covalent bonds. However, the dyes can react with the hydroxyl group of the water, instead of reacting with the hydroxyl groups of the cellulose, which highlights the importance of using exhaustion and fixation agents (Abo Farha *et al.*, 2010; Ru *et al.*, 2018). To improve the capacity of the fabric, especially cellulosic fibres to adsorb the dyestuff, the addition of inorganic electrolytes such as sodium chloride (NaCl) or sodium sulphate (Na_2SO_4) is necessary; this step constitutes the exhaustion of the dyeing process (Burkinshaw & Salihu, 2017). The addition of alkali (Na_2CO_3) constitutes the fixation step, which is also an essential step in the dyeing process of cotton using reactive dyes (Haque *et al.*, 2015). This fixing agent also helps in the hydrolysis of the dyes (Uddin *et al.*, 2014). According to Siddiqua *et al.* (2017), a reactive dyeing process can require 50 to 100 g/l of salt per process, depending on factors such as the expected colour of the fabric, the types of dyes and the dyeing process recipe.

Testing the colour fastness with respect to washing of the fabric is one of the very important tests carried out on the dyed fabric. The evaluation of the wash fastness can be carried out by comparing the difference between the treated and raw samples with greyscale for altering the colour of the dyed sample and discolouration of adjacent fabric in a colour-matching cabinet (Talukder et al., 2017). Table 2-1 represents the numerical rating for colour changing, which is based on the shade and alteration to the adjacent fabric.

Table 2-1: Colour fastness with respect to washing and rubbing grading assessment (Talukder et al., 2017)

Greyscale	
Numerical rating	**For wash and rubbing**
1	Poor
2	Moderate
3	Average
4	Good
5	Excellent

Therefore, each dyeing process is characterised by the types of metals, salts, surfactants, organic processing aids, sulphide and formaldehyde added to improve the dye adsorption of the fibres (Carmen & Daniel, 2012). Haque *et al.* (2015) studied the rate of exhaustion and fixation of dyeing on cotton fabric using three reactive dyes (Remazol Red RR, Remazol Yellow RR and Remazol Blue RR) at four different concentrations (0.5%, 1%, 2% and 3%). They found an excellent rate of exhaustion (88.5%) and fixation of 74% when they used reactive dye blue RR. Haque *et al.* (2015) also found that higher concentrations of dyes give poor compatibility. Therefore, they suggest that in order to improve dye compatibility with the fabrics, it is better to add more electrolytes, and reduce the temperature and the amount of alkali used.

Figure 2-3 shows the different steps involved in a typical dyeing process. This process depends on many parameters, such as the liquor ratio, dye type; dyeing time, temperature, salt and alkali concentration.

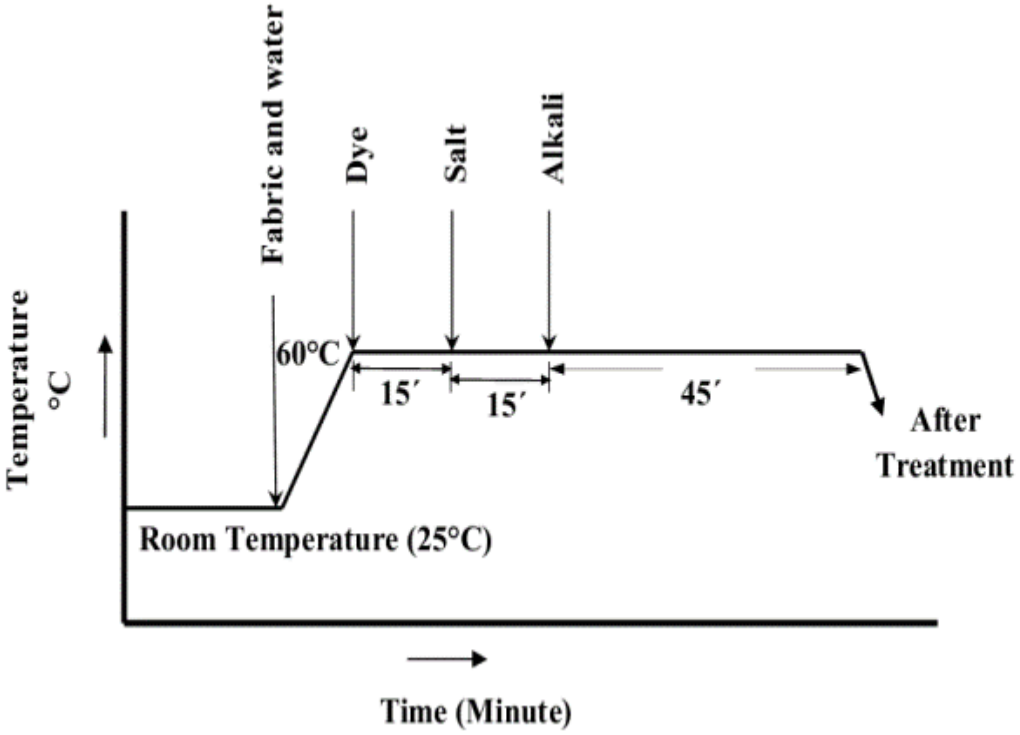


Figure 2-3: Dyeing curve (Naser & Haque, 2014)

2.3.2 Characterisation of textile effluent

Textile wastewater produced by the textile industry differs depending on the type of process, equipment used, the kind of fabric utilised and the amount of wastewater (Dilaver *et al.*, 2018; Koyuncu & Topacik, 2003). According to Rajasimman and Co-workers (2017), textile wastewater is characterised by chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS), total dissolved solids (TDS), high concentrations of chemicals, unfixed dyestuffs, inorganic salts and heavy metals such as plumbum, cadmium, zinc, manganese, nickel, copper iron and so on, as presented in Table 2-2 below. Nevertheless, during the pre-treatment of fabrics prior to dyeing, pH, alkali content and hydrogen peroxide are also some examples of physicochemical parameters that characterise the effluent water from the textile industry (Harane & Adivarekar, 2017).

Table 2-2: Example of characterisation of textile wastewater (Rajasimman *et al.*, 2017; Fazal *et al.*, 2018)

Characteristics	Units	Value
pH		5.6-9.0
Temperature	°C	35-45
Conductivity	mS	6.89
COD	mg O_2/L	250-8000
BOD	mg O_2/L	50-550
TSS	mg/L	100-700
TDS	mg/L	5000-10000
NH_4^{+1}	mg/L	50
NO_2^{-1}	mg/L	350
Total PO_4^{-1}	mg/L	4.0-12
SO_4^{-2}	mg/L	50-900

2.3.3 Effects of discharging the textile effluent into the environment

Textile wastewater is known to be one of the most hazardous wastewaters for the environment when discharged without any proper treatment (Hayat *et al.*, 2015). Due to its characteristics, effluent from the textile industry can be considered harmful to both the environment and human health (Rajasimman *et al.*, 2017). Groundwater and bodies of surface water can be affected by leaching to the soil when the effluent is discharged, because of its high colouration (Raman & Kanmani, 2016). According to Elfarash *et al.* (2017), textile effluent can cause the reduction of photosynthetic activity due to the presence of aromatic groups, metals and chlorides.

Vutskits *et al.* (2008) investigated the effects of methylene blue on human health and found that methylene blue has neurotoxic effects on the nervous system in high concentrations. Inflammatory alterations, skin necrosis and skin telangiectasias are also effects of methylene blue on the human body. The azo chromosphere in textile wastewater can be transformed into toxic, mutagenic and cancerogenic amines (Stagnaro *et al.*, 2015). The genotoxicity of Acid yellow 7 has been demonstrated by (Mansour *et al.*, 2007) who argue that Acid yellow 7 can cause skin irritation and allergy to humans body.

2.4 Treatment technologies applied to textile wastewater

Many technologies have been reported to treat textile wastewater, depending on the type of dyes used during the dyeing process. Figure 2-4 represents the corresponding diagram of the different methods of treatment applied to textile wastewater, and each type is discussed below.

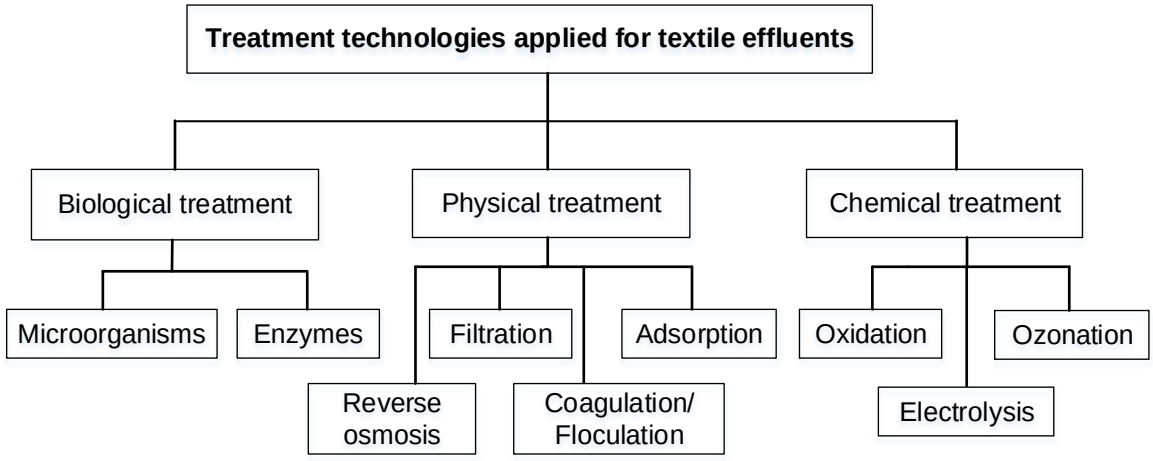


Figure 2-4: Different treatment technologies applied to textile wastewater diagram (Saratale *et al.*, 2011)

2.4.1 Biological treatment

Many studies have been conducted on the treatment of textile wastewater using biological methods. Biological methods used for the treatment of textile effluent can utilise microorganisms (bacteria, fungi and algae) or enzymes (Paz *et al.*, 2017). Paz *et al.* (2017) used culture media such as Nutrient Broth (NB), Luria-Bertani Broth (LB) and Trypticasein Soy Broth (TSB) to degrade three commercial dyes. Complete degradation of 150 mg/L of Coomassie Brilliant Blue G-250 was obtained at 37 °C (Paz *et al.*, 2017). The advantages of this treatment method are that it is environmentally friendly, there is less production of sludge and less consumption of water, full degradation of the pollutant and, finally, is applicable for a wide range of dyes (Solís *et al.*, 2012; Holkar *et al.*, 2016; Sahinkaya *et al.*, 2017). However, the main weakness of this treatment is the fact that the treated water is not in accordance with the standard disposal values from environmental regulations, as it contains recalcitrant organic compounds (Holkar *et al.*, 2016).

2.4.2 Physical treatment

2.4.2.1 Membrane filtration

Membrane technology has been studied for the treatment of textile wastewater. It can consist of ultrafiltration, microfiltration, nanofiltration, reverse osmosis and forward osmosis membranes. They present many advantages, such as the removal of any type of dye. For example, tight ultrafiltration membranes were found by Lin *et al.* (2016) to be effective for colour removal and salt removal in textile wastewater. However, as textile wastewater is highly salty, it can reduce membrane permeability and be the cause of membrane fouling, which results in high maintenance cost and short lifetime (Buscio *et al.*, 2015).

2.4.2.2 Adsorption

This technique is based on the capacity of dyes to attract adsorbents. The adsorption method is generally carried out using activated carbon, nanoparticulate absorbents. This technique has low budgets (low operating conditions), high treatment efficiency and reusability of the adsorbent (Ahmad *et al.*, 2015; Wong *et al.*, 2018). Although this technique has many advantages, it also presents some disadvantages, such as the high cost of replacement and regeneration of activated carbon and the limitation of usage (Santos & Boaventura, 2015).

2.4.2.3 Coagulation-flocculation

The coagulation-flocculation process is used as pre-treatment process, as it only focuses on removing suspended solids contained in wastewater. Therefore, it must be combined with other techniques, such as the Fenton process or membrane processes, for example, to obtain efficient treatment results (GilPavas *et al.*, 2018). Some drawbacks of this method are the production of highly concentrated sludge (Hassanzadeh *et al.*, 2017); and the fact that it is only effective on selective dyes for colour removal (Hai *et al.*, 2007).

2.4.3 Chemical treatment

Advanced oxidation processes are promising treatment methods for textile wastewater, as they produce hydroxyl radicals or sulphate radicals, which are strong oxidising agents. UV processes, chlorine, hydrogen peroxide, Fenton's reagent, ozone, or potassium permanganate are all promising oxidation processes for the treatment of textile wastewater (Sreeja & Sosamony, 2016). Although the advanced oxidation processes based on Fenton's reagent produce high amounts of iron and need neutralisation steps during treatment, it gives high COD and colour removal (Salim *et al.*, 2016). Oxidation processes using photocatalysts have the benefit of not requiring electricity during the process. One of the most-used catalysts is titanium dioxide (TiO_2) as it is cheap, stable and highly reactive (Verma *et al.*, 2012). Magnesium oxide (MgO) can also be used in the photocatalysis process, as it is a good semiconductor. However, it cannot be used for the treatment of industrial textile wastewater, as it has selective compatibility (Jorfi *et al.*, 2016). Therefore, the use of catalysts is important in oxidation processes.

The ozonation process has benefits, as it does not produce sludge because the only chemical used is ozone, and it dissolves into water and oxygen (Punzi *et al.*, 2015). In order to improve the efficiency of ozone, it can be combined with an alkaline solution, ultraviolet, peroxone, as well as catalytic ozonation (Ghatak, 2014). The disadvantages of the oxidation process utilising ozone is the production of highly toxic and difficult-to-degrade by-products during the treatment process (Verma *et al.*, 2012).

2.4.3.1 Advanced oxidation process with a focus on the persulfate radical

As mentioned previously, advanced oxidation processes (AOPs) have been found to be more efficient than conventional treatment methods for the treatment of the strong pollutants produced by textile industries. AOPs based on the production of sulphate radicals have shown some advantages, such as:

Sulphate radicals are strong oxidising agents with high oxidation potential (E°= 2,5~3,1) and are highly reactive.

They have a long half-life of 30-40 µs.

They are reactive within a wide range of pH (3-8).

They are stable at room temperature.

Transition metals, such as silver (Ag^{+}), cobalt (Co^{2+}), copper (Cu), iron (Fe^{2+}), manganese (Mn^{2+}), nickel (Ni^{2+}) and Ruthenium (Ru^{3+}) are used to activate persulfate and peroxymonosulfate via electron transfer for the generation of sulphate radicals (Xiong *et al.*, 2014; Fang *et al.*, 2017; Ma *et al.*, 2017). Equation 2.1 shows the activation of the persulfate process by ferrous ions (Liu *et al.*, 2018). Because of its low cost and its environmental friendliness, iron is the most-studied activator of the persulfate process. However, the sulphate radicals produced go through a fast reaction, due to the rapid reaction between ${F_e}^{2+}$ and ${S_2 0_8}^{2-}$ to form ${F_e}^{3+}$ ions (Wu *et al.*, 2015; Cai *et al.*, 2016).

$$ {F_e}^{2+} + {S_2 0_8}^{2-} \rightarrow {F_e}^{3+} + {S0_4}^{-\cdot} + {SO_4}^{2-} \qquad (2.1) $$

Consider Equation 2.2, which shows the activation of peroxymonosulfate by manganese metals (Xu *et al.*, 2017). Common metal oxides, such as manganese oxides, are highly reactive and also can be considered as commonly used in the persulfate process (Xiao *et al.*, 2018).

$$ M_n(III) + {S_2 0_8}^{2-} \rightarrow M_n(IV) + {S0_4}^{-\cdot} + {SO_4}^{2-} \qquad (2.2) $$

Zero valent aluminium ($ZVAl$) has also been found useful for the activation of peroxymonosulfate, as it presents a high efficiency in the decomposition of persulfate to produce sulphate radicals in water. Equation 2.3 shows how the $ZVAl/O_2/persulfate$ process degrades organic pollutants by producing sulphate radicals (Khatri *et al.*, 2018).

$$ 2Al^{\circ} + {S_2 0_8}^{2-} + 6H^{+} + 1.5O_2 \rightarrow 2Al^{3+} + 2{S0_4}^{\cdot -} + 3H_2O \qquad (2.3) $$

Granular activated carbon (GAC) as a catalyst has been known to be a good porous element for the activation of persulfate, due to its permeable structure and high porosity. GAC's micro and macroporosity are involved in the production of sulphate radicals, as seen in the following equations (Liu *et al.*, 2018).

$$GACSurface - OOH + S_20_8{}^{2-} \rightarrow S0_4{}^{-\cdot} + \text{GACsurface} - OO^- + HSO_4{}^- \quad (2.4)$$

$$GACSurface - OH + S_20_8{}^{2-} \rightarrow S0_4{}^{-\cdot} + \text{GACsurface} - OO^{\cdot} + HSO_5{}^- \quad (2.5)$$

Furthermore, Liu *et al.* (2018) used the sonoluminescence mechanism to form zinc oxide surface electrons ($ZnO_{Surf}e^-$) to react with persulfate to produce sulphate radicals, as seen in equation 2.6 below.

$$ZnO_{Surf}e^- + S_20_8{}^{2-} \rightarrow S0_4{}^{\cdot -} + SO_4{}^{2-} + ZnO_{Surf} \quad (2.6)$$

The following equation illustrates the use of zero-valent copper to produce copper ions for the decomposition of peroxymonosulfate to produce sulphate radicals (Ghanbari *et al.,* 2014).

$$Cu^+ + HSO_5{}^- \rightarrow Cu^+ + S0_5{}^{\cdot -} + OH^- \quad (2.7)$$

Wang *et al.*, (2017) used $Fe - Ag/GAC\ /Ps$ to degrade a strong dye, Acid Red 73. By doping the process withAg, rather than using simple iron, efficient colour removal and total carbon removal after an hour was achieved. Equation 2.8 shows the activation of $S_20_8{}^{2-}$ by Ag^+ to produce sulphate radicals and sulphate.

$$Ag^+ + S_20_8{}^{2-} \rightarrow Ag^{2+} + S0_4{}^{\cdot -} + SO_4{}^{2-} \quad (2.8)$$

Figure 2.5 shows the activation process of persulfate by iron-based metal-organic $MIL - 53$ for the catalytic degradation of Orange G by the production of sulphate radicals in aqueous solution by Pu *et al.* (2018).

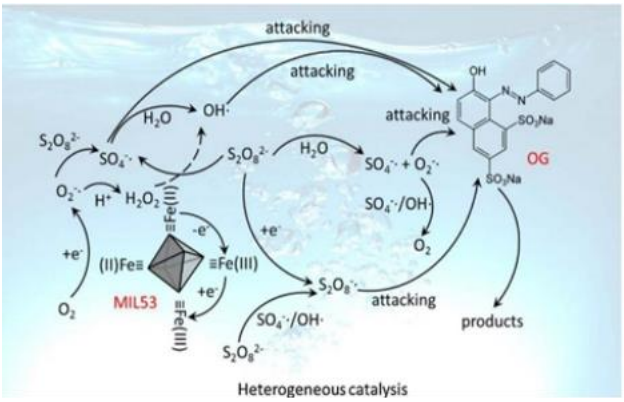


Figure 2-5: Activation process of persulfate by iron-based metal-organic $MIL-53$ (Pu *et al.*, 2018)

The activation of PMS by cobalt was found to be more efficient than the traditional Fenton reaction at neutral pH with a lower dosage of reagent. The production of sulphate radicals by the activation of PMS can be represented by the following equations. $CoOH^+$ is the most active species to activate PMS, (Equation 2.9). The next equation (2.10) illustrates the maintenance of the concentration of cobalt at low dosage during the regeneration of $Co^{2+}$by the reduction of Co^{3+} (Hu & Long, 2016).

$$CoOH^+ + HSO_5^- \rightarrow CoO^+ + SO_4^{\cdot -} + H_2O \qquad (2.9)$$

$$Co^{3+} + HSO_5^- \rightarrow Co^{2+} + SO_5^{\cdot -} + H_2O \qquad (2.10)$$

An illustration of the activation process of PMS via cobalt is presented in Figure 2.6.

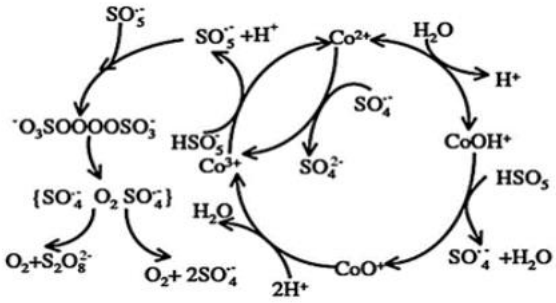


Figure 2-6: Activation process of PMS via cobalt oxide catalyst (Hu & Long, 2016)

Table 2-3 below shows some studies in which AOPs focused on sulphate radicals have been used for the treatment of textile effluent. In this table, iron aggregates, manganese oxide and nanoparticle cobalt oxide were used to activate persulfate and peroxymonosulfate for the treatment of different types of azo dyes. In this table, the results are focused in terms of colour removal and COD/TOC removal during the decolourisation of different dyes. None of these processes were applied in the reuse of treated textile effluent.

Table 2-3: Application of advanced oxidation processes (AOPs) based on persulfate/peroxymonosulfate in the treatment of textile wastewater

AOP focus on persulfate	Dye types	Colour removal	COD/TOC removal	References
Fe^0aggregates/persulfate (PS/Fe^0)	Direct dyes		COD: 85% 5	Liu *et al.* (2018)
Persulfate activation by Fe/SBA-15	Acid Orange II	≤94.5%	COD: 75.4% TOC: 46.3%	Cai *et al.* (2016)
$\boldsymbol{MnO_2}$ to activate (PDS)	Acid Orange 7	> 76.8%	-	Xu *et al.* (2017)
$\boldsymbol{ZVAl}$/persulfate	-	97.9%	COD:94.4%	Khatri *et al.* (2018)
$\boldsymbol{Fe-Ag/GAC}$ catalytic persulfate	Acid Red 73	98.4%	TOC: 84.1%	Wang *et al.* (2017)
Activation of persulfate by $\boldsymbol{MIL-53}$	Orange G	≥99%	COD :74%	Pu *et al.* (2018)
$\boldsymbol{UV-LED/FeTiO_3}$ activated persulfate	Disperse Blue 3	92%	TOC:95%	Silveira *et al.* (2018)
$\boldsymbol{Ultrasound/ZnO-GAC/persulfate}$	Acid Orange 7	91.2%	TOC:83.1%	Liu *et al.* (2018)
$\boldsymbol{ZVI}$ activated $\boldsymbol{PMS}$	-	95.6%	-	Ghanbari *et al.* (2014)
$\boldsymbol{Ultrasound/Fe^{2+}/UVC/Ps}$	Azorubine	81.2%	TOC:68.35%	Chakma *et al.* (2017)
$\boldsymbol{Persulfate\ (PS)/BiOI/Fe_3O_4}$	Rhodamine B	-	TOC:44.9%	Liu *et al.* (2018)
Nano C_3O_4 activate $\boldsymbol{PMS}$	Acid Orange 7 (A07)	-	TOC:70%	Chen *et al.* (2008)

2.4.3.2 Effects of parameters on advanced oxidation process focused on persulfate radical

Stoyanova and co-workers (2014) investigated on the degradation of acid orange 7 (AO7) by activating peroxymonosulfate (PMS) with cobalt (Co) and iron-cobalt ($CoFe_2$) oxides nanoparticles supported on MgO. They studied the variation of the catalyst from 0.15 g/l to 0.5 g/l with constant PMS/AO7 molar ratio of 10:1. It was found that with Co/MgO, Co_2Fe/MgO and $CoFe_2$ /MgO at 0.15 g/l, a complete degradation of AO7 was observed at 13, 15 and 25 minutes respectively. Processes run with 0.5 g/l of catalyst led to obtained 100% dye degradation in 7, 9 and 14 minutes for Co/MgO, Co_2Fe/MgO and $CoFe_2$ /MgO respectively. On other hand, the effects of the variation of the concentration of PMS were also studied by them at constant concentration of AO7 (50 mg/l) with 0.15 g/l of Co/MgO catalyst. When PMS/AO7 molar ratio was 40:1, a complete degradation was observed in less than 10 minutes; while with molar ratio of 2:1 of PMS/AO7 complete dye degradation was observed in 30 minutes.

The degradation of methylene blue (MB) using supported cobalt oxide on MgO by activating PMS were done by Zhang et al. (2010). They found a complete degradation of MB concentration with Co/MgO in less than 8 minutes with 0.5 mM of Oxone in 200 ml of MB solution.

The removal of methylene blue was also studied by Wang et al (2016) using waste material of incineration ash (IBA) to support cobalt oxide catalysts for the production of sulphate radicals. The optimisation of Co/IBA led to obtain 81% in 20 minutes when 50 mg of Co/IBA was applied while 99% was observed in 8 min when 250 mg of catalysts were used for 0.1 mM of MB solution and 0.4 mmol of Oxone. Dosage of Oxone was also optimised; it was observed that with 0.2 mmol of Oxone 71% of MB degradation was obtained in 20 minutes. When the amount of Oxone increased to 0.5 mmol, complete colour degradation was observed in 8 minutes with a constant amount of catalyst (250 mg) and 0.1 mM of MB solution in both cases.

Thus, more catalyst accelerates the production of persulfate radicals from Oxone activation responsible for colour degradation; the higher the amount of Oxone is used during the treatment process, the higher is the dye removal efficiency.

2.5 Water reuse concept in the textile industry

The reusability of treated textile effluent is a relatively new concept, and few investigations in this topic are found in the literature. The requirement for the reuse of textile wastewater is that the treated effluent should not compromise the quality of the fabric properties (Harane & Adivarekar, 2017). The efficiency of the reuse process depends on prior treatment applied to treat the effluents (Yuzer *et al.*, 2014). According to Moussa *et al.* (2013), in order to evaluate the success of a dyeing process from treated effluent, three criteria must be validated:

Colour conformity.

Levelness.

Colour fastness of the dyed samples.

The standard value accepted by the textile industry for the colour difference is usually less than 1 (ΔE<1) between the quality performance of two dyed samples. As the colour difference value approaches zero, the closer the recycled water is to the standard (Farias *et al.*, 2017). Different steps applied before reusing a treated effluent are described by (López-Grimau *et al.*, 2011):

Adjust the pH to 7 after the effluent treatment

Quantification of the salt residuals (NaCl and Na_2SO_4) in order to know the amount of salt that still needs to be added.

Reconstitution of the initial dyebath volume, adding water if necessary.

Add dyestuff and start a new dyeing process.

2.5.1 Colour conformity

Laboratory-scale ceramic membrane ultrafiltration with various sizes (300KDa, 50KDa, 15KDa and 3KDa) have been used for the regeneration and reusability of hot discharge textile waste (Dilaver *et al.*, 2018). Ceramic membrane with molecular weight cut-off (MWCO) of 3KDa was found to give treatment efficiency. Hence, the MWCO of 3KDa was for the treatment of mixed hot discharge printing washing baths for their reuse in dense dyeing and printing bath washings. Although the application of this method led to the reuse of 22% of the total water consumption in laboratory scale, an optimisation of the membrane filtration operating conditions and cleaning procedures needs to be studied for printing baths of hot effluents. Furthermore, a ceramic microfiltration membrane made of alumina and clay was combined with a bio-sorbent from sugarcane bagasse for the treatment of industrial textile wastewater in batch scale prior to reuse in the dyeing of cotton fabrics using reactive dyes (Red 198, Yellow 198 and Blue 171) by Bhattacharya *et al.* (2015).

Although the results showed that the reuse for blue dyes was not in the acceptable range, further studies need to be performed for scaling up this process.

Harane and Adivarekar (2017) studied the reuse of textile wastewater treated by microfilters of 0.45 µm pore sizes in textile pre-treatment processes such as de-sizing and scouring. They explain that the wastewater obtained from the pre-treatment process of the fabric can be reused without being filtered,

as there is not a significant difference between the fabric pre-treated with treated wastewater and the untreated wastewater.

The cotton fabrics pre-treated with reused wastewaters were then dyed with CBFIX Navy Blue HER and CBFIX Yellow HE6G dye. The colour difference of the fabrics shown that navy blue dyed fabrics had colour difference (ΔE) less than 1, while the yellow dyed fabrics had ΔE above 1, whether the water was passed through the filters or not. This was explained by the fact that during the scouring process, the whiteness index of the fabrics de-sized was lower. Compared to the standards (fabrics dyed with normal pre-treated process), improvements in terms of washing fastness, rubbing fastness and light fastness properties of the samples dyed with reused water were observed, with grading of 4-5; 4-5 and 6 respectively, which mean “Good” to “Excellent”.

Harane and Adivarekar (2017) also managed to save 40% of the full processing cost of fabric by saving 50% and 19% of water and chemicals respectively when the process was applied in a cotton textile processing mill with a production of 1 ton per day. However, combined methods such as homogenisation-decantation treatment and polyvinylidene difluoride (PVDF) ultrafiltration membranes by Buscio *et al.* (2015), led to colour difference of less than 1.5 when reusing the treated effluent in the next dyeing process, for 100% permeate with one dye and 50% diluted permeate with three dyes. This value should be less than 1, but 1.5 is described as acceptable by the authors. Buscio and co-workers, (2015) used two different pilot membranes to treat the effluent after the homogenisation and decantation treatment. The first pilot plant was a laboratory PVDF ultrafiltration membrane (U-1b) and the second membrane was a semi-industrial membrane (U-4). The results showed that U-4 membranes have 33% higher colour removal efficiency than U-1b membranes. The use of this process shows promising results in reuse studies, as in laboratory dyeing process of polyester fabrics using disperse dyes.

Nevertheless, Do *et al.* (2005) found industrially-acceptable values of 0.9 colour difference for cotton fabrics dyed with treated effluent using bioprocess combined with an ultrafiltration membrane made with mini-cassettes of cellulose triacetate and Optisal Red 7B dye. The laboratory-scale continuous system was used to recycle a treated effluent prior to dye without altering the quality of the fabrics. Therefore, the amount of salt left in the treated effluent was considered in the reused dyeing process.

Treated textile effluents were reused for the dyeing and bleaching of cotton fabrics by Yuzer *et al.* (2014) using granular activated carbon (GAC), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) processes for the treatment of collected biologically-treated textile wastewater (BTWW) from five cotton fabric plants. The treated effluent from the nanofiltration membrane was treated by the lime-soda

softening method before its reuse as saline dyeing liquor. In a benchmark, the reuse of each treated effluent was carried out using Ramozol yellow, red, and blue reactive dyes. The treated effluent was also used in washing and bleaching of 100% cotton fabrics. Acceptable colour difference (less than 1.0) was observed for NF and RO membranes, while the opposite was observed for UF and GAC.

Bhuiyan *et al.* (2014) studied the reusability of treated effluent irradiated by cobalt-60 gamma radiation for the dyeing of cotton fabrics with three reactive dyes (blue, yellow and red). A comparison of the fabric samples dyed with treated effluent and the ones dyed with tap water revealed "Good" to "Excellent" ratings for colour fastness with respect to washing measured by greyscale (4 to 5) for both types of fabrics. The analysis of variation of shade was found in an acceptable range of 0.02 to 0.9 colour difference. Treated effluent from cotton fabric processing was also reused in the irrigation of Malabar (India) spinach plant by Bhuiyan *et al.* (2016). The wastewater treatment by gamma irradiation was found to have fertilizing properties, as the nitrogen content increased during treatment. Hence, the irradiated wastewater was appropriate for the growth of spinach plants and was satisfactory for reuse in wet processing in the textile industry.

Senthilkumar and Muthukumar (2005), Hu *et al.* (2016) and Bilińska *et al.*, (2019) investigated the reusability of textile dyeing effluent using advanced oxidation processes based on ozone and catalytic ozonation respectively. Senthilkumar and Muthukumar (2005) tried the reuse of the treated wastewater five times, using reactive dyes Red 5MR and Golden Yellow MR on cotton fabrics. Comparisons between the standards and the fabrics dyed with red 5MR led to 1.39 colour difference in the third recycle and 2.68 in the fifth. The same thing was observed with Golden Yellow MR dye, as in the third cycle the ΔE was in the acceptable range of 1.01, while the ΔE was above the acceptable range, with a value of 2.16, in the fifth reuse. Thereafter, the evaluation of the visual appearances of hues of the fabrics was either Excellent or Good for every sample (high or low colour difference). Therefore, Senthilkumar and Muthukumar (2005) concluded that the reusability of treated textile effluent using ozonation was possible for only three reuse cycles, and improvements on the recycling process needed to be undertaken to produce more products with acceptable quality.

Bilińska *et al.*, (2019) investigated the use of ozone for the treatment of industrial textile wastewater and its reuse up to four times in laboratory scale. In this study, reactive (yellow 145, red 195 and black 5) dyes were used to dye cotton fabric. During the recycling process of treated effluent, extra salt (NaCl) was not added. The colour difference of the first reuse was equalled to 1.16. Contrary to reuse II to IV, where ΔE was more than 1.5 which is not in the acceptable range. However, Hu *et al.* (2016) combined ozone with mesoporous carbon aerogel supported by cobalt oxide catalyst for the treatment of reactive dyeing

wastewater in laboratory-scale. The efficiency of the treatment using catalytic ozonation increased the COD removal by thirty per cent (30%) compared to a simple ozonation process. The authors managed to reuse the treated effluent twice, and the quality of the dyed fabric was found with ΔE of 0.19 and Good colour fastness, with ratings of 4.5 ratings compared to the standard.

However, Mittersteiner *et al.* (2017) investigated treated textile wastewater using industrial waste with an eye towards its reuse for dyeing cotton fabric using Direct Black 22 dye. When the dye concentrations were 0.5, 1.0 and 1.5%, the weight of the fabrics and the colour difference with respect to the standard were 0.7, 0.46 and 0.32 respectively, with thermally treated industrial effluent. Colour fastness of all the samples was 4-5 ratings.

Nautiyal and Shukla, (2018) studied the possibility of reusing treated effluent from nylon, silk and wool fabrics using C.I. Acid Red 249 dye. After the treatment of the wastewater with a non-sulphur agent, sodium borohydride and silver nanoparticles, the reuse studies were carried out 5 times without adding any extra salt. Colour fastness was identical for all samples. However, the colour difference was 0.8 for the first three reuse cycles, then 0.7 for the fourth reuse, and finally 1.2 for the fifth reuse.

2.5.2 Colour

Moussa and colleagues (2013) evaluated the possibility of reusing treated effluent from acid dye (Blue Marine Inganol 2RLS) and reactive dye (Blue Lanesyn BLS) for wool dyeing. The residual wastewater was reused 20 times, using a dye concentration of 1%. To minimise error, each dyeing was carried out twice and the reconstitution of the dyeing recipe was carried out using the analytical method. At each reuse, the wastewater was diluted with no more than 10 ml of freshwater as initially, the volume of the water was 200 ml. Colour fastness with respect to washing was evaluated at each reuse and Good to Excellent (4 to 5) grading was obtained for fabrics dyed with reactive dye. Ratings of 5 were obtained for dyed fabrics with acid dyes. No significant deterioration of shade was found, as the colour difference of every sample was less than 1.

López-Grimau *et al.*, (2011) studied the possibility of reusing treated effluent and recovering salt after dyeing the cotton using reactive dyes (navy blue, crimson red and Yellow Procion H-EXL). The colour difference between the fabrics dyes used with treated effluent was less than 1.

Furthermore, López-Grimau *et al.*, (2013) worked on reusing the treated effluent in 10 successive cycles in a benchmark scale. Seventy per cent (70%) of total water and an average of 60% of salt (NaCl) was saved in this work. Colour difference (ΔE) with respect to the reference was less than 0.5 for the first and

second reuse; then ΔE was between the 0.5 to 1.5 for the next reuse cycles for reactive red and yellow. The colour difference of fabric dyed with blue reactive dyes give acceptable colour difference (ΔE less than 1.5) in the first reuse; from the second to the tenth cycle ΔE was more than 1.5.

Biological treatment using enzyme horseradish peroxidise was applied for the reuse of treated textile effluent by Farias *et al.* (2017) in pilot scales. The reuse was carried out by diluting 50% of dyeing solution with 50% of clean water. The reuse process was attempted twice on cotton fabric using reactive dyes (blue and red). In the first cycle, ΔE equalled 0.6, and Good colour fastness of 4 was obtained; while the second dyeing yielded colour difference of 1.08, with the colour fastness grading of 3, due to the prohibitions of protein adsorption of the dye by the fibre, leading to colour failure.

The combination of reverse osmosis concentrate with persulfate oxidation and lime-soda softening was used for the treatment of real textile wastewater by Zheng *et al.*, (2015). The treated effluent was reused three times using Yellow X-G, Red X-3B and Blue X-R reactive dyes on cotton fabric. Here the authors considered ΔE more than 1 as unacceptable. Therefore, with the first reuse, ΔE was 0.63 for yellow and more than 1 in the other two cycles. With red dyes, dE was 0.24 and 0.85 for both first and second reuses. With blue dye, ΔE was 0.17 and 0.47 for reuse I and reuse II respectively. Colour fastness was Good to Excellent (4-5) with all three types of dyes in the first reuse. In the second reuse with yellow, the colour fastness was 2-3. For red and blue, the ratings were 3-4. For reuse 3, colour fastness ratings were 1, 1-2 and 2 for reactive dyes yellow, red and blue respectively.

2.5.3 Summary of fabric properties obtained with treated textile effluent

Table 2-4 below presents a review of the reuse concept of treated textile wastewater in dyeing processes, using mostly azo dyes from 2005 to 2019. In this table, the number of reuse cycles varies from two to twenty. The results are focused on the dyed fabric's properties, such as colour difference and colour fastness at the end of each cycle.

Table 2-4: Review of the reuse concept of the treated textile effluent

Methods used	Colour difference	Colour fastness	Reuse cycles	Dye types	Fabrics types	Authors
Bioprocess combined with cellulose triacetate ultrafiltration membrane	0.9	-	-	Reactive	Cotton	Do *et al.* (2005)
Ozonation	< 1.5 for reuse I to III	-	5	Reactive	Cotton	Senthilkumar and Muthukumar (2005)
Water dyebath reconstitution by dilution	< 1	4-5	20	Acid/Reactive	Cotton	Moussa *et al.* (2013)
Electrochemical decolourisation	< 0.5 for reuse I to II	-	10	Reactive	Cotton	López-grimau *et al.* (2013)
Nanofiltration with lime soda	< 1	-	-	Reactive	Cotton	Yuzer *et al.* (2014)
Cobalt-60 gamma radiation	0.02 to 0.9	4-5	-	Reactive	Cotton	Bhuiyan *et al.* (2014)
Homogenisation-decantation and PVDF ultrafiltration membranes	<1.5 for 100% Permate 1 dye <1.55 for 50% permeate with three dyes	-	1	Polyester	Disperse	Buscio *et al.* (2015)

Reverse osmosis with a combination of persulfate oxidation and lime-soda	<1 reuse I and II > 1.5 reuse III	4-5 reuse I 3-4 reuse II 1-2 reuse III	3	Reactive	Cotton	Zheng *et al.* (2015)
Catalytic ozonation	0.19	4.5	2	Reactive	Cotton	Hu *et al.* (2016)
Enzymatic: Horseradish peroxidase	0.6 reuse I 1.08 reuse II	4 reuse I 2-3 reuse II	2	Reactive	Cotton	Farias *et al.* (2017)
Microfiltration	<1 for blue > 1 yellow red dyes	-	-	Reactive	Cotton	Harane and Adivarekar (2017)
Adsorption	<1.5	-	-	Direct	Cotton	Mittersteiner *et al.* (2017)
Ceramic membrane ultrafiltration	-	-	-	Disperse, reactive	Cotton	Dilaver *et al.* (2018)
Catalysed silver nanoparticles Sodium borohydride	0.8 reuse I to IV 1.2 reuse V	-	5	Acid	Nylon, silk, wool	Nautiyal and Shukla (2018)
Low-cost adsorbent	<1.5	4-5	-	Reactive	Cotton	Leal *et al.* (2018)
Combination of electrocoagulation and ozone	1.16 reuse I > 1.5 reuse II to IV	-	4	Reactive	Cotton	Bilińska *et al.* (2019)

2.6 Design of experiments (DoE)

Design of experiments (DoE) is a statistical methodology through which effective experimentation in engineering processes can be achieved to determine cause-and-effect relationships, in particular where it is not possible to explore all possible combinations of the levels of the causing factors. In engineering, DoE is used for the exploration, estimation and confirmation of processes (Antony, 2014). The theory of DoE is applied to setups such as randomised, screening, factorial and split-plot designs, to build linear and response surface statistical models, and to use these for optimisation of the process (Morris, 2011).

2.6.1 Response surface methodology (RSM)

Using DoE helps to vary many factors simultaneously and to establish the relations between independent variables (factors or parameters) and dependent variables (responses). Response surface methodology (RSM) is used for the optimisation of the response with reduced numbers of experiments (Hassanzadeh *et al.*, 2017), which is the determination of optimum operating conditions, such as determining factor levels that lead to the maximum or minimum estimated response (Murray *et al.*, 1990). RSM is a collection of several designs such as central composite (CCD) and Box-Behnken designs (BBD). In this work, a BBD design was employed.

2.6.2 Analysis of variance (ANOVA)

The analysis of variance (ANOVA) is an analytical technique used to identify the significance of the model terms using Fisher's F-test, by calculating the F-ratio, sum of squares (SS), degrees of freedom (DF), mean sum of squares (MS) (Box *et al.*, 2005). By using BBD, a second-order quadratic polynomial regression model equation is developed to fit to the experimental data by application of the Design-Expert software (Noordin *et al.*, 2004; Dhawane *et al.*, 2015) as seen in the equation below:

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} {X_i}^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} b_{ij} X_i X_j$$

Here b_0, b_i, b_{ii}, b_{ij} represent the regression coefficients and X_i (*i = 1, … , k*) are the coded independent variables. The F-test and its p-value are used to determine the significance of the regression coefficients. The significance of the model terms is determined by using p-values less than 0.05, indicating the statistical significance at 95% confidence level (Noordin *et al.*, 2004; Nautiyal & Shukla, 2018). The comparison of the effect of all the variables at a particular point in the design space is carried out by using perturbation plots. The perturbation plots read the effect of two factors, while one factor is kept constant at the reference midpoint of all factors (Morero *et al.*, 2017).

According to Murray and co-workers (1990), two-dimensional and three-dimensional surface plots are used to define the interaction effects of two factors as the third one is held constant. The only reason for

that is because only graphs in two dimensions can be carried out. The desirability of the response from numerical optimisation is an objective function by which the desirability of the response ranges between 0 and 1, where 0 means least desirability and 1 most desirability.

2.7 Conclusion

In summary, the textile industry mostly uses synthetic dyes, as a large range of these is found in the marketplace and they present good colour fastness with respect to washing, unlike natural dyes. Among synthetic dyes, azo dyes are the most important types, due to their global production (and thus availability), as well as cost-effectiveness. Their major drawback, however, is their high resistance to degradation because of their structure. Reactive dyes are the most common types of azo dyes used, due to their high production and the fact that they can be used at high temperatures, and at a wide range of pH. They also have high affinity to bonding with cellulosic fibres. However, they have low fixation rates onto the fabrics, due to their high affinity to react with water instead of the fabrics. Most reactive dyes are used to dye cellulosic fibres (cotton, linen, rayon and jute fibre) due to the fact that a chemical reaction occurs between their reactive groups. Cotton and polyester fibres are the most important fibres used by the textile industry. However, polyester fibres are only dyed with disperse dyes, due to their lack of chemical groups in their structure.

To avoid the reactive group of reactive dyes reacting only with the hydroxyl groups of water instead of the hydroxyl group of cotton fabrics, exhaustion (addition of salt) and fixation (addition of soda ash) steps are carried out during the dyeing process of cotton fabrics using reactive dyes. Colour fastness in washing is performed to evaluate the quality of the dyed fabrics, as the principal objective of the dyeing process is to change the shade of the fabrics without altering the quality of the dyed fabrics.

The waste effluent produced by the textile industry is highly polluted. This waste effluent, when discharged without proper treatment, is hazardous to the environment and to human health. Many treatments, such as biological, physical and chemical processes, have been used for the treatment of textile wastewater. All these treatments present many disadvantages, such as high energy consumption, being financially costly, and producing highly toxic by-products, among others.

The reuse of treated textile wastewater is a new practice in textile wastewater treatment. The main objective of this method is to treat an effluent and reuse the same treated effluent in multiple reuse cycle without altering the properties of the dyed fabrics. However, limited investigations are found in literature relating to the reuse in dyeing of textile dyeing effluent. None of the studies on textile dyeing effluent treated with a cobalt oxide-mediated persulfate radical-based advanced oxidation process was further

evaluated for the reuse of the treated effluent in the available literature. Therefore, further studies need to be carried out to assess the reusability of these effluents produced via the sulphate radical-based advanced oxidation process.

Chapter 3: Research methods

3.1 Introduction

This chapter explains in detail the different procedures and the corresponding apparatus used for a complete reuse dyeing process using cobalt oxide and carried out to obtain a sulphate radical-based advanced oxidation process. The experimental work consisted of firstly dyeing cotton fabric; secondly treating the wastewater using a cobalt oxide mediated sulphate-radical advanced oxidation process (CO-SR-AOP) for reuse, and lastly analysis of the resulting fabric (colour fastness) and quality of the treated wastewater.

3.2 Fabric dyeing process and characterisation

3.2.1 Pre-treatment

Initially, cotton grey fabric contains impurities and dark starch; therefore, it was important to perform a cotton fabric pre-treatment for the removal of impurities and starch in order to improve the fabric whiteness prior to the dyeing process. Untreated cotton fabric (6 m^3) was cut, and then put in a laboratory washing machine. The washing machine was set to 90°C, and 500 ml of hydrogen peroxide and sodium hypochlorite respectively were added, with 2 g/l of soap. The washing machine was set to 1 hour for 1 cycle. Figure 3-1 shows pictures of untreated fabrics and treated fabrics.

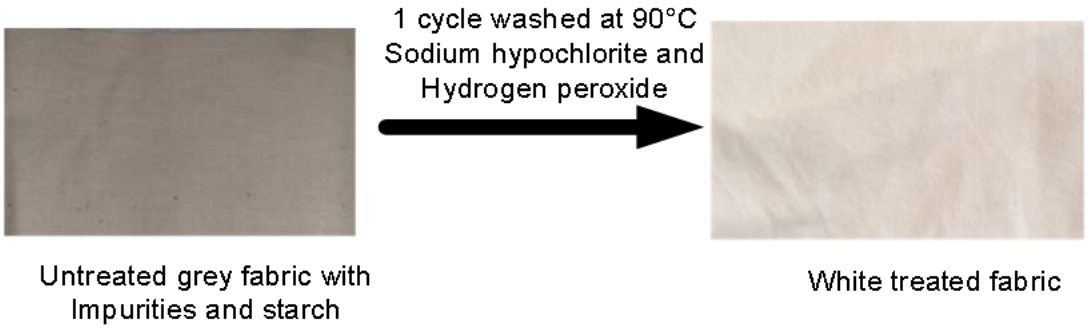


Figure 3-1: Pictures of the untreated cotton fabric (left) and treated cotton fabric (right)

3.2.2 Dyeing procedure

The dyeing process was carried out by using the PYROTEC MB2 dyeing machine for the production of textile wastewater and the dyed fabrics. The machine can accommodate up to fourteen dye tubes in a single dye cycle. This process was carried out using the recipe below. Calculations were performed to determine the total mass of the fabrics. Knowing the liquor ratio (50:1) and the maximum amount of water the dyeing tubes could take (150 ml), the mass of the fabric was calculated as follows:

$$mass\ of\ fabric\ (g) \times liquor\ ratio = 150ml \tag{3.1}$$

Therefore, the mass of the fabric is:

$$mass\ of\ fabric = \frac{150ml}{50ml} = 3g$$

The mass of dye was obtained as follows:

$$dye\ mass = percentage\ of\ dye \times mass\ of\ the\ fabric \tag{3.2}$$

The calculated mass of the reactive dye was poured into a beaker with 150 ml of cold water and the solution's temperature was set to 40°C. The Pyrotec MB2 dyeing machine was heated to 80°C and the dye solution was added in the dyeing tube. Cotton fabric (3 g) was immersed in the dyebath solution and the dyeing machine was kept running for 20 minutes. After the first 20 minutes, the exhaustion step, which was the addition of 80 g/l of salt (Na_2SO_4) to the dye bath, was implemented, and the mixture run for another 20 minutes. The fixation step was carried out, which was the addition of 20g/l of soda ash (Na_2CO_3), and the fabric was kept there for 30 minutes. Finally, the fabric was rinsed with cold water for 10 minutes, after which the fabric was boiled in a solution of 1 to 2 g/l soap and 1 to 2 g/l soda ash for about 10 minutes. Lastly, the fabric was rinsed with warm water at 50°C for 10 minutes, and the rinsed fabric was dried at ambient temperature. Figure 3-2 presents the dyeing process diagram at each step, with the temperature and time variations.

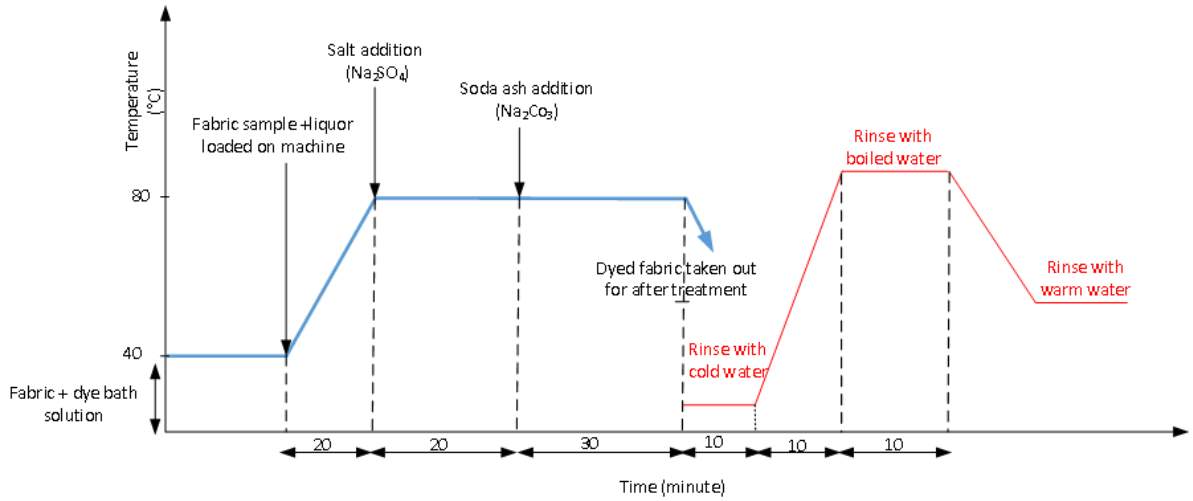


Figure 3-2: Dyeing process diagram

3.2.3 Colour fastness

After the rinsing step of the dyeing process, the fabric was left to dry at ambient air temperature. Colour fastness with respect to washing was completed according to the ISO recommendation No.1.5, using the

washing machine (WASHTEC-P) to wash the dyed fabrics. This machine can accommodate twelve metallic pots of 500 ml each during the same washing test cycle. The evaluation of wash fastness by the WASHTEC-P machine was helpful to contrast the treated and untreated sample with greyscale for the changing colour of the dyed samples. Colour fastness of the dyed fabrics was carried out in two steps.

The first step was to prepare the washing solution by adding 5 g of soap without optical brightening agent (ECE formulation phosphate reference detergent) in 1 L of water. In the next step, a piece of multifibre was cut. This multifibre piece was taken as a measurement to cut the dyed fabric to the same size. Then, the two fabric pieces were sewed together with a white sewing thread. The liquor ratio used was 50:1. The sewed fabrics were weighted to perform calculations to determine the amount of washing solution. The amount of washing solution used per washing pot was found by multiplying the obtained mass by the liquor ratio. The sewed fabric was then washed in the WashTech machine for 30 minutes at 40°C. After 30 minutes, the sewed fabrics were rinsed thoroughly with tap water and dried at ambient air temperature.

The second step consists of performing the colour fastness analysis. This test was carried out in the colour machine cabinet (Figure 3-3 a). The purpose of this test was for viewing, comparing, analysing and matching the colour of two samples under different lighting conditions. The change in the colour test was assessed using a greyscale, as seen in Figure 3-3 b).

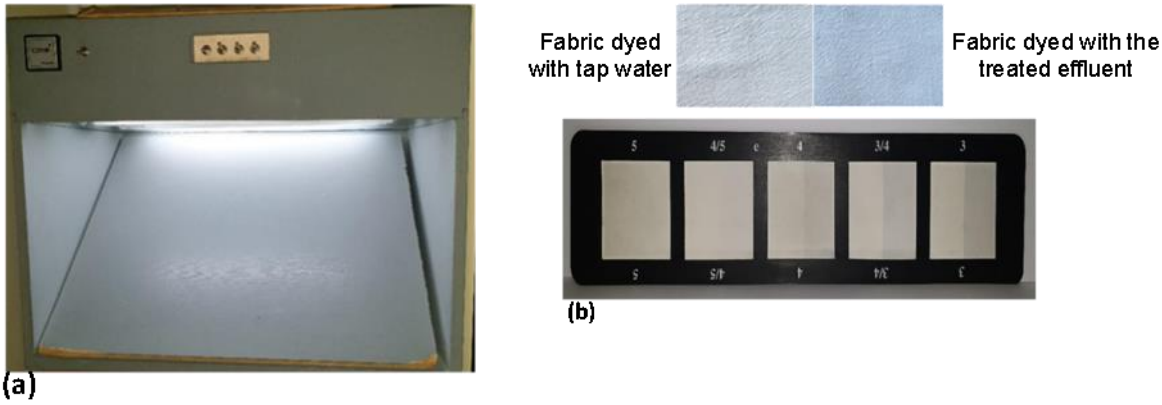


Figure 3-3: a) Colour matching cabinet and b) assessment of colour fastness test using a greyscale Wastewater treatment and characterisation

3.2.4 Catalyst preparation and characterisation

The preparation of cobalt oxide catalyst was carried out by hydrothermal synthetises using a Teflon-lined autoclave. Cobalt chloride (18 g) were measured in a beaker and added to 600 ml of ethanol. The solution

was stirred until the cobalt chloride powder was completely dissolved. The pH was adjusted by adding ammonium hydroxide drop-wise while stirring until a pH of 8.10. The solution was then poured into the one-litre Teflon-lined autoclave reactor. The autoclave temperature and time were set to 105°C for 6 hours. After 6 hours, the supernatant was decanted. The next step was to centrifuge the bottom product and rinse with deionised water and ethanol. The bottom product was put in the oven at 30°C to dry in order to obtain cobalt hydroxide (CoOH). Finally, CoOH was crushed before its calcination in the furnace at 300 °C for 3 hours to produce the cobalt oxide catalyst, as seen in Figure 3-4.

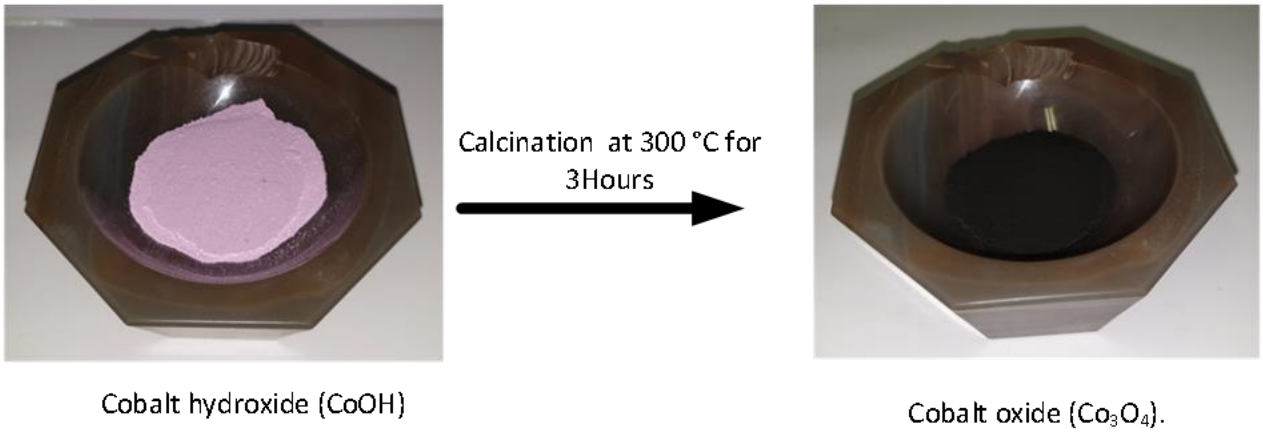


Figure 3-4: Pictures of cobalt hydroxide and cobalt oxide after calcination

The laboratory synthesised cobalt oxide catalyst was analysed by performing XRD (Figure 3-5) SEM analysis at different sizes (Figure 3-6) and the TEM analysis (Figure 3-7).

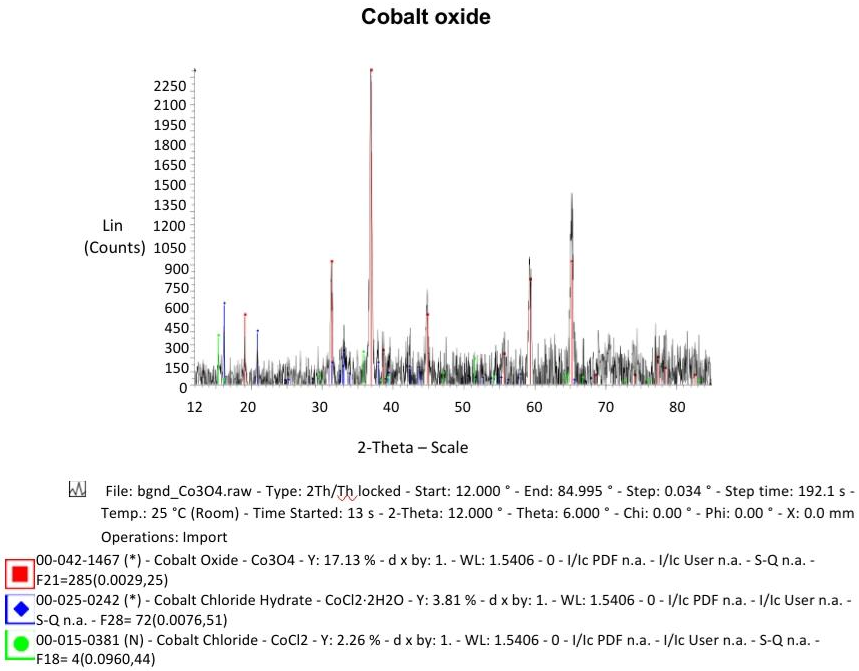


Figure 3-5: Cobalt oxide catalyst XRD analysis

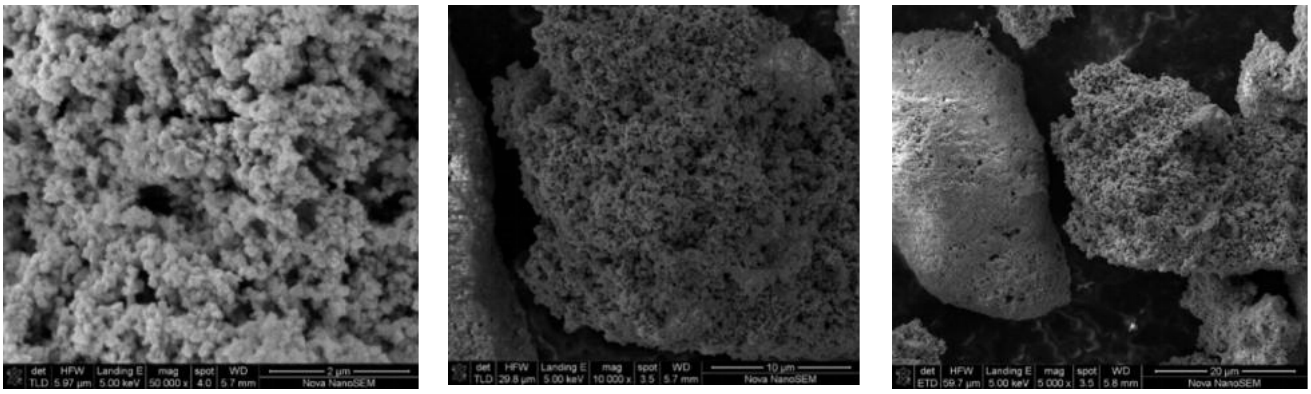


Figure 3-6: SEM analysis of cobalt oxide at different magnification (a) 2 µm, (b) 10 µm and (c) 20 µm sizes

TEM analysis of cobalt oxide catalyst is presented in Figure 4-3 showing the particles have a typical square to hexagonal shape with wide size distribution.

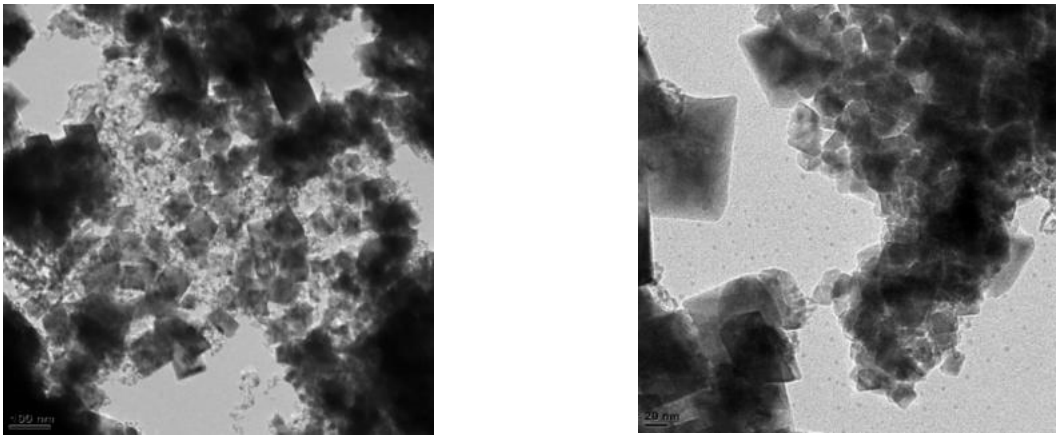


Figure 3-7: TEM analysis of cobalt oxide at different size

3.2.5 Water treatment reactor set up

The permeable reactive barrier (PRB) containing the catalyst was manufactured by a protected patent method. The PRB contained 0.3 g of cobalt oxide catalyst and is shown in Figure 3-8. For each run, a fresh permeable reactive barrier was prepared to minimize the number of variables that could influence the performance of the system.

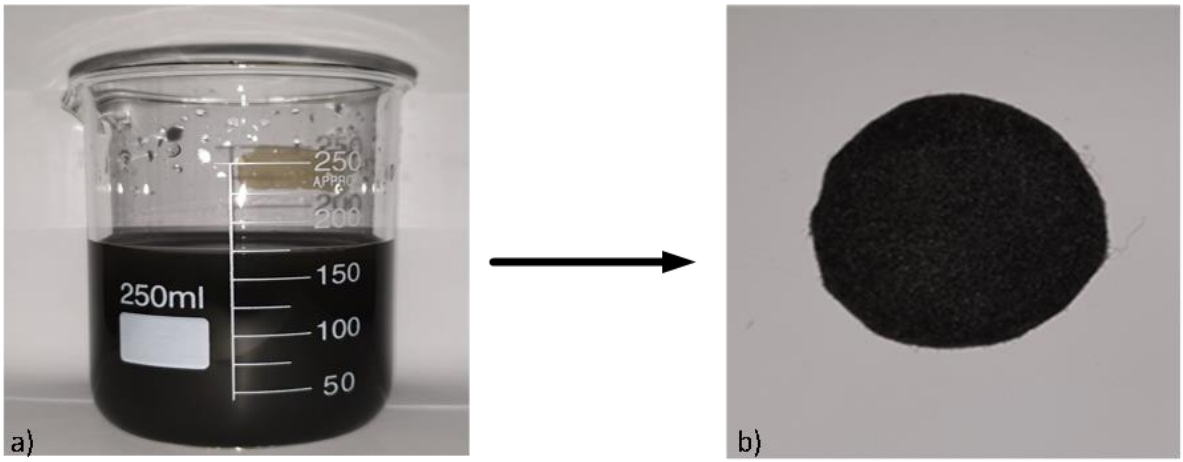


Figure 3-8: (a) shows the black substrate and (b) the permeable reactive barrier

Figure 3-9 shows the bench-scale model of the in-house developed one-step continuous water treatment reactor. This reactor was used for the treatment of the produced textile dyeing effluent. The reactor consists of a feed pump (1) in Figure 3-9which is responsible for pumping the wastewater to the reactor. The PRB was inserted in the reactor at point (2) as shown in Figure 3-9. A known amount of Oxone, the trade name for peroxymonosulfate, was added to the wastewater and stirred for five minutes. The wastewater was then pumped through the fitted piping at a speed of 40 m/s until it reached the PRB. The contact between the PMS and Co_3O_4 led to the activation of PMS to produce sulphate radicals responsible for the colour degradation. Samples of the treated effluent were then taken for further analysis. The analysis was carried out the next day to allow any residual reaction between PMS and Co_3O_4 to be completed.

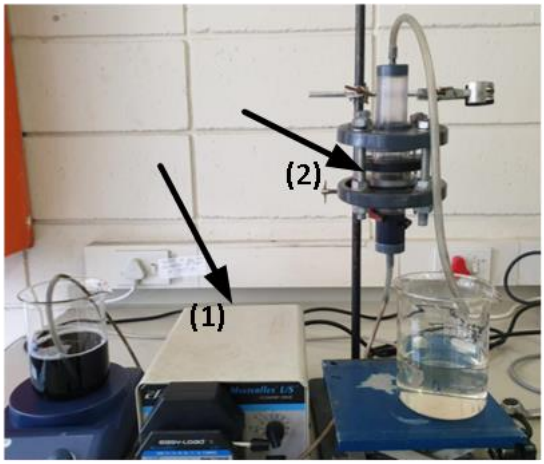


Figure 3-9: Bench-scale wastewater treatment reactor system

Figure 3-10 shows the colour degradation curve rate of treated effluents over the time. The waste effluents were treated with different concentrations (0.3 g/l and 1.5 g/l) and the amount

of cobalt oxide on the filter remained constant (0.3 g/l). The percentage of colour degradation was taken every fifteen minute during an hour.

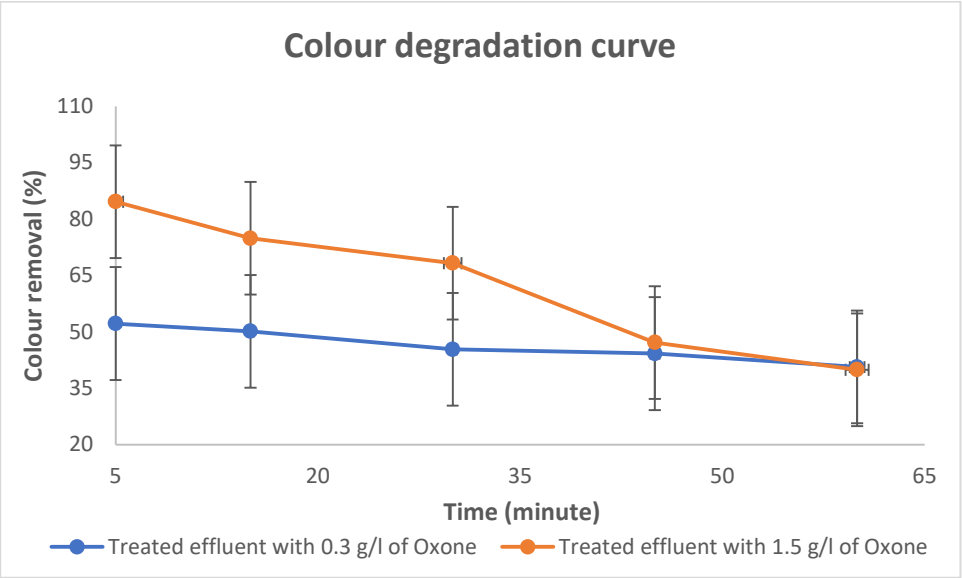


Figure 3-10: Reaction rate graph during water treatment

3.2.6 Colour, conductivity, COD, sulphate and cobalt analysis

The treated wastewater was analysed by measuring the colour degradation, the conductivity, COD, sulphate and cobalt in the effluent after each treatment. Figure 3-11 presents the pictures of the portable Lovibond colourimeter (Figure 3-11 a), Lovibond SD 320 waterproof handheld conductivity meter (Figure 3-10 b), and the DR1900 spectrophotometer (Figure 3-10 c).

Figure 3-11: (a) Lovibond colourimeter, (b) Lovibond SD 320 Conductivity waterproof Handheld meter and (c) DR1900 spectrophotometer

Colour measurement of the treated wastewater

The colour of the wastewater was assessed by measuring the colour degradation of the treated water using a portable colourimeter (Figure 3-11 a). The readings were taken three times to minimise the

percentage error. The colour of the treated wastewater was measured the day after the treatment process to allow the sulphate radicals responsible of the colour degradation to be completed.

Conductivity analysis

The conductivity of the treated wastewater was analysed after each treatment using the Lovibond SD320 Con waterproof handheld meter. This was undertaken to see how the conductivity of the treated wastewater behaves during the treatment process.

COD analysis

COD vials with a range between 250 and 15000 mg/l were selected to analyse the COD. For the preparation of the blank, the cap from the vial was removed, the vial was held at an angle of 45 degrees. A cleaned pipet was used to add 2.00 ml of deionised water to the vial. The program 435 COD HR was started on the DR1900 instrument. The blank sample cell was cleaned and inserted in the blank holder. The zero button was pushed, and the display showed 0.0 mg/l COD. For the prepared sample cell, the read button was pressed, and the results were shown in mg/l COD.

Cobalt analysis

On the DR1900 machine, the program cobalt 110 was started, then the blank was prepared by filling a sample cell with 10 ml of de-ionised water. The second sample cell was filled with 10 ml of treated effluent. In each sample cell, the contents of one phthalate-phosphate reagent powder were added. The sample cells were closed immediately and were shaken to dissolve the reagent completely. 0.5 ml of 0.3% PAN indicator solution was added to each cell. The stopper of each cell was put in place, and each cell was inverted several times to mix everything. The DR1900 instrument timer was set to wait 3 minutes. During this time, a colour change for the treated effluent and the blank was observed. The contents of one EDTA reagent powder pillow was added to each cell when the timer expired; then the sample cells were closed and shaken to dissolve the reagent powder. The blank cell was cleaned and inserted into the cell holder, zero was pushed, and the instrument showed 0.00 mg/l Co. The same procedure was performed for the sample cell in this case. The Read button was pushed and the amount of cobalt in the treated effluent was determined.

Sulphate measurement

For this analysis, 2 ml of treated effluent was pipetted into the TNT 865 vial tube. One dosing spoon of reagent A was added. Then, the vial was closed and inverted repeatedly for 1 minute. The vial was left for

30 seconds before it was cleaned and inserted into the corresponding cell holder of the DR1900; on the machine, the corresponding test was selected, the measurement carried out and the result displayed.

3.3 Reuse of treated textile effluent

Prior to reusing the treated wastewater, the pH of the water was adjusted to 7 with 1 mol/l of sodium hydroxide (NaOH) to avoid an unsuccessful reuse dyeing process. The reuse dyeing procedure was exactly the same as the dyeing procedure used with tap water, except for the fact that tap water was replaced by the treated effluent. The exhaustion and fixation steps were kept the same. Figure 3-12 illustrates the flowchart of the full process from dyeing with tap water to three reuse cycles.

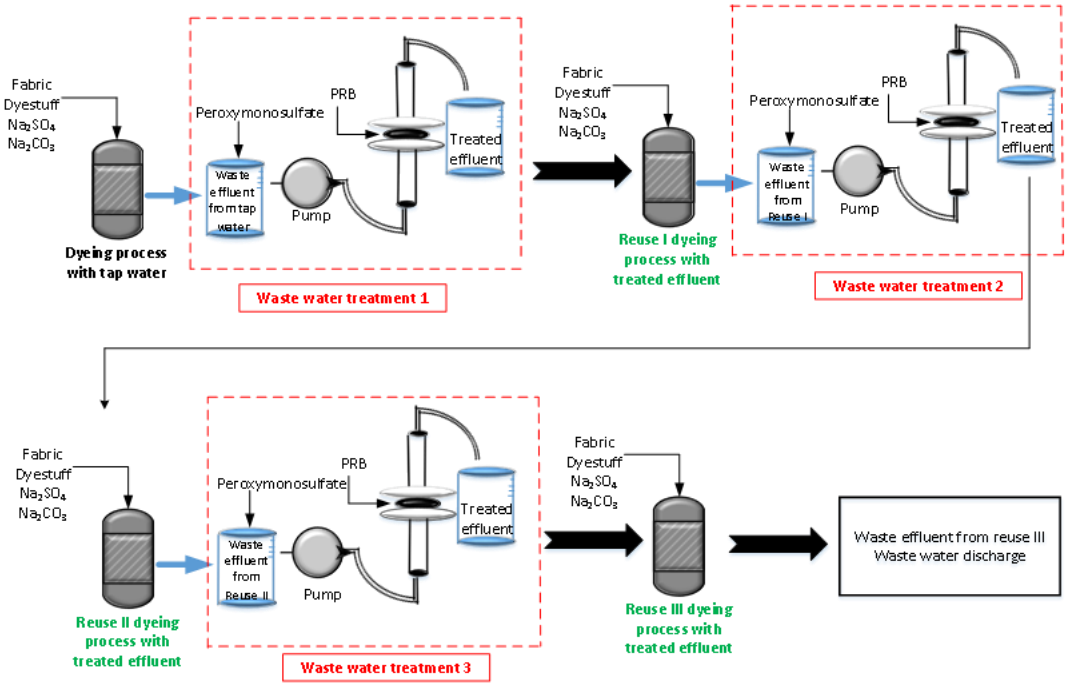


Figure 3-12: Flowchart of three reuse cycles

3.4 Factorial design analysis and presentation of results

For further studies, Design-Expert software version 11.1.2.0 was used for the factorial trial using Box-Behnken design from response surface methodology. Oxone level added during the water treatment process, dye concentration added during the dyeing process, and the number of reuse cycles of the treated waste effluent were studied at three different levels: low, medium and high, with coded levels values of -1, 0 and 1. The corresponding actual values for each factor are given in Table 3-1. The effect of each factor on the colour fastness of the dyed fabrics was studied.

Table 3-1: Levels of factors for design of experiment

			Levels used		
Factor	Name	Unit	Low	Medium	High
A	Oxone level	g/l	0.5 (-1)	1.0 (0)	1.5 (+1)
B	Dye concentration	%	3.0 (-1)	5.0 (0)	7.0 (+1)
C	Reuse cycles	-	1.0 (-1)	2.0 (0)	3.0 (+1)

Table 3-2 shows the experimental setup of the Box-Behnken design matrix of each factor and their actual values. Fifteen experiments were run for each combination of the factor levels selected by the software.

Table 3-2: Box-Behnken factorial trial for colour fastness

		Factor 1: A	Factor 2: B	Factor 3: C
Standard Order	Run Order	Oxone level (g/l)	Dye Concentration (%)	Reuse cycles
1	14	0.5	3	2
2	3	1.5	3	2
3	11	0.5	7	2
4	2	1.5	7	2
5	12	0.5	5	1
6	10	1.5	5	1
7	6	0.5	5	3
8	1	1.5	5	3
9	8	1	3	1
10	7	1	7	1
11	15	1	3	3
12	13	1	7	3
13	4	1	5	2
14	9	1	5	2
15	5	1	5	2

3.5 Conclusion

In conclusion, the different equipment used to study the reusability of the reactive textile waste effluent treated by cobalt-mediated sulphate radical-based advanced oxidation process were presented. Three different procedures were described in this chapter: the dyeing process, wastewater treatment and reuse dyeing process. Three factors at three levels were selected to evaluate their effects on colour fastness of

the dyed fabrics. The preliminary results using the different methods are discussed in Chapter 4 and the results from the factorial trial are discussed in Chapter 5.

Chapter 4: Preliminary studies

4.1 Introduction

The first part of the research design consisted of preliminary test runs to determine the treatment conditions for wastewater prepared at different dye concentrations, to measure the number of obtainable reuse cycles that will provide good colour fastness, as well as evaluate the effects of the variation of dye concentration on the treated effluent and the effects of standing time and dilution of the treated waste effluent on colour fastness.

4.2 Characterisation of the treated textile effluent from cobalt oxide and sulphate radical-based advanced oxidation

4.2.1 Colour degradation and conductivity of the treated effluent

As mentioned earlier, the purpose of this work was to study the reusability of waste effluent from a dyed cotton fabric using reactive dye and treated with the continuous reactor system. Taking into account the fact that effluents from reactive dyes are difficult to treat (Singh, 2014; Elfarash et *al*., 2017; Karim et *al.*, 2018), investigations were undertaken to determine the treatment conditions at which the reactive wastewater will be degraded and reused in three reuse dyeing processes. Therefore, process conditions were studied for textile waste effluents obtained at different dye concentrations (3% and 8%) and treated with different ranges of Oxone (0.5 g/l and 3.5 g/l) when reused three times. Table 4-1 shows the different processes carried out with the variation of dye and Oxone concentrations. To study the treatment process conditions, colour removal and conductivity after the treatment were measured. The reason for measuring the conductivity is the fact that the conductivity shows the amount of salt in the effluent (Rosa et *al.,* 2015; Hu et *al.*, 2016). Also, the sulphate radicals produced extra salt in the treated effluent.

Table 4-1: Reuse processes with varied conditions

Process Conditions	Dye concentration (%)	Oxone concentration
Conditions 1	3	0.5
Conditions 2	3	3.5
Conditions 3	8	0.5

4.2.1.1 Colour degradation of the treated effluent

Figure 4-1 shows the colour degradation curves of treated effluents after each reuse cycle. In this figure, three colour degradation curves are presented at different process conditions when the effluent is reused three times.

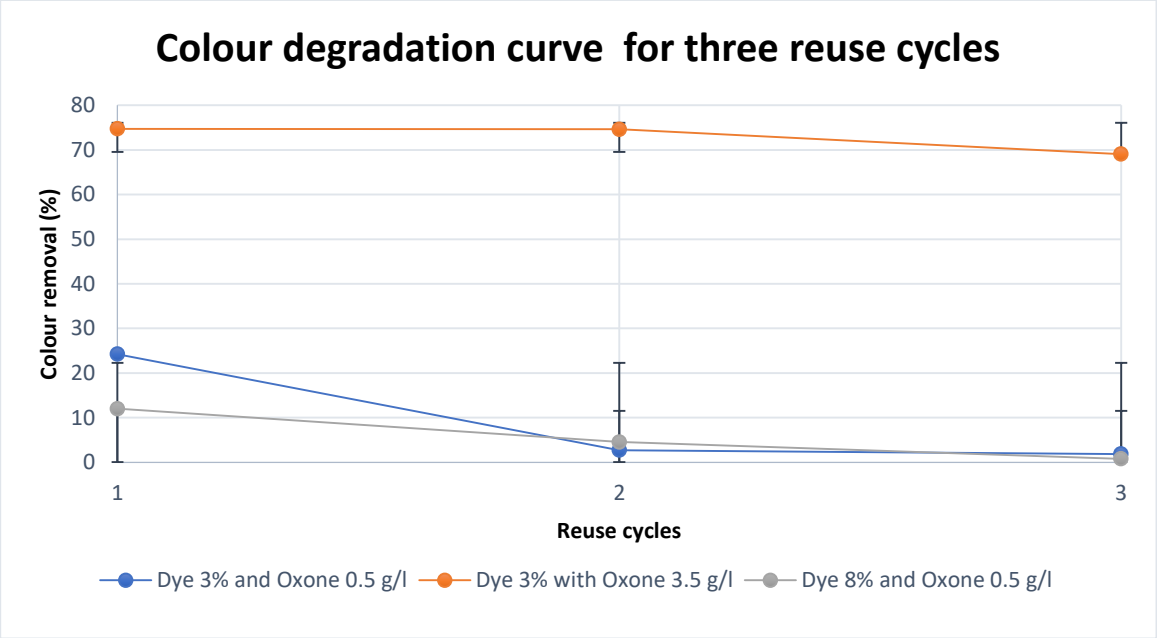
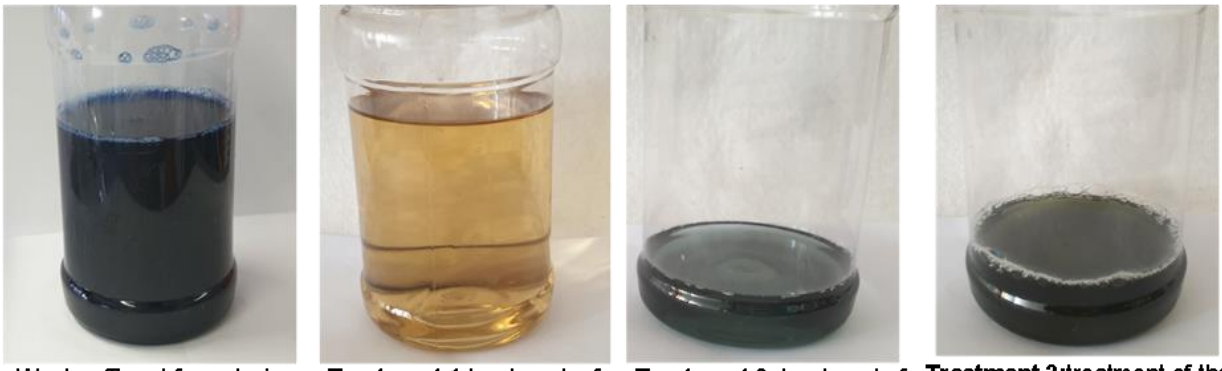


Figure 4-1: Colour degradation curves of treated textile effluents at different process conditions

The following figures (Figure 4-2, Figure 4-3 and Figure 4-4) show pictures of the different treated textile effluent at different process conditions after 24 hours of standing time. Figure 4-2 conditions are 3% dye concentration and 0.5 g/l of Oxone, Figure 4-3 conditions are 3% dye concentration and 3.5 g/l of Oxone and Figure 4-3 conditions are 8% dye concentration and 0.5 g/l of Oxone. From Figure 4-1, it can be seen that the percentage of colour removal of the treated effluent decreases as the number of reuse cycles increases. When the same dye concentration (3%) was maintained, and when treated with a different amount of Oxone (0.5 g/l and 3.5 g/l), colour removal was 24% when the effluent was treated with 0.5 g/l and 75% when it was treated with 3.5 g/l of Oxone for the first reuse cycle. For the second reuse, similar types of degradation were observed, poor colour removal (3%) was observed for treated effluent with 0.5g/l of Oxone and good colour removal (75%) was observed for treated effluent with 3.5 g/l of Oxone. Lastly, for reuse cycle number three, percentages of colour removal were 2% and 69% for the same effluent treated with 0.5 g/l and 3.5 g/l of Oxone respectively.

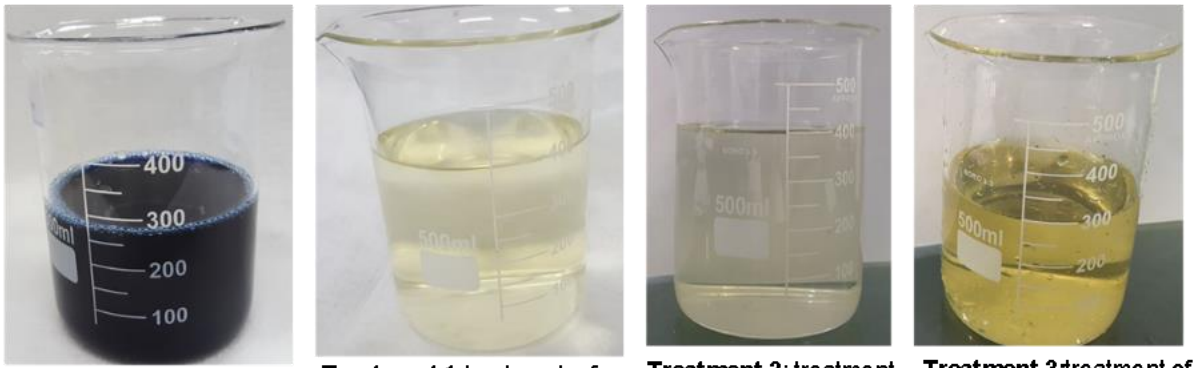
With the process condition dyed with 8% and effluent treated with 0.5 g/l, poor colour degradation in the three cycles was observed. Colour removal of 12 % in reuse cycle number one was observed, followed by 5% colour removal in reuse two, and the last reuse cycle yielded 0.8% colour removal. This is explained by

the fact that a low amount of Oxone (0.5 g/l) was used to treat a highly concentrated effluent (8% dyeing concentration).



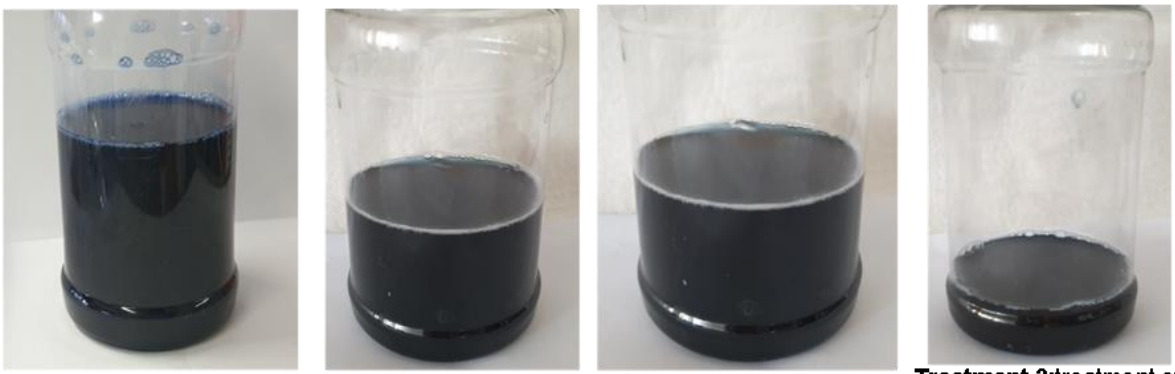
Waste effluent from dyeing with tap water | **Treatment 1**:treatment of the effluent obtained from tap water | **Treatment 2**: treatment of the effluent after reuse I | **Treatment 3**:treatment of the effluent reuse II

Figure 4-2: Treated effluent at 3% dye concentration and 0.5 g/l of Oxone concentration



Waste effluent from dyeing with tap water | **Treatment 1**:treatment of the effluent obtained from tap water | **Treatment 2**: treatment of the effluent after reuse I | **Treatment 3**:treatment of the effluent after the reuse II

Figure 4-3: Treated effluent at 3% dye concentration and 3.5 g/l of Oxone concentration



Waste effluent from dyeing with tap water | **Treatment 1**:treatment of the effluent obtained from tap water | **Treatment 2**: treatment of the effluent after reuse I | **Treatment 3**:treatment of the effluent after reuse II

Figure 4-4: Treated textile effluent at 8% dye concentration and 0.5 g/l of Oxone concentration

4.2.1.2 Conductivity of the treated effluent

Initially, the conductivity of tap water was 0.55 µs/cm. After the dyeing process, the conductivity of the waste effluent obtained from dyeing with tap water increased to 1.69 µs/cm and 2.3 µs/cm from dyeing with 3% and 8% of dyed concentrations respectively. The conductivity (1.69 µs/cm) of the treated effluent increased to 2.6 µs/cm, 4.1 µs/cm for processes dyed with the same amount of dye (3% dye concentration) and treated with 0.5 g/l and 3.5 g/l respectively after the first treatment. For the waste effluent with a conductivity of 2.6 µs/cm, an increase to 6.1 µs/cm was observed after the first treatment. Figure 4-5 presents the conductivity measurement of the treated effluent when the water was reused three times at different treatment process conditions. It was observed that the conductivity increased as the treated effluent was reused. The first process conditions (3% dye concentration and 0.5 g/l) had the lowest conductivity: 2.6 µs/cm, 4.6 µs/cm and 5.1 µs/cm for reuse one, two and three respectively. For the second process conditions (3% dye concentration and 3.5 g/l), the conductivity increased to 4.1 µs/cm, 7.6 µs/cm and 15.1 µs/cm for the three reuse cycles respectively. For the last process conditions (8% dye concentration and 3.5 g/l), for reuse one; two and three, the respective conductivities were 6.1 µs/cm, 11.3 µs/cm and 17.2 µs/cm.

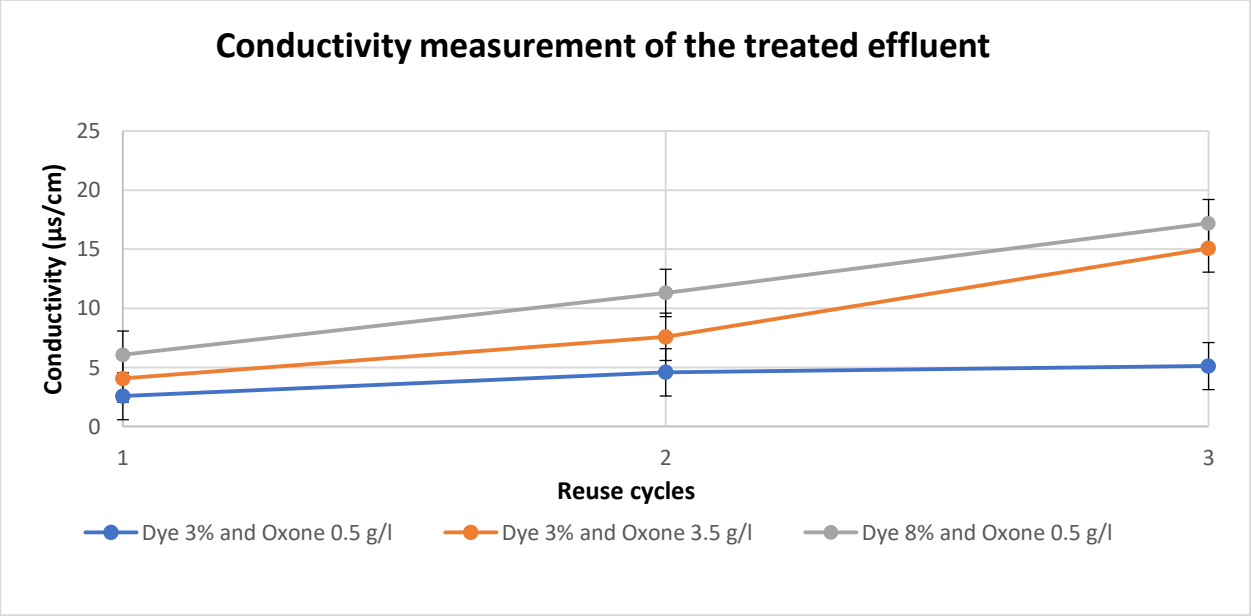


Figure 4-5: Conductivities of treated textile effluents at different process conditions when reuse three times

As mentioned earlier, the conductivity of the waste effluent shows the amount of salt in the treated effluent. Therefore, the increase of conductivity in the treated effluent corresponded to the increase of the amount of salt in the same effluent. A trial was performed to see if the extra salt present in the treated effluent could be recovered by modifying the dyeing recipe without adding the salt (sodium sulphate) during the exhaustion step. The reason for doing this trial was to see if the extra salt produced by the sulphate radicals when Oxone was activated by cobalt oxide catalyst could be taken as sodium

sulphate (Na_2SO_4) in the dyeing recipe. This trial was carried out at process conditions of 3% dye concentration, 0.5 g/l of Oxone and reuse in three cycles.

Figure 4-6 shows the conductivity of the treated effluent after each reuse cycle, dyed from reuse dyeing processes with the standard dyeing recipe and the modified dyeing recipe. It was observed that for both cases, the conductivity of the treated effluent increased as the treated effluent was reused. This increase is due to the structure of the reactive dye used during the process. However, the conductivity of the treated effluent dye reused in the dyeing process with the standard recipe is higher than the one dyed using the modified recipe. Before the first reuse cycle, the conductivity of the treated effluent was $\pm$ 2.6 µs/cm in both cases. Then, in the second reuse cycle, the conductivity of the treated effluent increased to 3.1 µs/cm and 4.6 µs/cm for treated effluent dyed in the reuse dyeing process using the modified dyeing recipe and the standard dyeing recipe respectively. In the last reuse, the conductivity of the effluent dyed in the reuse dyeing process using the modified dyeing recipe was 5.1 µs/cm. For the one dyed using the standard dyeing, this measurement was 3.9 µs/cm.

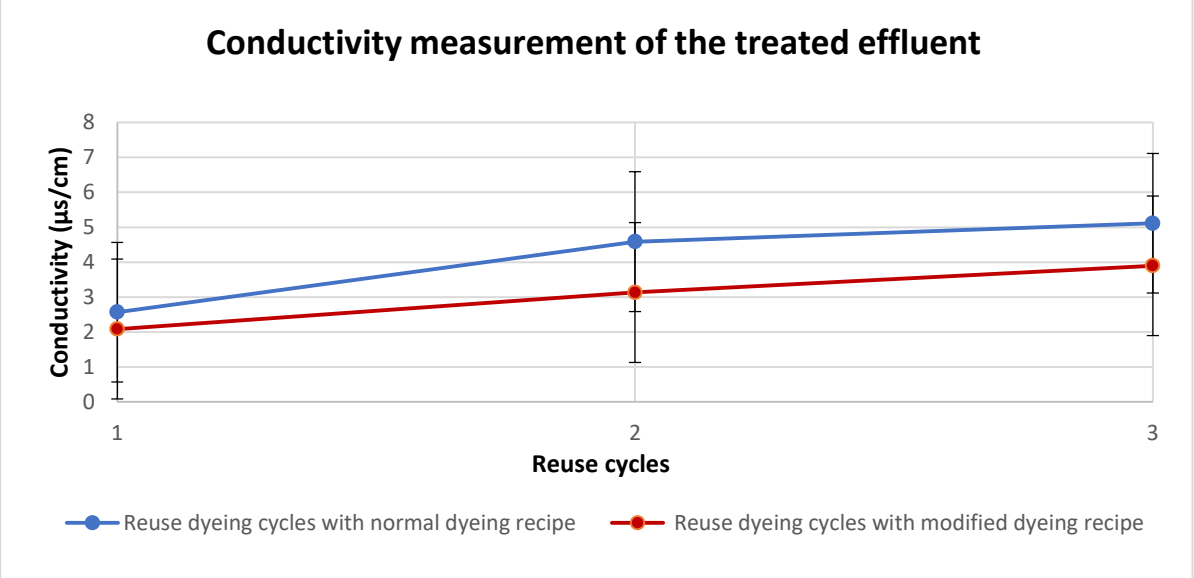


Figure 4-6: Conductivity of the treated effluent dyed in the reuse dyeing process using the standard and the modified dyeing recipe

4.2.2 Evaluation of the variation of dye concentration at constant Oxone concentration during treatment process

This section discusses the role of variation in dye concentration at constant oxone concentration during treatment process.

4.2.2.1 Effects of COD of the treated effluent when reused three times with variation in dye concentrations

The chemical oxygen demand (COD) of the treated effluents at various dye concentrations of 2%, 4%,6% and 8% and treated with the same amount of Oxone concentration (0.5 g/l) when the effluent was reused twice, are shown in Figure 4-7. Poor COD removal was observed in treated effluents in all reuse cycles.

It was observed that the percentage of COD decreased as the amount of dyed concentration increased, while the amount of Oxone added during the different treatment processes was the constant. Two percent dye concentration (2%) treated effluent gave COD readings of 7% and 5% percentage removal for reuse cycles I and II. With 4% dye concentration, the percentage COD removals were 6% and 4% for reuse I and II. Finally, for dye concentrations of 6% and 8%, the percentage of COD removals are the same in reuse cycles one (5%) and two (0.05). The reason for the poor COD removal is due to the fact that the more the treated effluent is reused, the higher the conductivity of that effluent is. Also as poor COD removal was observed, the more the COD of the treated effluent increased, as more salt was added after the treatment process due to the action of the sulphate radicals.

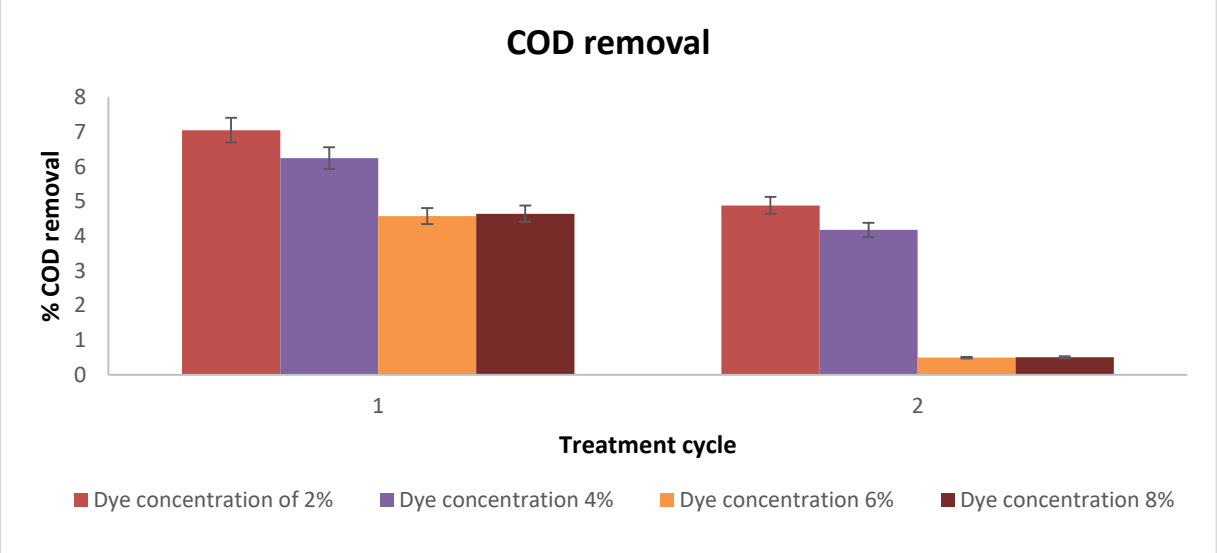


Figure 4-7: Chemical oxygen demand (COD) measurement of textile waste effluent reused once

4.2.2.2 Effect of sulphate and cobalt amounts in the treated effluent when reused three times with variation of dye concentrations

Figure 4-8 presents the amount of sulphate measured in the treated effluents at various dye concentrations of 2%, 4%, 6% and 8% and treated with the same amount of Oxone concentration (0.5 g/l) when the effluent was reused twice.

It was observed that there was an increase of sulphate amounts in the treated effluent as the effluent was reused and as the concentration of dye increased. Initially, the amounts of sulphate in the waste effluents obtained from dyeing processes with tap water were 734.3 mg/l, 933.4 mg/l, 1043.3 mg/l and 1052.1 mg/l, for 2%, 4%, 6% and 8% dye concentrations respectively. The presence of sulphate in the initial waste effluent can be explained by the fact that during the exhaustion step of the dyeing process, sodium sulphate was added. The increase of sulphate as the concentration of dyes increased is explained by the presence of sulphate in the reactive dyes' compositions. After the first treatment, the amount of sulphate in the treated effluent increased to 869.2 mg/l, 999.8 mg/l, 1267.3 mg/l and 1649.2 mg/l for dye concentrations of 2%, 4%, 6% and 8% respectively. After the second treatment, the amounts of sulphate increased again to 1984 mg/l, 2162 mg/l 2431 mg/l and 3398.8 mg/l. The increases of sulphate amounts in the treated effluents were also due to the presence of sulphate radical residuals in the treated effluent, produced by the activation of peroxymonosulfate by the cobalt oxide catalyst during the treatment process.

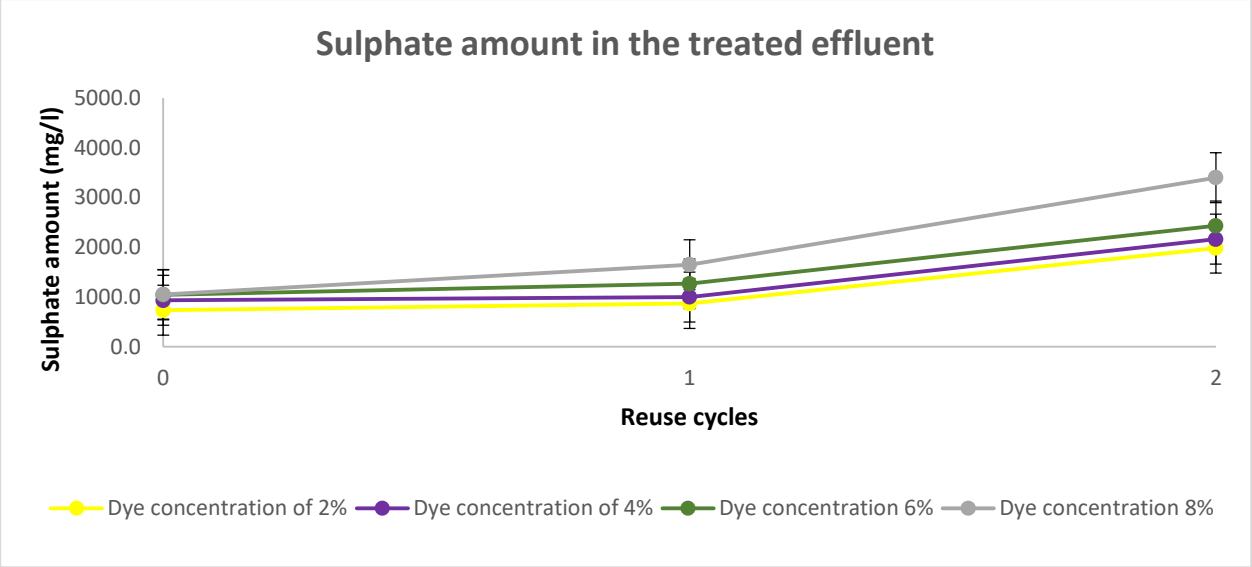


Figure 4-8: Amount of sulphate measured in the effluent at different dye concentrations

Figure 4-9 shows the amount of cobalt measured in the treated effluents for two reuse cycles at various dye concentrations of 2%, 4%, 6% and 8%, and treated with a constant Oxone concentration (0.5 g/l). Here, the amount of cobalt in the treated effluent increased as the effluents were treated and reused with the different concentrations of dyes. The increase of cobalt in the treated effluent was due to cobalt leaching from the catalyst during the treatment process, as the activation of Oxone by cobalt oxide catalyst results in an acidic pH of the treated effluent (Zhang *et al.*, 2010; Stoyanova *et al.*, 2014; Wang *et al.*, 2016). After the first treatment, the increase of cobalt was due to the residual amounts of cobalt present in the passage of the effluent through the permeable reactive barrier in the continuous reactor system.

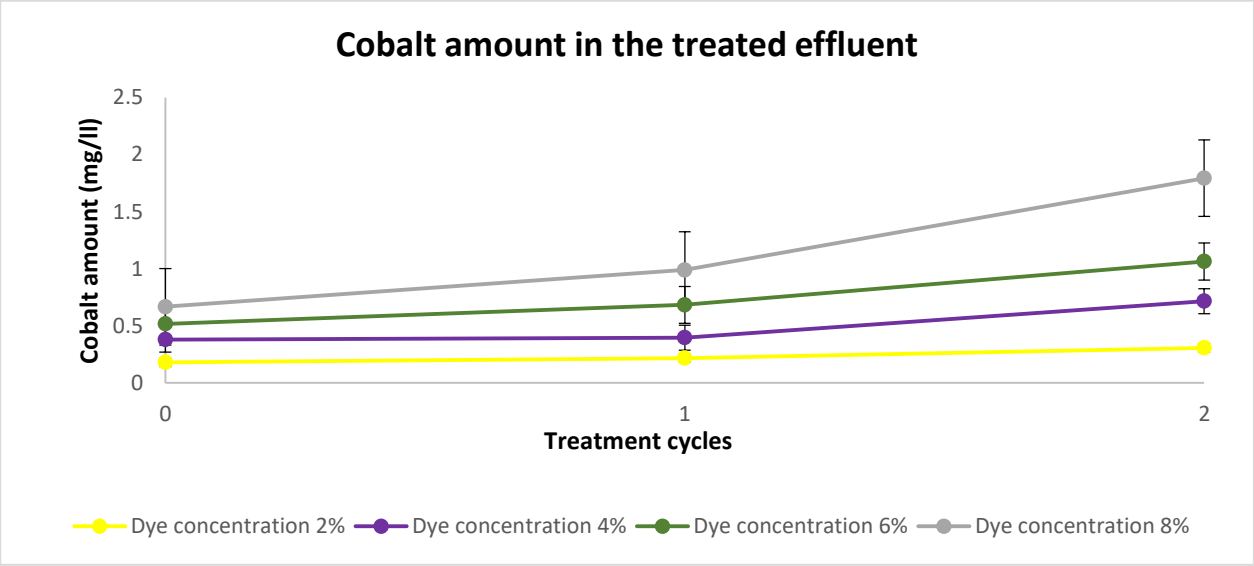


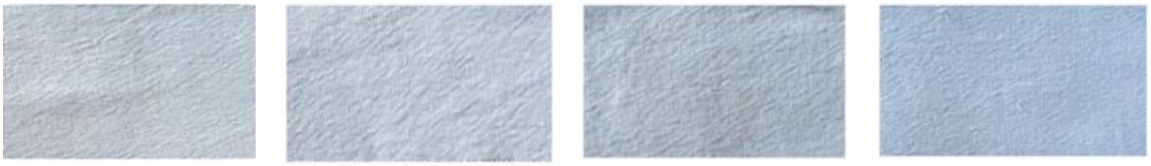
Figure 4-9: Amount of cobalt measured in the effluent at different dye concentrations

4.3 Colour fastness of the fabrics dyed with an effluent treated from cobalt oxide and sulphate radical-based advanced oxidation

4.3.1 Colour fastness of the dyed fabrics at each process condition

Colour fastness of the fabrics dyed at each treatment process condition (discussed in section 4-2-1) are recorded in the following figures. The fabric dyed with tap water was taken as the reference in all cases. It was observed that colour fastness ratings were Good in reuse one and two. For the third reuse, colour fastness ratings started to decrease. In Figure 4-10, the process conditions were 3% of dye concentration and 0.5 g/l of Oxone. It was observed that reuse cycles I and II yielded colour fastnesses of Good to Excellent (4/5). The fabric obtained in reuse III had a darker shade, while colour fastness of fabric obtained from reuse III was Moderate (2).

In Figure 4-11, the dye and Oxone concentrations were 3% and 3.5 g/l respectively. The colour fastness based on the comparison with the standard (fabric dyed with tap water) was found to be Good to Excellent (4/5) for reuse I and II. With reuse III, the colour changed slightly, yielding a rating of Good (4). Figure 4-12 represents the colour fastness of the fabric dyed with 8% of dye concentration and effluent treated with 0.5 g/l of Oxone concentration. The shade of the dyed fabric is darker due to the high concentration of dye used (8%). For reuses I and II the grading were Good, contrasting with reuse III, where the shade of the fabric was Moderate (2).

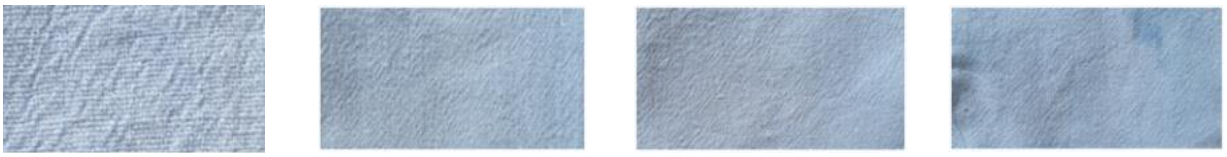


Tap water Reuse I: 4/5 Reuse II: 4/5 Reuse III: 2

Figure 4-10: Colour fastness of the dyed fabrics at 3% dye concentration and 0.5 g/l of Oxone concentration

Tap water Reuse I: 4/5 Reuse II: 4/5 Reuse III: 4

Figure 4-11: Colour fastness of the dyed fabrics at 3% dye concentration and 3.5 g/l of Oxone concentration



Tap water Reuse I: 4/5 Reuse II: 4 Reuse III: 2

Figure 4-12: Colour fastness of the dyed fabrics at 8% dye concentration and 0.5 g/l of Oxone concentration

4.3.2 Effects of recycling salt found in the treated effluent on the colour fastness of the fabric

Colour fastnesses of the dyed fabric from dyeing in reuse dyeing without adding extra salt in the reuse process are shown in Figure 4-13. It appears that, compared to the standard (fabric dyed with tap water and exhaustion step), the fabrics dyed with the treated effluent without adding extra salt in the dyeing recipe are darker in shade. Therefore, in the first reuse cycle, the colour change is higher, giving a colour fastness of Moderate (2). A small improvement in colour fastness was observed, producing a rating of Average (3), in reuse cycles two and three.

Tap water Reuse I: 2 Reuse II: 3 Reuse III: 3

Figure 4-13: Effect of recycling the salt of the treated effluent on the colour fastness of the dyed fabrics

4.3.3 Evaluation of the effects of standing time of the treated effluent on colour fastness

The effects of the standing time of the treated effluent at treatment process conditions of 3% of dye concentration and 0.5 g/l, as well as treated effluent reused three times, on the colour fastness of the

dyed fabrics are shown in the Figures below. In Figure 4-14, the water was reused 5 hours after treatment and in Figure 4-15, the water was reused 48 hours after treatment. As seen in both cases, reuse cycles I and II yielded a colour fastness of 4/5 (Good to Excellent) and in the third reuse cycle, colour fastness decreased to 3 (Average). The standing time of the treated effluent had no effect on the properties of the dyed fabrics in the reuse process. As it did not matter whether the treated effluent was reused after 5 or 48 hours after treatment of the effluent, the colour fastness of the dyed fabrics was still the same. The following results are supported by the results found in Figure 4-10, in which the treatment process conditions were the same (3% and 0.5 g/l of dye and Oxone concentrations respectively and reused three times) except that the standing time of the treated effluent was 24 hours and the colour of the reactive was blue. Colour fastness of the dyed fabrics was the same, with reuses I and II producing a Good to Excellent rating of colour fastness and reuse III Average colour fastness.

Tap water | Reuse I: 4/5 | Reuse II: 4/5 | Reuse III: 3

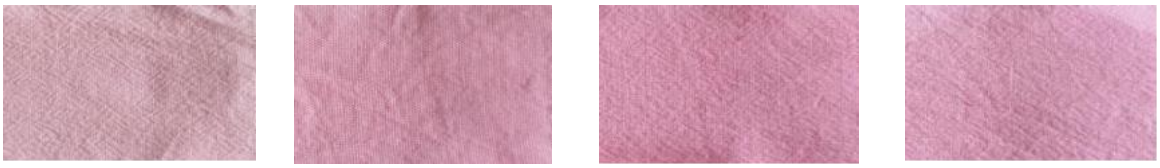
Figure 4-14: Colour fastness of the dyed fabrics after 5 hours standing time of the treated effluent before reuse

Tap water | Reuse I: 4/5 | Reuse II: 4/5 | Reuse III: 3

Figure 4-15: Colour fastness of the dyed fabrics after 48 hours of standing time of the treated effluent before reuse

4.3.4 Evaluation of the effects of dilution of the treated effluent on colour fastness

The following figures (Fig. 4-16 and Fig. 4-17) show the dyed fabrics obtained from diluting the treated effluent at 25% and 50% dilution factors, with tap water at treatment process of 3% and 0.5 g/l of dye and Oxone concentrations. The shade of the fabrics became darker and the difference between the standard (fabric dyed with tap water) and the fabrics dyed with diluted effluent is high in both figures. Colour fastness of the fabrics was 3 for reuses I and II and decreased to 2 for reuse III in in the cases of both 25 and 50% dilutions. Therefore, it can be concluded that the dilution parameter on the reuse process does not have a significant effect on colour fastness of the dyed fabrics, as regardless of whether the dilution factor was changed from 25% to 50%, the colour fastness of the dyed fabrics remained unchanged.



Tap water | Reuse I: 3 | Reuse II: 3 | Reuse III: 2

Figure 4-16: Colour fastness of the dyed fabrics at 25% dilution factor of the treated effluent before reuse

Tap water | Reuse I: 3 | Reuse II: 3 | Reuse III: 2

Figure 4-17: Colour fastness of the dyed fabrics at 50% dilution of the treated effluent before reuse

4.4 Conclusion

The number of reuse cycles, dye and Oxone concentrations have significant influences on the treated effluent and the colour fastness of the dyed fabrics. Treatment process conditions with low amounts of dye and Oxone concentrations when reused in three cycles, yielded poor colour degradation with low levels of conductivity of the treated effluent, with Good to Excellent colour fastnesses of the dyed fabrics in reuses I and II and Moderate colour fastness in reuse III. Process conditions with low dye concentrations and high levels of Oxone produced high colour degradation and high conductivity of the treated effluent, as well as colour fastness of Good to Excellent in reuse I and II. In the last reuse cycle colour fastness was Good. COD, levels of sulphate and cobalt residuals increased in the treated effluent as it was reused. Their presence also increased with the increase in dye concentration.

Due to cost considerations and the fact that the purpose of this work is to study the reusability of a treated textile effluent, process conditions with low amounts of dye and Oxone concentration were used to study the effects of standing time of the treated effluent. Also under analysis was the dilution of the treated effluent before reuse and the effects of reuse without adding extra amounts in the next dyeing process on the colour fastness of the dyed fabrics. Parameters such as standing time of the treated effluent, dilution of the treated effluent before reuse and the effect of reusing without adding extra amount of the treated effluent on the colour fastness of the dyed fabrics were found to be not relevant, as no significant changes were found. The results obtained informed the parameters selected for the factorial trial.

As previously mentioned, three factors were selected at three different levels (low, medium and high). From this chapter, it is apparent that the significant factors influencing the colour fastness of the dyed fabrics are Oxone level, dye concentration and the number of reuse cycles of the treated effluent. Oxone

levels during the treatment process are 0.5 g/l, 1 g/l and 1.5 g/l, while the concentrations of dyed used during the dyeing process are 3%, 5% and 7%. Finally, the number of reuse cycles undergone by the treated effluents is from one to three reuse cycles. The effects of these factors are discussed in Chapter 5.

Chapter 5: Effect of process parameters and their interactions on colour fastness of the dyed fabrics

5.1 Introduction

The aim of this research was to study the reusability of treated textile effluents from cobalt oxide and sulphate radical-based advanced oxidation processes. In this chapter, the effects of Oxone level, dye concentration and reuse cycles are evaluated at different levels by measuring colour fastness of the dyed fabrics. The use of Design-Expert software through Box-Behnken design led to the utilisation of an analysis of variance, a regression analysis, determining the interaction effects of the process factors on colour fastness and finding the optimum conditions for this process on the colour fastness of the dyed fabrics. Table 5-1 shows the experimental of responses for the Box-Behnken design of colour fastness at each value of the factors and the corresponding pictures of the treated effluent and dyed fabrics.

Table 5-1: Box-Behnken factorial trial for colour fastness

		Factor 1: A	Factor 2: B	Factor 3:C	Response		
Standard Order	Run Order	Oxone level (g/l)	Dye concentration (%)	Reuse cycles	Colour fastness	Treated effluent	Dye fabrics
1	14	0.5	3	2	4		
2	3	1.5	3	2	3		
3	11	0.5	7	2	3		
4	2	1.5	7	2	3		

5	12	0.5	5	1	4		
6	10	1.5	5	1	3		
7	6	0.5	5	3	3		
8	1	1.5	5	3	4		
9	8	1	3	1	4		
10	7	1	7	1	3		
11	15	1	3	3	4		
12	13	1	7	3	3		
13	4	1	5	2	4		
14	9	1	5	2	4		
15	5	1	5	2	4		

5.2 Optimisation of parameters using Box-Behnken design with RSM and its validation

5.2.1 ANOVA and estimated regression coefficients for colour fastness

The results of analysing the measured colour fastness of the dyed fabrics using Design-Expert software, the significance test for the regression model and the significance test of individual model coefficients were all determined by the software. A backward stepwise regression model was selected for a quadratic model with no transformation. The non-significant effects were eliminated, and a simpler hierarchical model was obtained with significant terms, as shown in Table 5-2.

ANOVA results for colour fastness obtained from Box-Behnken design analysis are given in Table 5-2. Probability (p = 0.0025) of the model was less than 0.05, and therefore it can be concluded that the model is significant, at a 5% significance level (Hassanzadeh et *al.*, 2017; Nautiyal & Shukla, 2018). Table 5-2 indicates that dye concentration (B) is the only independent variable with a significant effect, as its p-value is 0.0015. In this case, the other significant model terms are AB, AC, A^2 and B^2, with respective p-values of 0.0015, 0.0020, 0.0121 and 0.0121. The significance of this model can also be supported by the F-value of 11.13. This value leads to the conclusion that there is only 0.25 % chance that the F-value could occur due to noise.

The adjusted coefficient of determination (Adj.R^2) between the experimental and model predicted values obtained from the colour fastness response is 0.8352. This value indicates a good model fit. This value showed a good correlation between the observed and predicted values of colour fastness.

Table 5-2: Analysis of variance (ANOVA) for colour fastness response

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3.43	7	0.4894	11.13	0.0025	Significant
A – Oxone level	0.1250	1	0.1250	2.84	0.1356	
B – Dye concentration	1.13	1	1.13	25.59	0.0015	
C – Reuse cycles	0.0000	1	0.0000	0.0000	1.0000	
AB	0.2500	1	0.2500	5.69	0.0485	
AC	1.0000	1	1.0000	22.75	0.0020	
A^2	0.4959	1	0.4959	11.28	0.0121	

B^2	0.4959	1	0.4959	11.28	0.0121	
Residual	0.3077	7	0.0440			
Lack of fit	0.3077	5	0.0615			
Pure error	0.0000	2	0.0000			
Cor Total	3.73	14				
Adjusted R^2	0.8352					

Where A is the amount of Oxone used in the treated effluent; B is the dye concentration in function of the weight of the fabrics; C is the number of reuse cycle of the treated effluent; AB is the interactions between Oxone level and dye concentration; AC is the interaction between Oxone level and reuse cycles; and A^2 and B^2 are the quadratic effects of the Oxone level and dye concentration, respectively.

5.2.2 Model determination

Table 5-3 shows all the terms involved for the determination of the predicted model for colour fastness and the most significant coefficients. To study the reusability of a waste effluent from a dyed cotton fabric using reactive dye and treated with the continuous reactor system, all variables presented in Table 5-3 have significant effects on this process and cannot be neglected.

Table 5-3: Variables terms with their coded and actual coefficients

Terms	Coded coefficient	Actual Coefficient
Constant	$C_0 = 3.92$	$C_0 = 4.615$
A – Oxone level	$C_1 = -0.125$	$C_1 = -0.577$
B – Dye concentration	$C_2 = -0.375$	$C_2 = 0.476$
C – Reuse cycles	$C_3 = 0.000$	$C_3 = -1.000$
AB – Oxone level *Dye concentration	$C_{12} = 0.250$	$C_{12} = 0.250$
AC – Oxone level * Reuse cycle	$C_{13} = 0.500$	$C_{13} = 1.000$
A^2 Oxone level²	$C_{11} = -0.365$	$C_{11} = -1.462$
B^2 Dye concentration²	$C_{22} = -0.365$	$C_{22} = -0.091$

Equation 5-1 is a relationship between the response, also called the dependent variable (colour fastness) and the independent variables (Oxone level, dye Concentration and reuse cycles). The response surface equation for colour fastness with the coded factors is given by Equation 5-1 below. This equation can be

used to predict the colour fastness of the dyed fabrics within the range of the factorial trial, by substituting the values of A, B and C or their codes (-1 to 1).

It is important to note that Equation 5-1 is useful for identifying the relative impact of the factors by comparing the factor coefficients. In Equation 5-1 a positive sign before a term indicates an increasing effect, while a negative sign indicates a decreasing effect on colour fastness. The presence of binary terms such as AB and AC in Equation 5-1 indicates that colour fastness of the dyed fabrics depends on both single and mixture variables. These binary terms show that there is an increasing effect between Oxone level and dye concentration (AB) and Oxone level and reuse cycles (AC) on the colour fastness of the dyed fabrics.

$$Y = C_0 + C_1A + C_2B + C_3C + C_{12}AB + C_{13}AC + C_{11}xA^2 + C_{22}B^2 \quad (5\text{-}1)$$

The calculated equation in actual values of the factors was:

$$Y = 4.615 - 0.577A + 0.476B - 1C + 0.25AB + 1AC - 1.462A^2 - 0.091B^2 \quad (5\text{-}2)$$

Where Y represents the colour fastness of the dyed fabrics.

In Equation 5-2, the coefficients are scaled to accommodate the units of each factor and the intercept is not at the centre of the design. This equation indicates that the Oxone level was the dominant factor, followed by the interaction effect of Oxone level and reuse cycles among the selected parameters. It was followed by the reuse cycles of the treated effluent, dye concentration and interaction effect of Oxone level and dye concentration.

5.2.3 Model validation

The diagnostic analysis was carried out to investigate the validity of the goodness of fit of the proposed model. Figure 5-1 illustrates externally studentised residuals versus the predicted values for the colour fastness of the dyed fabrics. It was noticed that all colour points describing the values of colour fastness were within the limits (red lines) close to zero-axis, which led to the absence of constant error for colour fastness. Therefore, it can be concluded that all the values are constant and thus the F-tests were valid.

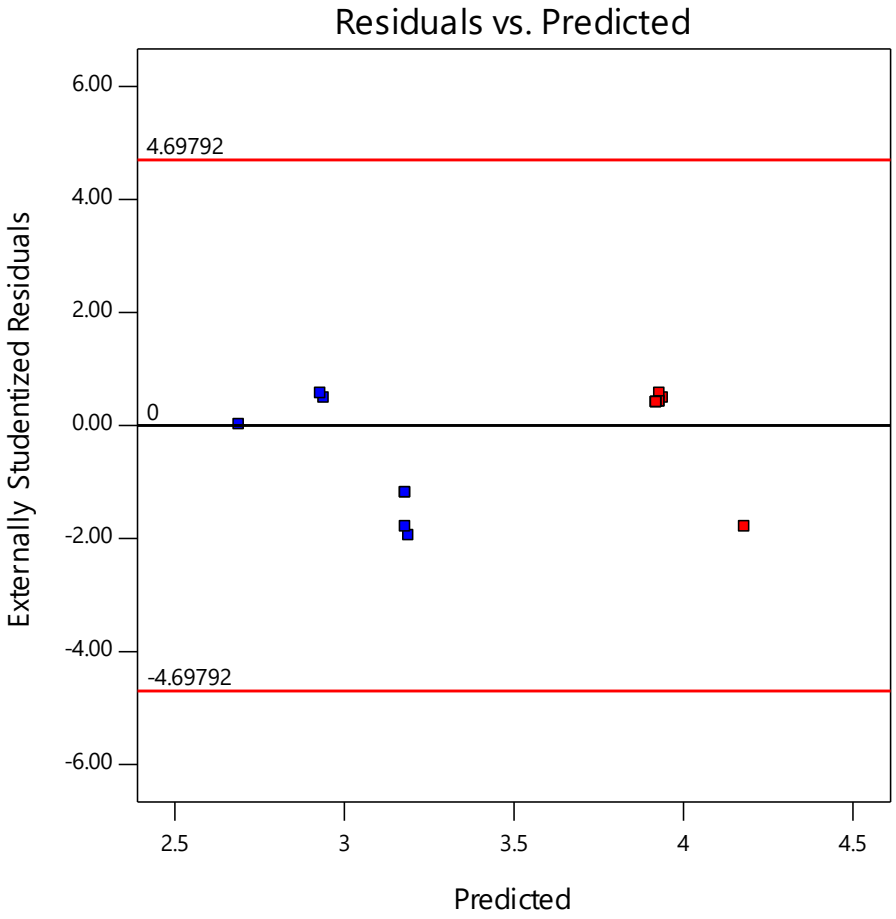


Figure 5-1: Diagnostic plot for colour fastness: externally studentised residuals vs predicted colour fastness values

5.3 Interaction effect of variables on colour fastness of fabric dyed with treated effluent

5.3.1 Interaction effect of Oxone level and dye concentration on colour fastness of the dyed fabrics at constant reuse cycles

This section discusses the response surface of colour fastness as a function of the selecting parameters. A two–dimensional (2D) contour and three-dimensional (3D) surface plots of the interaction effect of Oxone level and dye concentration, with constant number of reuse cycles to 2, are shown in Figure 5-2. The values of colour fastness of the dyed fabric at 0.5 g/l (-1), 1 g/l (0) and 1.5 g/l (+1) levels of Oxone concentration used during the treatment of the waste effluent were 4 (Good), 4 and Average (3.4) respectively. These results were similar to that obtained from dyeing fabrics with a treated effluent from a reverse osmosis process with a combination of persulfate oxidation and lime soda for reuse I and II by Zheng et *al*. (2015). However, the cost associated with reverse osmosis treatment is significant in terms of both electricity cost as well and maintenance of the membrane, where in the work presented a similar result was obtained without further treatment of the treated effluent, making it more cost effective. With an increase of Oxone level in the treatment process from 0.5 g/l to 1 g/l and from 1 g/l to 1.5 g/l, 15%

decrease in the colour fastness of the dyed fabric was observed. Therefore, when the concentration of Oxone increased from 0.5 g/l to 1.5 g/l, a decrease of only 15% in the colour quality the dyed fabric was observed. The decrease in colour fastness is due to the increase of salt in the treated effluent, as during the treatment process, the activation of Oxone by cobalt oxide catalysis leads to the production of sulphate radicals residuals (extra salt) in the treated effluent (Zhang et al., 2010; Stoyanova et al., 2014; Hu et al., 2016). In the next reuse dyeing process, during the exhaustion step, sodium sulphate was added, which produced a more concentrated dyeing solution causing a difference in shade between the fabric dyed with tap water (reference) and the fabric dyed with the treated effluent.

Colour fastness of the dyed fabrics at 3%, 5% and 8% (-1, 0 and +1) dye concentrations were 4, 3.8 and 3, respectively. With the increase of dye concentration from -1 to 0 levels (3% to 5%) and from 0 to +1 (5% to 7%), respectively, 5% and 21% decreases in colour fastness of the dyed fabrics were observed. In general, with the increase of dye concentration from -1 to +1 levels (3 to 7%), about 25% decrease in colour fastness of the dyed fabric was observed, which resulted in darker shades of dyed fabrics. This can be explained by the shade of the dyed fabrics increasing with an increase of dye concentration during the dyeing process, which makes the dyeing solution more concentrated (in term of dye). Therefore, the percentage of fixation rate of the dye increases, as it is known that reactive dyes have low fixation rates when used to dye cotton fabrics (Christie, 2007).

Finally, the effects of Oxone level and dye concentration on colour fastness of the dyed fabrics shows that Medium (0) levels of Oxone content (1 g/l), dye concentration (5%) and reuse cycles (2) resulted in the colour fastness of the dyed fabrics of Good (4). This value represents the optimised region for the selected reuse process conditions. These findings were opposite to the ones obtained from dyeing cotton fabric with reactive dye using a treated effluent from enzymatic horseradish peroxidase treatment process by Farias et *al*. (2017), with colour fastness of 4 and 2-3 in reuse I and II respectively.

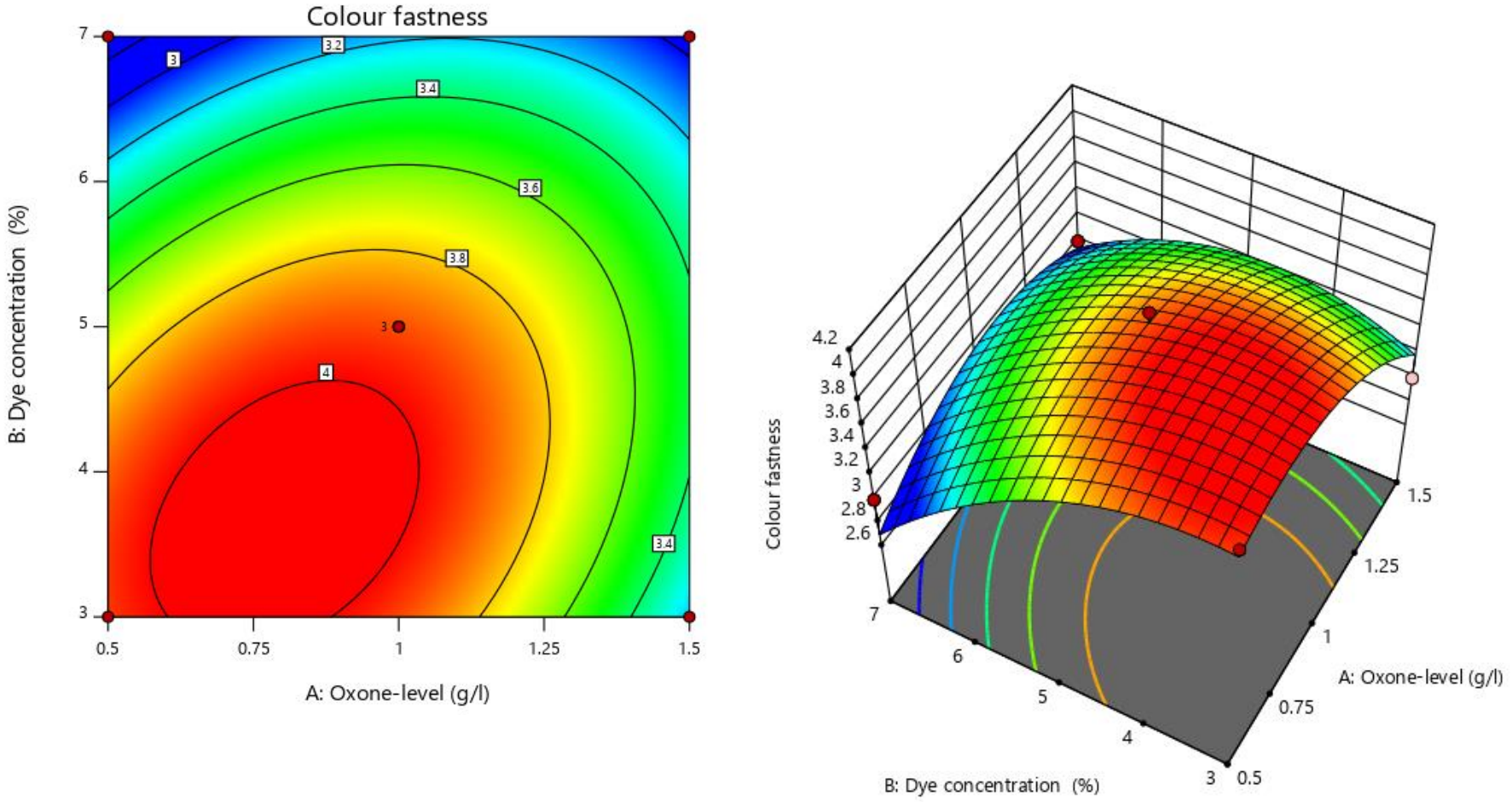


Figure 5-2: 2D contour and 3D surface plots showing the interaction effects of Oxone level and dye concentration on colour fastness at constant reuse cycle of 2

5.3.2 Interaction effect of Oxone level and reuse cycles on colour fastness of the dyed fabrics at constant dye concentration

The interaction effects of the Oxone level and reuse cycles on colour fastness with constant dye concentration of 5% are shown in Figure 5-3. The values of colour fastness at 0.5, 1 and 1.5 g/l (-1, 0 and +1) levels of Oxone level were 4, 4 and 3 respectively. Therefore, with the increase in Oxone level during the treatment of the effluent from -1 to +1 (0.5 g/l to 1.5 g/l), 25% decrease in colour fastness of the dyed fabric was observed. This decrease in colour was due to the presence of sulphate radical residuals in the treated effluent, produced during the treatment process and the concentration of dye (5%).

Colour fastness of the fabrics dyed with the treated effluent at 1, 2 and 3 (-1, 0 and +1) levels of the number of reuse cycles of the treated effluent were 4, 3.8 and 3.4 respectively. With reuse cycles of the treated effluent from 1 to 2 (-1 to 0) levels and reuse cycles from 2 to 3 (0 to +1) levels, 5% and 11% decreases of colour fastness of the dyed fabrics were respectively observed. Therefore, with the increase of the number of reuse cycles of the treated effluent from -1 to +1 (1 to 3) level, about 16% decrease in colour fastness of the dyed fabrics was observed. Again, the decrease in colour fastness is due to the fact that as the water was reused, it became more concentrated. Finally, the combined effect of Oxone levels and reuse cycles shows that 1 g/l level of Oxone level (0), 2 level of reuse cycles (0) and 5% level of dye concentration (0) resulted in a Good (4) rating of colour fastness of the dyed fabrics. The above parameters represent the optimised region at these process conditions. Here, colour fastness of the dyed fabrics at reuse II is slightly different from the fabrics dyed with an effluent treated by a catalytic ozonation process given a colour fastness of 4.5 (Hu et *al*., 2016). However, during catalytic ozonation process, the production of ions in the treated effluent is observed; causing a secondary pollution of the treated effluent which leads to further treatment of that same effluent and increasing the costs of the treatment process; contrary to the work presented where a similar colour fastness of the dyed fabrics was obtained from a single treatment process.

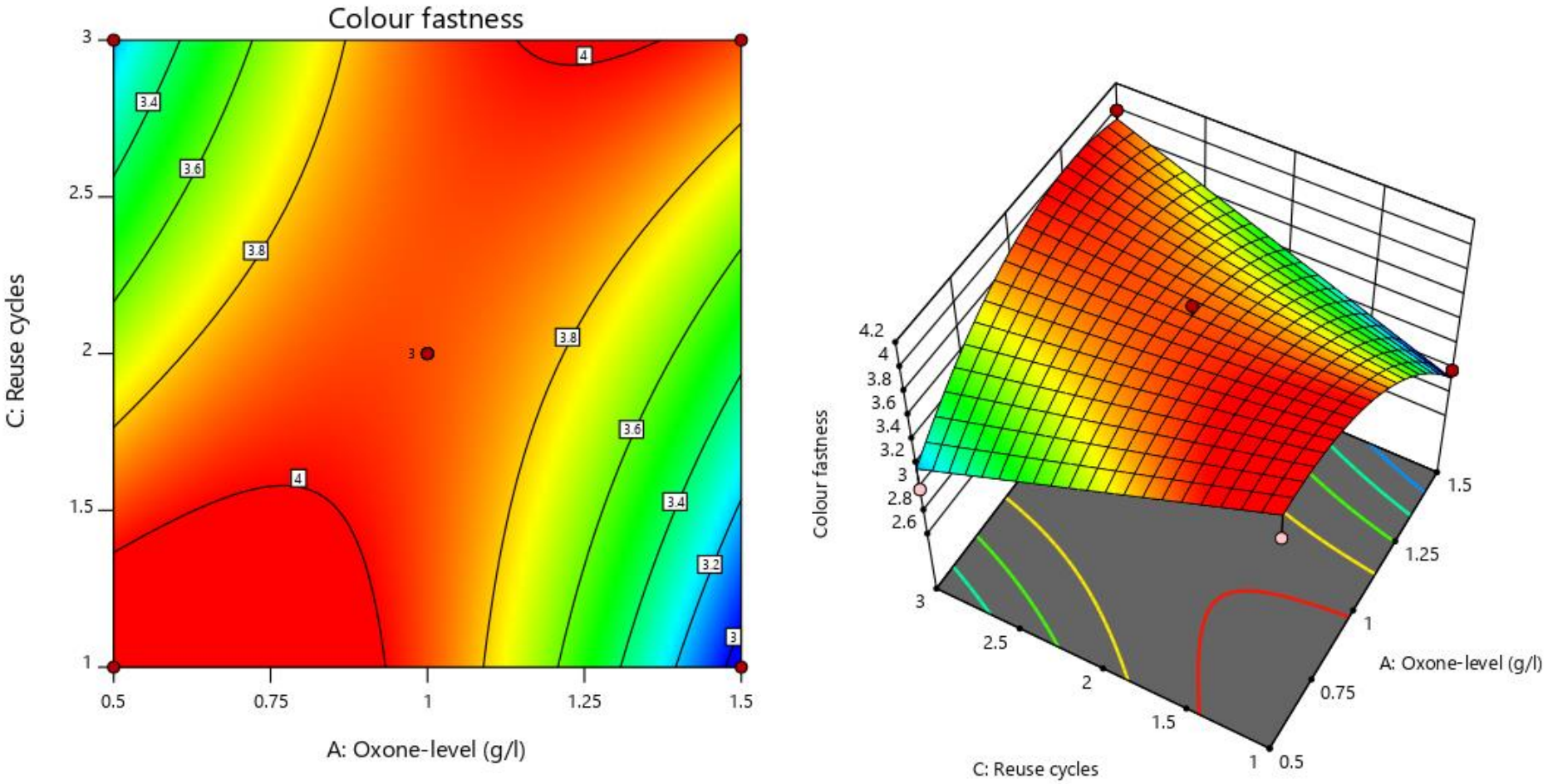


Figure 5-3: 2D contour and 3D surface plots showing the interaction effects of Oxone level and reuse cycles on colour fastness at constant dye concentrations of 5%

5.4 Optimum conditions for colour fastness

5.4.1 Criteria for optimisation

To determine the optimum conditions at which the maximum colour fastness of the dyed fabrics could be found, the criteria shown in Table 5-5 were defined. The purpose of this is to determine at which conditions the maximum high rating of colour fastness can be obtained by reusing the treated effluent multiple times at the lowest cost (meaning using low levels of Oxone and dye concentration). In this table, the criteria were set, as all three factors (Oxone level, dye concentration and reuse cycles) were kept in their respective range, and the importance of each factor was at an interval of 3. The goal for colour fastness was set to obtain the maximum grading of 5 (Excellent colour fastness of the dyed fabric with the treated effluents).

Table 5-4: Criteria for optimisation

Name	**Goal**	**Lower Limit**	Upper limit	Importance
A: Oxone level	is in range	0.5	1.5	3
B: Dye concentration	is in range	3	7	3
C: Reuse cycles	maximise	1	3	3
Colour fastness	maximise	3	4	5

5.4.2 Predicted values of colour fastness at the optimum settings

The optimum conditions for the colour fastness of the dyed fabrics with an effluent treated with cobalt oxide catalyst and sulphate radicals AOP are presented in Table 5-6. After numerical optimisation, the predicted values at the optimum settings with their confidence intervals were found as: dyeing process must be with 4.398% of reactive dyes concentration, the effluent must be treated with 1.322 g/l and the treated effluent must be reused thrice. These settings are desirable at a level of 1.

Table 5-5: Optimum conditions in reuse of treated textile effluent operational parameters

Oxone level g/l	Dye concentration %	Reuse cycles	Colour fastness	Desirability
1.322	4.398	3	4.044	1

Figure 5-4 shows the colour fastness of the fabrics dyed at the optimum conditions. Colour fastness of Good to Excellent (4/5) was observed in the first reuse. A decrease of 11% of colour fastness was observed in the second and third reuse with a rating of 4 (Good).

Tap water | Reuse I: 4/5 | Reuse II: 4 | Reuse III: 4

Figure 5-4: Colour fastness of the dyed fabrics from dyeing at the optimum conditions

5.5 Conclusion

The purpose of this chapter was to characterise the effects of the process parameters and their interactions on the colour fastness of the fabrics dyed with treated effluent from cobalt oxide and sulphate radical-based advanced oxidation processes using a continuous reactor system and reused several times. This study was conducted by doing factorial trial runs using a Box-Behnken design. The influences of Oxone level, dye concentration and reuse cycles at three (low, medium and high) levels on colour fastness of the dyed fabrics were studied and the optimum process conditions were determined. A predicted model for colour fastness was found at 95% confidence, with an adjusted coefficient of correlation of 83%. Among the selected factors, Oxone level was the dominant factor, followed by the interaction effect of Oxone level and reuse cycles influencing the colour fastness of the dyed fabrics, followed by the reuse cycles, dye concentration and interaction effect of Oxone level and dye concentration. Colour fastness of 4 (Good) of the fabrics dyed using this process was found when the treated effluent was reused twice, with a treated effluent dyed with 5% dye concentration and treated with 1 g/l of Oxone.

The interaction effects of all the process parameters have significant influence on the colour fastness of the dyed fabrics. The predicted optimum conditions for this process are that 1.3 g/l of Oxone must be used for the treatment of the waste effluent dyed with 4.4% of dye concentration and reused in three cycles.

Chapter 6: Conclusions and recommendations

6.1 Introduction

The optimisation of the three principal processes of dyeing, wastewater treatment and recycling processes was carried out by studying the effects of dye concentration, Oxone level and the number of reuse cycles on the colour fastness of the dyed fabrics with an effluent treated by cobalt oxide mediated sulphate radicals advanced oxidation (CO-SR-AOP) using a continuous reactor system and reused several times.

6.2 Conclusions

6.2.1 Preliminary studies

To obtain more or less 80% colour removal during the treatment process in three reuse cycles, the waste effluent from dyeing at 3% dye concentration must be treated with high Oxone concentration (3.5 g/l), with very high levels of salt in the treated effluent. To obtain low amounts of salt in the treated effluent using the same concentration of dye, the waste effluent must be treated with 0.5 g/l of Oxone. Standing time and dilution of the treated effluent do not have any significant effects on the colour fastness of the dyed fabrics. The recycling process of the amount of salt present in the treated effluent gives poor colour fastness results, with resultant darker shades of the dyed fabric. The preliminary studies showed that reuse I and II gave Good to Excellent colour fastness, while in reuse III the colour fastness of the dyed fabrics decreased when dyed with the treated effluent.

6.2.2 Colour fastness of the fabrics dyed with the treated effluent

In terms of colour fastness of the dyed fabrics, a significant model was found to predict the colour fastness of dyed fabrics with an effluent treated with the continuous reactor system using Oxone activated by Co_3O_4. The adequacy of the obtained model was proven by the finding that there was not a significant difference between the predicted data and the experimental data. A diagnostic plot from the analysis of colour fastness showed a goodness of fit of the predicted and obtained models. The study of the interaction effects of all three parameters (dye concentration, Oxone level and reuse cycles) concluded that they had significant effects on determining the colour fastness of the dyed fabrics.

The optimised region found from this process at which a Good colour fastness of the dyed fabric is obtained is as follows: the waste effluent must be obtained from dyeing with 3% dye concentration, then treated with 1 g/l of Oxone and reused in two reuse cycles. Finally, the predicted optimum process

conditions at which colour fastness obtained will be Good (4) and the treated effluent reused in three successful cycles are with a level of Oxone of 1.3 g/l and dye concentration of 4.4%.

6.3 Recommendations

From the findings presented previously, it can be concluded that using cobalt oxide and sulphate radical-based advanced oxidation process to treat and reuse an effluent from reactive dye and cotton fabrics is feasible. However, this process presents some weaknesses by which their improvement would lead to improving the quality of dyed fabrics and more reuse cycles of the treated effluent. Below are suggestions to improve on the established process:

To recover the amount of salt in the reuse dyeing process, the conductivity of the treated effluent can be fixed by calculating the amount of salt found in the treated effluent.

To obtain dyed fabrics with the same shade of colour for both tap water and treated effluent, the use of less concentration in the next dyeing process will be helpful.

Darker shades of the dyed fabrics usually found in third reuse cycles and also found in the modified reuse dyeing recipe can be obtained to dye denim jeans, as their dyeing procedure requires a large amount of salt and high dye concentration.

Furthermore, a detailed costing analysis to determine the exact amount of water that can be saved using such a process should be done for further promotion of the technology toward implementation.

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Appendices

Appendix A: Percentage colour removal and conductivities of the treated effluent

The measurement of percentage colour removal and conductivities of the treated effluent at different process conditions are presented in Appendix A.

Table A. 1: Colour removal of the treated effluent under different process conditions

Number of reuse cycles	3% dye and 0.5 g/l Oxone (%)	3% dye and 0.5 g/l Oxone (%)	3% dye and 0.5 g/l Oxone (%)
1	24.24	75.24	11.99
2	2.72	74.02	4.56
3	1.84	69.97	0.77

Table A. 2: Conductivity measurement of the treated effluent under different process conditions

Number of reuse cycle	% dye and 0.5 g/l Oxone (µm/cm)	% dye and 0.5 g/l Oxone (µm/cm)	% dye and 0.5 g/l Oxone (µm/cm)
1	2.6	4.1	6.1
2	4.6	7.6	11.3
3	5.1	15.1	17.2

Table A. 3: Conductivity of the treated effluent under different process conditions

Reuse cycles number	Conductivity (µm/cm)
1	2.1
2	3.1
3	3.9

Table A. 4: Conductivity measurement of the treated effluent at 25 and 50% dilution

Number of reuse cycles	25% dilution: conductivity (µm/cm)	50% dilution: conductivity (µm/cm)
1	2.36	2.36
2	3.99	3.43
3	4.99	3.88

Table A. 5: Conductivity measurement of the effluent after 4- and 48-hours' standing times of the treated effluent

	5 hours' standing time: conductivity (µm/cm)	48 hours' standing: conductivity (µm/cm)
T.1	2.36	2.36
T.2	4.39	4.5
T.3	6.22	6.28

Appendix B: COD, sulphate and cobalt residual amounts in the treated effluent

Appendix B represents the measured data for COD, cobalt and sulphate in the treated effluent at different dye concentrations during the preliminary work.

Table B. 1: COD measurement at different dye concentrations

DYE CONCENTRATION (%)	Reuse 1 (%)	Reuse 2 (%)
2	7.1	4.9
4	6.3	4.2
6	4.6	0.5
8	4.7	0.5

Table B. 2: Sulphate amount in the treated effluent at different dye concentrations

DYE CONCENTRATION (%)	Effluent from tap water (mg/l)	Reuse 1 (mg/l)	Reuse 2 (mg/l)
2	743.3	869.2	1984
4	933.4	999.8	2162
6	1043.3	1267.3	2431
8	1052.1	1649.3	3398.8

Table B. 3: Cobalt measurement at different dye concentrations

DYE CONCENTRATION (%)	Effluent from tap water (mg/l)	Reuse 1 (mg/l)	Reuse 2 (mg/l)
2	0.18	0.22	0.31
4	0.38	0.40	0.72
6	0.52	0.68	1.06
8	0.67	0.99	1.79