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# Decolouration of Reactive Dyes with Ozone in a Semi-Batch and a Continuous Stirred Tank Reactor

**Mohammad Taghi Fardin Tabrizi**

A thesis submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in fulfilment of the requirements for the degree of Doctor of Philosophy.

Johannesburg, 2013

# DECLARATION

I declare that this thesis is my own, unaided work, unless otherwise stated. It is being submitted for the Degree of Doctor of Philosophy to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

……

Mohammad Taghi Fardin Tabrizi

…… day of ……, 2013

# ABSTRACT

The aim of the thesis was to model and interpret the behaviour of ozone when utilised to decolourise reactive dye solutions in textile dyeing applications. The purpose of ozonating the dye solutions is to remove dyes from the waste streams produced in order to conserve the water and eliminate the impact associated with these industrial processes.

In order to explain the decolourisation process, ozonation experiments were conducted in a continuously stirred tank reactor (CSTR) and a semi-batch reactor (SBR). Experimental results at both steady state and unsteady state were obtained from both reactors.

Stoichiometry revealed that many dye molecules were decoloured per ozone molecule consumed (58 mole of dye solution per one mole ozone). This suggests that decolouration was taking place via a radical chain reaction. Different coloured dyes had different rates of decolouration. This implied the rates were not totally mass transfer controlled. It was found that the higher the initial dye concentration, the lower the rate of decolouration. This was an unexpected result when needed to be explained using the model. The effect of different gas-phase ozone concentrations appeared to be negligible.

For the SBR, there was a difference (what do you mean??) between the results of experiments. These occurred when the dye was added before the solution was pre-ozonated and when it was not. The former gave more consistent results and showed slightly higher initial rates. Because, for the CSTR, there are wide ranges of steady states as a function of residence time, the major benefit of using the CSTR rather than an SBR is that one can explore different regions of the reaction space. Thus, in doing modelling, one is in a position to assess the kinetic model against a wider variety of conditions.

A mathematical model was developed to describe the kinetic behaviour of the reactive dye degradation by ozone. The basis for the model took into account the phenomena observed as a consequence of exploring the implications of the experimental results described above. The model had three unknown constants and these were estimated by regressing on all the SBR data simultaneously. The fit between experimental and model data was found to be good. As a final verification of the model, it was used to predict the CSTR unsteady/steady-state data. Again, the fit was found to be good ($R^2$ =0.9897 Model versus experimental) thus suggesting the kinetic model captured all the important aspects of the

reaction kinetics. This model thus becomes potentially important for the design of future facilities for the degradation of a reactive dye by ozone.

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**List of Abbreviations:**

a=A/VL volumetric interfacial area

AOPs advanced oxidation process

Bé Bohme

C* the equilibrium ozone concentration in the liquid

$C_{dye}$ the concentration of dye in the liquid

$C_{dye}^{\circ}$ the concentration of dye in the feed stream

$C_{dye}^{ss}$ the dye concentration in steady-state

$C_{ozone}$ the concentration of ozone in the liquid

$C_{ozone}^{*}$ the equilibrium concentration of ozone in the liquid

$C_{ozone}^{ss}$ the ozone concentration in steady-state

CG concentration of ozone in the gas phase

CGI concentration of ozone in the gas phase at the interface

CL concentration of ozone in the liquid phase

CLI concentration of ozone in the liquid phase at the interface

COD chemical oxygen demand

$C_{radical}$ the concentration of dye decolouration

CSTR continually stirred reactor

D molecular diffusion coefficient

DDye decoloured dye

$dye^{\circ}$ the initial dye concentration

K mass transfer coefficient of film

| | |
|---|---|
| $K_{La}$ | the volumetric liquid controlled mass transfer coefficient for ozone |
| M | precise mass transfer rate |
| N (0.5 – 1) | varying on system turbulence |
| nm | nanometre |
| Q | the volumetric flow-rate of the liquid |
| $R_{dec}$ | the rate of dye decolouration |
| $R_{dye}$ | the rate of consumption (decolouration) of the dye. |
| $R_{ozone}$ | the rate of ozone formation |
| $R_{radical}$ | the rate of radical formation |
| $R_{term}$ | the rate of radical termination |
| USS | unsteady-state |
| t | time |
| SS | steady-state |
| UV/Vis | ultra violet/visible |
| V | volume of the liquid contents of the vessel |
| VL | liquid volume |
| λ max | maximum wavelength |

# 1. Chapter One: INTRODUCTION

## 1.1 Overall Introduction

The textile industry needs wet processing in order to convert raw materials to finished goods such as dyed and printed yarn as well as fabrics. For this purpose, the best and most used solvent by volume is pure water. Enormous quantities of water are used for the wet stages which includes sizing, desizing, bleaching, mercerizing, dyeing, printing and the processing of yarns and fabrics.[1-2] Textile mills are large industrial factories which generally use 0.2 – 0.5 $m^3$ of water to produce 1 kg of textile finished goods [3]. There are contaminants such as dust, grease, dirt, oil, colours of animal fibres, unused and dead dyes, organic and inorganic chemicals, polymers and fibres that, during the wet processing, are removed from the textiles chemically or by mechanical means. Ultimately, there are toxic organic and inorganic materials that pollute the remaining wastewater and this water has to be treated before it is released into the environment [4-9].

In the 21$^{st}$ century, with increasing world population, the consumption of water has also increased. Hence, as water is becoming a more valuable commodity, it is becoming more expensive. For this reason, most governments are making their emission regulations more stringent, making it compulsory for almost all industries to have a purification system for wastewater and effluents. Wastewater from textile industries is known to have a high chemical oxygen demand (COD), high alkalinity, medium biochemical oxygen demand (BOD) and also high content of total solids [10-12].

In the last decade, experimental investigations related to treatment of textile effluents have focused on the capabilities of traditionally-used treatment (oxidation) methods which are now deemed destructive. One question to ask is the following: are these technics really capable of removing coloured compounds in an economically feasible but also environmentally safer way?

The perceived advantage of chemical oxidation techniques lies in the avoidance of sludge generation and associated disposal costs. In the near future, it is more likely that destructive treatment methods will gain and more attractive at the expense of those that simply separate or concentrate pollutants.

Decolourisation of secondary treated dye-house effluents and the practical oxidation of raw textile waste water to promote its biodegradability by 'advanced oxidation processes' (AOPs) are currently under investigation. AOPs are based on the complete or partial mineralisation of organic pollutants by a complex radical mechanism mainly involving hydroxyls radicals ($^{o}OH$) at reaction rates with pollutants being appreciably higher than that of conventional oxidants. [13-16]

To date , AOPs have mainly focused on fundamental research or application oriented investigations on the degradation of dye, simulated dye-bath effluents or real textile wastewaters. With the aim to gain more insight on AOPs, the experimental work described in this thesis cundocted the treatment of reactive dyes with ozone in a SBR and CSTR.

## 1.2 Aims of Thesis

The operational problems and costs of various methods are major unresolved problems in wastewater treatment. Developing better mechanisms and methods for the textile industry to reduce environmental impact of its activities and improve its environmental performance is a critical phase towards more sustainable practices. This is especially so in South Africa.

### 1.2.1 Overall research strategy

The main aim of this research is to investigate the use of ozone for decolouring of azo dye solutions in wastewater to a standard at which it may be reused in the process or to be safely

discarded into the environment. In this research four reactive dye with colour index number (Red 198, Blue 21, Black 31 and Orange 107) were used.

### 1.2.2 Method and techniques

Ozone decolouration experiments with a range of azo dye solutions and concentrations were performed in a semi-batch reactor (SBR). In most experiments, a UV-vis spectrophotometer was used to measure the dye concentrations. These experiments were followed by the use of apparatus for CSTR experiments enabling a greater range of experimental conditions to be studied.

A kinetic model based upon the experimental observations was devised and fitted into the experimental results.

## 1.3 Thesis Overview

Chapters 3-5 in this thesis have been written in the style of journal articles. Each of these chapters has been published, submitted for publication, or prepared for submission in a reputable international journal. The current status of the each paper is given at the beginning of each chapter. As the chapters were written independently, repetition of the basics and some experimental results occur from one chapter to the other. However, this does allow each chapter to be read independently with each having its own abstract, introduction, approach and conclusion. The outline of this thesis is given as follows:

**Chapter 1** Introduction

**Chapter 2** In this chapter, we offer a review of the published literature related to wastewater treatment by ozone. The review covers major aspects of textile wastewater, dyes and dye auxiliaries, plus advanced oxidation process.

**Chapter 3** In this chapter, we describe all experimental techniques and procedures in the semi- batch reactor used to carry out the experiments on which the thesis is based. We also explain the methodology used to analyze and calculate the experimental data.

We measured the mass transfer coefficient and the solubility of ozone in water experimentally as well as determine its relationship to the ozone efficiency of decolouring.

**Chapter 4** The study in this chapter commenced with an investigation of the decolouration effect of ozone on the reactive dye in a CSTR. The effect of flow rate and the initial concentration their intensity as a function of time at steady state were measured. As well, the rate of decolouration was calculated under both steady and unsteady state conditions. The CSTR was run with various initial dye concentrations, dye solutions, as well as at various flow rates.

**Chapter 5** From the experimental data obtained in Chapter 3 and 4, a kinetic model was developed to simulate dye decolouration of the reactive dye using Ozone. The experimental results from the SBR were regressed against the model which had three unknown rate constants. Subsequently the model was verified against the CSTR results.

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# 2 Chapter Two: LITERATURE SURVEY

## 2.1 Wastewater in Textile Industry

One of the main consumers of water is the textile industry. Its output of wet processing generates wastewater with high pollution levels. Moreover, it is not easy to purify water with traditional methods such as biological and coagulation treatment. Nowadays, in order to achieve the completed supplies in the course of wet processing, the textile industry uses enormous amounts of water along with chemicals. The process consists of printing, finishing and dyeing. In a very wide ranging cycle, there are many different chemical materials utilized in this industry. Examples of these chemical compositions consist of inorganic chemicals, polymers and organic components [1].

The textile industry is well known for its immense up-take of water throughout its wet process . It is also well known for discharging large amounts of wastewater. For this reason, we are unable to use methods like organic, biological and coagulation as it is difficult to monitor the textile and wastewater through commonly used techniques with low efficiency [2].

The textile industry is the second-most chemically comprehensive industry in the world and follows agriculture as the largest polluter of pure water [3].

Table 2.1 provides a review of chemicals and substances applied in each procedure as well as the characteristics of wastewater effluent occurring in these processes. [4].

Table 2.1: Summary of Potential releases Emitted during Textiles manufacturing [4]

| Process | Air Emission | Wastewater | Residual Wastes |
|---|---|---|---|
| Fibre preparation | Little or no | Little or no wastewater generated | |
| Yarn spinning | | Little or no wastewater generated | |
| Slashing/Sizing | | BOD; COD; metals ;cleaning waste, size | |
| Weaving | | Little or no wastewater generated | |
| Knitting | | Little or no wastewater generated | |
| Tufting | | Little or no wastewater generated | |
| Desizing | | BOD from water-soluble sizes, synthetic size; lubricants; biocides; antistatic compounds | |
| Scouring | | Disinfectants and insecticide residues; NaOH; detergents; fats; oils; pectin; wax; knitting lubricants; spin finishes; spent solvents | |
| Bleaching | | Hydrogen peroxide, sodium silicate or organic stabilizer; high pH | |
| Singeing | | Little or no wastewater generated | |
| Mercerizing | | High pH; NaOH | |
| Heat setting | | Little or no wastewater generated | |
| Dyeing | | Metals; salt; surfactants; toxics; organic processing assistants; cationic materials; colour; BOD; COD; sulphide; acidity/alkalinity; spent solvents | |
| Printing | | Suspended solids; urea; solvents; colour; metals; heat; BOD; foam | |
| Finishing | | BOD; COD; suspended solids; toxics; spent solvents | |
| Product fabrication | | Little or no wastewater generated | |

Amounts assigned to textile sewage disposal have a high degree of TDS (1000 mg/l – 10000mg/L), COD (approximately 600 mg/L-4000mg/L) which are approximately 2 up to 5 times of the BOD level, alkalinity sum of (300mg/l-900mg/L), medium power of BOD (200mg/L-1800mg/L), chromium or copper ions which are initiated from certain dyestuffs (0mg/L-25mg/L) and an altering pH (5-12;mainly alkaline). The general volume of sewage disposal per Kg of processed textile commodities varies from167L - 834L. All these processes contribute towards toxicity of the wastewater needing to be characterized for possible treatment [2, 5].

Organic materials including dyes, detergents and starches often initiate chemical and biological changes within textile sewage. These changes tend to destroy marine life by consuming dissolved oxygen gained from rivers, drains, etc. To prevent 'septic conditions," it is important to eliminate these organic pollutants, including soluble inorganic salts, before they are released into the environment. Such waste water is completely inappropriate for farming, manufacturing, public and home use as it has a corrosive effect on boats and other structures (such as bridges) coming into contact with it. [6]

Other metals that should also be removed before being released into the environment are copper, zinc and chromium, which are all toxic. Therefore, to put this into effect, governments of the world are increasingly more strict about permit limitations involved in the purification of wastewater [6].In order to meet sewage removal constraints – specifically in relation to colour, pH, heavy metals, ionic salts, COD and dissolved solids – it has become commonplace for the textile industry to face enormous impediments [7-9].

Even though the majority of colours are not really bio toxic, they are difficult to purify water back to a point where it is suitable for drinking. Textile industry chemicals such as phenol can be toxic and also alter the taste and smell of water. As a result meeting government standard regulations for discharging wastewater is becoming more difficult every day. To minimise contamination released into the environment, very special and efficient treatment methods need to be set into motion.

Years of experience have shown treating textile wastewater via conventional methods is a very difficult task. This effluent has a very high concentration of ecological dyes and inorganic salts. [10]. Dye-baths include up to 50g/l of total solids, 4g/l $BOD_5$ and 30-40g/l COD. In practice, the input of contamination load of dye with consequent washing and rinsing processes may not be more than 20-40%, but the volume is significantly outsized and normally less than 50% of the total [10].

Removal of colour, in particular, is the primary environmental challenge facing textile manufacturing. This is especially true today with the advent of synthetic dyestuffs which can be non-biodegradable and even toxic [11]. In the following section, more comprehensive information about dyestuffs and auxiliaries found in the dye house wastewater are discussed.

## 2.2 Dyestuffs in Textile Industry

In 1856, William Henry Perkin invented and initiated the first production of synthetic dyes on a large scale basis [12].

Typically, dyeing is done in a number of ways. What is presented in (Table 2.2) is the most frequently used dyes in textile manufacturing along with their descriptions and the representative related fibres. Today's dyes, because have an elevated and brilliant wet fastness as well as an extremely bright saturated colour. Therefore, the utilization of reactive dye-stuffs is in a prime position for high level growth.

Particular consideration needs to be given to dyes and their chemical binding agents with fibres to lessen colour release into the sewage disposal system. However, because of the low degree of fixation (50%-85%) possessed by reactive dyes [13] cotton, wool as well as several

man-made fibres – polyamide and synthetic cellulose fibres such as viscose rayon – could be dyed by reactive dyes if they are suitably pre-treated and accustomed [13-14].

An English company called ICI established the first reactive dyes in 1956. These dyes comprised the covalent link connecting the dye and the fibre. Through this form of reaction, remarkably positive changes were introduced. Innovations such as straightforward dying techniques, exclusive of any oxidation or reduction in the dying system resulted in a stronghold of properties and an enormous improvement for the dyeing of cellulosic fibres [15].

Adding to the density of the procedure are the various techniques used, as well as the employment of new dyes and auxiliaries. Different types of dyes are used according to their fibre categories. These are illustrated in Table 2.2[4].

Table 2.2: Typical Characteristics of Dyes Used in Textile Dyeing Operations

| Dye class | Description | Method | Fibres typically Applied | Typical Fixation (%) | Typical Pollutants Associated with Various Dyes |
|---|---|---|---|---|---|
| Acid | Water-soluble anionic compounds | Exhaust/Beck/Continuous (Carpet) | wool<br>nylon | 80-93 | Colour, organic acids, unfixed dyes |
| Basic | Water-soluble, applied in weakly acidic dye baths, very bright dyes | Exhaust/Beck | Acrylic some polyesters | 97-98 | N/A |
| Direct | Water-soluble, anionic compounds; can be applied directly to cellulosic without mordant (or metals like chromium and copper) | Exhaust /Beck/Continues | Cotton<br>Rayon<br>Other cellulosic | 70-95 | Colour, salt; unfixed dye; cationic fixing agents; surfactant; de foamer; levelling and retarding agents; finish, diluents |
| Disperse | Not water – soluble | High temperature /exhaust/Continuous | Polyester/acetate<br>Other synthetics | 80-92 | Colour; Organic acids; Carriers; Levelling agents; phosphates; defoamers; lubricants; dispersants; delustrants; diluents |
| Reactive | Water soluble, anionic compounds; largest dye class | Exhaust/Beck/Cold pad batch/Continuous | Cotton<br>Other cellulosic<br>wool | 60-90 | Colour, salt; alkali; unfixed dye; surfactants; defoamer; diluents; finish |
| Sulphur | Organic compounds containing sulphur or sodium sulphide | Continuous | Cotton<br>Other cellulosic | 60-70 | Colour; alkali; oxidizing agent; reducing agents; unfixed dye |
| Vat | Oldest dyes; more chemically complex; water-insoluble | Exhaust/package/ Continuous | Cotton<br>Other cellulosic | 80-95 | Colour; alkali; oxidizing agent; reducing agents |

## 2.2.1 Reactive Dye as largest category in textile industry

### 2.2.1.1 Chemical specification of reactive dye

Reactive dyes are known as colour compounds which consist of groups able to create covalent bond between a carbon atom of the dye ion or molecule and an oxygen-nitrogen- or sulphur –atom of a hydroxyl or amino group of the fibres respectively [16].

Dichlorotriazine and nucleophilic aromatic substitution are utilized as a reactive connector by reactive dyes. It requires a nucleophilic group on the chromophore and can acquiesce to a broad range of chromophores in its formation [17].

In order to create a dye fibre bond, the pH needs to increase in order to achieve the creation of cellulosate. Therefore, nucleophilic addition is supported. Groups are classified according to information cellulose, protein and nylon fibres contain – forming groups able to react as nucleophilic substrates.

These dyes can be created in three categories :

A) a group able to react with nucleophilic addition-elimination – (heteroaromatic) substitution mechanism. The following representatives are part of this group: monoclorotriazines (Procion MX/H, Cibacron dyes), trihalogenpyrimidine (Drimarene X/F, Verofix), dichloroquinoxalines (Levafix E,Cavalite), dichloropyridazone (Primazin P)

B) a group which reacts with the addition of the nucleophilic group of the substrate to a-C=C- double bond on the reactive group. Sulphuric acid esters of B-hydroxyethylsulphones (Remalan and Remazol dyes) which from vinilsulphones (Hostalan & Remazolan dyes), and sulphuric acid esters of B-hydroxy/chloropropionamides (Primazin dyes)

C) a group which reacts under acidic conditions. They contain N-methylol groups (Calcobond dyes).

Solubility of the dye in water is indicated by the number of sulphonated acids within the group. Reactive dyes for cellulose and protein fibres generally require two or three sulphonated acid groups [16].

The number of sulphonated acid groups determines the solubility of the dye in water. A minimum of two to three sulphonated acid groups are essential for the reactive dyes to penetrate cellulose and protein fibres. (Bird and Boston,1975) [16].

#### 2.2.1.2 Benefits and flaws of reactive dyes

The benefits of reactive dyes consist of the following: by having covalent links among the fibres and the dye, the colour fastness advances extraordinarily. Additionally, the dye method is also made easier.

The main flaws of this method is it requires an additional washing procedure and huge amounts of electrolytes are essential to bond the dye with fibres. Lastly, through the dying stage, certain components of the dye hydrolyse, turn into dead dye in the water solution.

## 2.2.2 Reactive dye auxiliary chemicals

### *2.2.2.1* Electrolyte (Salt*)*

Electrolyte can be defined as any substance that dissociates into ions when dissolved in a suitable medium or melted, thus forming a conductor of electricity. In order to displace the dye in the fibre, electrolyte has to be added to it. It is essential to utilise a great quantity of ordinary salt (NaCl) or Glabuber's salt (hydrated $Na_2So_4$) in order to consign the dying process with the reactive dyes.

NaCl is dissolved more easily than Glauber's salt. If electrolyte is not free from alkali, premature fixation or hydrolysis of the dye may occur. Some factors like impurity are able to critically influence the dying reproducibility. These are earth alkali (Ca, Mg) or transition metals (Cu, Fe). However, this situation is controllable by sequenctrating agents like EDTA. But, one must be aware that if EDTA is used in an uncontrolled manner, it can result in hue change and a decrease in light fastness [13].

### 2.2.2.2 Alkali

Alkali is a substance producing hydroxide ions, OH- when dissolved in water. The term originates from the Arabic al-qili, "ashes of the saltwort plant".

Alkali is created in order to encourage reaction amid the dye and the fibre as well as acting as a pH barrier. The most well-known alkalis are Caustic soda, soda ash, caustic sodium silicate as well as various phosphates. Usually used as the concentrated liquors of well-known concentration (i.e.48Be) [13].

#### 2.2.2.3 Other dye auxiliary chemicals

Wetting agents, levelling agents and antifoam are other auxiliaries in a reactive dye-bath and in some types of dyeing, for example exhaust dyeing, it is not essential to add wetting of levelling agents. In Jet or overflow machines, created foam can be controlled by adding selected antifoam agents in the dye-bath. At high temperatures – more than 70 °C – some reactive dyes may incur reduction. This is due to the combined effects of heat, alkali and aldehydic groups present within cellulose. In this case, it is advised to add 1-2g/L of sodium m-nitrobenzene sulphonate to resolve the problem.

#### 2.2.2.4 Dye residues in dye bath

In the dyeing process, up to 50%, of reactive dyestuffs (colour) may be lost in dye house wastewater. However, this effluent cannot be reused or recovered. Today, following much effort, reactive dyes with higher fixation rates have been developed. These dyes are specifically designed to minimise the level of hydrolyzed dye in waste water [13].

New types of bio-functional dyes include two reactive anchors in the dye molecule and are very suitable for the fixation of dye into fabrics, raising fixation efficiency from 70% to 91%. In bio functional dye, the overall fixation rate is 77% and dye lost into effluent water is therefore a maximum of 23%. The addition of this second reactive group results in a reduction of 40% of colour loss into effluent water [5].

## 2.3 Wastewater Treatment in Textile Industry

### 2.3.1 Conventional methods

There still exists a huge challenge on the issue of disposing the effluent streams without having negative effect on receiving water bodies. Many avenues have been taken – preservation, procedure alteration and better housekeeping – to decrease the strength and volume of waste water. However, there are numerous waste water treatment techniques and these vary from one mill to the other. Possible treatment processes have been offered up by the mills but these 'solutions' are hinged upon existing types of treatment services, the kind of waste water involved and the level of treatment required. A cornucopia of issues arise from textile processing sewage disposal. These most often include: colour resolution, temperature, surplus in pH, foaming, as well as heavy metals initiated by dye sewage disposals [14, 18].

In the course of traditional textile techniques in wastewater treatment, a combination of various methods is used. These include biological, chemical and physical techniques [19-21].

Some traditional methods employed include: separation (of process sewage disposals needing particular treatment), broadcasting, mechanical filtration, equalisation and neutralisation as the primary steps. This is usually followed by chemical solidification, flocculation, flotation and biological treatment or a combination of these as a secondary treatment technique. In this way, the reduction of organic load is aimed and finally, an optional tertiary polishing treatment (chemical oxidation) and disinfection via chlorination or ozonation.

Textile effluents free of toxic materials can be easily processed by organic oxidation after an initial equalisation/neutralisation of the unprocessed sewage through the traditional methods. Due to the low costs and simplicity a number of methods – like activated sludge, trickling

filters, unlimited aeration, long-lasting aeration and internal breathing – they are consistently being used in the textile industry for wastewater purification.

Less space and expenditure is required in the process of activated sludge. However, it is considered more susceptible than dripping filters to changes in pH, shock loading and toxic sewage disposal. Though progress has been made in other techniques, probabilities are up to 99% of treatment efficiencies are for COD [22].

Another technique used is oxidation ponding. This is a cost-effective technique and encircling temperatures are high with the easily obtainable land area. The anaerobic method of this style is chosen if the organic loading rate is likely to be high. In the case of textile wastes – including dyestuffs that absorb solar exposure and therefore, reducing the O2 generation treatment effectiveness – choosing the aerobic type can be challenging. Typically, coagulation is the method most useful for textile effluents, which follows the organic method. This method may also be predominantly beneficial for alkaline sewage disposal.

Inexpensive waste ferrous sulphate, with its higher pH rate, may also be used. An added benefit of this alternative is that it concurrently neutralises sewage disposal. The percentage of removal of parameters is shown in Table 2.3[18].

Table 2.3: Percentage of the removal of parameters

| Parameter | Removal (%) |
|---|---|
| BOD5 | 40-55 |
| COD | 35-40 |
| Colour | 80-95 |
| SS(Suspended solids) | 85-95 |

Some heavy metals as well as sulfides are accelerated and assimilated on ferrous hydroxide flocks. The batch coagulations/flocculation (C/F) executed in sequencing analogous tanks is currently deemed a more capable method than constant flow technique [18].

Because exponential growth of the population accelerates rising drains of resources in the manufacturing sector, traditional water and wastewater treatment is rapidly becoming outdated. And, as greater quantities of pollutants enter into the world's waterways, sources of potable water are equally reduced.[23].

In order to treat textile wastewaters, numerous processes have been considered. Nonetheless, their function in an industrialised plant is complicated by inherent problems and issues related to costs. Biological management via activated sludge does not entirely eliminate the colour of water nor does it adequately deal with continuing problems such as the appearance of bulking. However, this process does offer high propensities for COD deduction. For separating treated wastewater from the activated sludge, flotation is used as an alternative to sedimentation and resolves this problem. However, it increases depuration expenses and complicates plant operations [24, 25].

Using the flotation method as an alternative to sedimentation, the treated wastewater from the activated sludge can solve this problem but it raises depuration expenses and complicates processes at the mills [24, 25].

## 2.3.2 Colour removal of textile effluents in advanced treatment

### 2.3.2.1 Adsorption

In colour removal of textile effluents, the most useful adsorbent is activated sludge and has been broadly studied in numerous dye modules. Other cheaper adsorbent materials have also

been studied. These include the use of peat, sawdust, meat, chitin, clay, activate alumina, wheat, bentonite, $MnO_2$, rice bran, turkey feathers and even activated sludge [26].

Dye characteristic can broadly determine "adsorbability" and normally, in the presence of hydroxyl group, $No_2$ and –N=N (Aza) groups, this increases. In the presence of sulphonated acid groups, "adsorbability" will reduce [26].

The removal of dye requires the use of a combination of carbon active ingredients with polymer flocculation, chemical reduction or biodegradation to become efficient. The upside of this process is: it's very economical.

#### 2.3.2.2 Filtration with membrane

A primary concern of textile manufacturing industry is the reduction of waste at the source coupled with the recovery and reuse of waste water. Attending to water flow following purification and eliminating the remaining waste is a component of textile manufacturing which cannot be ignored. The membrane method has been assigned to the recycling of wastewater. This involves wet processing effluents as well as the application and reuse of dyestuffs. Osmosis and ultra-filtration can be very efficient in the removal of dye colour from the effluents in all types of dyes [5, 26].

For revival of the vat dye, various membrane filtration methods have been stated in the literature [5, 14, 26].

By using membrane in combination with physic-chemical methods, water shows a great undertake for reusing treated water in the industry, but because of the limit in membrane

application due to the blocking and uncleaned filters is not completely promising technique [24, 27-29].

The use of membranes is still not favourable in the textile industry and can only concentrate for the recovery of sizing agents in the process of desizing separate effluents and also recovering of indigo dye from normal dye wastewater by ultra-filtration [24, 28, 30].

In the course of these methods, saturated salts, caustic soda and low molecular liquid – which include heavy pollutants – are treated by employing ordinary wastewater treatment facilities. Following this, they are released into the environment.

Treating wastewater containing reactive dyestuffs via the membrane method has been widely studied [31, 32].

To remove dyestuffs, a nanofiltration unit can be used. This colour free liquid is mixed with salts and low pollutant molecules can be released or reused. The hydrolysed reactive dyes remaining in this system can be removed by the chemical method.

In reverse osmosis processes, the osmosis membrane is used on stainless steel or porous ceramic in the form of tubes. This efficiently removes TOC (>85 %) and colour %-80% [30].

Polysulfone membrane has extremely high resistance to solvents, strong acids and high temperature [14, 30, 31].

Vat dyestuffs are insoluble in the water and cannot penetrate into the membrane. The membrane method is used for this type of colourant. A two phase membrane method is utilised to concentrate non-biodegradable natural materials (dyes and auxiliaries) prior to

their successive chemical destruction. The chemical structure of some dyes has greater control over selective removal than their molecule weight [30].

However, according to the reports, the use of membrane methodology in the textile industry remains uncommon. Usage, instead, is concentrated on the recovery of sizing agents and materials from desising effluents. This also can include ultra-filtration recovery of indigo vat dye from dyeing effluents [33,27,29].

#### 2.3.2.3 Ozonation

a. General Aspects

Ozone is a molecule that consists of three negatively charged oxygen atoms. The ozone molecule is very unstable and has a short half-live, causing it to fall back into its original form after a while, according to the following reaction mechanism:

$2O3 \rightarrow 3O2$

Principally, an ozone molecule is nothing but an oxygen molecule that has received an extra oxygen atom by electric high voltage. Ozone is naturally produced through certain types of chemical reactions. The most commonly known example is the ozone layer, in which ozone is produced by ultra violet rays (UV), which derive from the sun. Ozone is also formed during thunderstorms, in waterfalls and – although this is a less natural process – in photochemical smog which forms in summer. In thunderstorms, ozone forms as a result of the high voltages that are involved. The specific fresh scent after a thunderstorm is caused by ozone formation.When one speaks of ozone, the above-mentioned examples are immediately associated with it. It is however less known that ozone can be artificially produced, so that it can be used for water treatment. Ozone generators can create ozone artificially by means of extremely high voltages or by means of UV-light. Both methods involve the decomposition

of the oxygen molecule. This causes oxygen radical formation. These oxygen radicals can bind to oxygen molecules, forming ozone (O3). [34]

Ozone ($O_3$) at room temperature is a colourless and an allotropic type of oxygen gas. To form O3 from oxygen, an enormous quantity of energy is needed. O3 is one of the greatest oxidizing agents and can oxidize almost all organic complexes.

Temperature and pH are effective in ozone stability. Ozone has an oxidation potential of 2.07V, compared to chlorine's (=1.36V). In the category of powerful oxidizing agents, ozone is listed fifth – after OH, O, $F_2$ and $F_2O$.

In distilled water, the half-life of ozone is known to be about 20 minutes and ozone doses are considered potentially serious above 50 ppm [31].

Ozone's reaction with biological mixtures can be categorized as 1, 3-addition, 1, 3-insertion, electrophilic, nucleophilic and electron transfer reactions [30]. Among them, electrophilic attack and the 1, 3-addition reaction are the most commonly known and studied reactions of ozone. Ozone readily attacks unsaturated –N=N and –C=C double bonds.

b. Ozone-Dye Chemistry

To decolourize dye, we must involve ozone with the oxidative cleavage of a conjugated system of the dye molecule. Table 2.4 illustrates the reaction mechanism of dye class.

Table2.4: Ozonation of different Dye Classes [31].

| Dye Class | Reaction Mechanism |
|---|---|
| Stilbene | Attack of the central olefinic bond (1,3-addition) |
| Indigoid | Attack of the central olefinic bond (1,3-addition) |
| Azomethine | Electrophilic Attack of the N-atom |
| Azo | Electrophilic Attack on the hydrazine isomer, main product: N2 gas |
| Anthraquinone & Tripheniylmethane | Attack of the carbon skeleton |
| Xanthene | 1,3-insertion reaction at the C-H bond of the 9-position |

Reaction of $O_3$ can differ with different types of dyes – from 0.0046 to 0.0123K/S-1( First order reaction rate constants).Dyes with olefinic and hydrazine groups of dyes, reaction occurs readily by $O_3$, but complex and anthraquiniod dyes are rather stable in the presence of $O_3$ [30].

On the other hand, ozone molecular reactions are selective and in most cases they proceed through electrophilic attack; though ozone can react through nucleophilic or oxygen transfer pathways. The electrophilic attack occurs on sites possessing high negative charge density including multiply bonded species such as –C C– or –N N–, and atoms such as N, P, O, S. Direct reactions of ozone with compounds having ortho- and para-directing substituent (i.e. electron donors) such as as –OH, –CH3, –OCH3, –NH2 may also occur [35]. Several studies have shown that it is the molecular ozone reaction mechanism that is responsible for the partial oxidation of azo dyes (i.e. colour removal) [36-38] and it was suggested that the first stage of decolourisation occurs through ozone reaction with the double bond azo chromophoric group–N N– or with the double bond of the –C C– connecting aromatic rings. Generally the decolourisation with ozone occurs rapidly due to the rapid destruction of the

conjugated chains of the dye molecules that are responsible for colour. Rate constants of ozone reactions with dyes in the range of 103 and higher than 107 L/mol s have been reported in the literature [39,40].

In wastewater, ozone can be used as a pre-treatment to increase biodegradability. However, ozone treatment still needs to be made cost effective. For example, the cost of ozone treatment of effluent is (1.57USD/t effluent for 100 tonnes of wastewater). While, compared to activated sludge (bio treatment), reclaiming dye wastewater the cost is only (0.72USD/t effluent) [31].

The $O_3$ requirement in a defined form mainly depends on the background COD and TOC. For example: For 150mg/l-70mg/l O3 is required in 10-15min of treatment. For minimum ozone demand, pre-treatment is advisable [31].

## 2.4 Advanced Oxidation Processes (AOPs)

Oxidation is usually used for the chemical alteration of a pollutant to become extra oxygenated types in water and wastewater treatment preparations. This is done by ways of reaction with oxidizing means, namely oxygen ($O_2$), ozone ($O_3$), hydrogen peroxide ($H_2O_2$), or sodium hypochlorite (NaOCl)[41].

One of the most useful amongst all wastewater treatment techniques is the advanced oxidation process ($AOP_S$). This technique uses Ozone, $O_3/H_2O_2$ and $H_2O_2$/UV-C oxidation that seems to be the capable applicant for complete dye house sewage decolourization. [42].

At present, no useful technology – at economical cost – has been created to accomplish colour deduction [43].

One of the main difficulties facing manufacturers discharging wastewaters containing a substantial variety of dyes is wastewater decolourization. Furthermore, the most capable technique for effluent decolourisation is the procedure referred to as Ozonation – the advanced oxidation process (AOPs) [44- 50].

Several European countries are obliged to decrease the colour in the dye house effluent even though highly developed destruction treatment techniques – namely, photochemical or photo catalytic oxidation – are somewhat costly [42].

At the complete finishing point of the oxidation procedure, contaminants are generally transformed into water and carbon dioxide. However, hypothetically, reaction time for the absolute oxidation of industrialised effluents would certainly be longer. Therefore, this makes it impossible as a function of sewage disposal. In highly developed oxidation, when the rate of oxidation is taken as a whole, it has been observed it becomes significantly larger when compared to levels achieved when adding oxidising agents. This process is achieved by the creation of extreme reactive initiators (radicals) such as hydroxyl radical ( $^{\cdot}$OH) in APO's [51-52]. In Table 2-5, reaction time constants (k, M-1 s-1) of ozone vs. hydroxyl radical is explained and in Table 2-6, Oxidizing potential for conventional oxidizing agents is shown.

Table2.5: Reaction time constants (k, M-1 s-1) of ozone vs. hydroxyl radical [53,54 ].

| Compound | O3 | $^{\cdot}OH$ |
|---|---|---|
| Chlorinated alkenes | $10^3$-$10^4$ | $10^9$-$10^{11}$ |
| Phenols | $10^3$ | $10^9$-$10^{10}$ |
| N-containing organics | 10-$10^2$ | $10^8$-$10^{10}$ |
| Aromatics | 1-$10^2$ | $10^8$-$10^{10}$ |
| Ketones | 1 | $10^9$-$10^{10}$ |
| Alcohols | $10^{-2}$-1 | $10^8$-$10^9$ |
| Alkenes | $10^{-2}$ | $10^6$-$10^9$ |

Table2.6: Oxidizing potential for conventional oxidizing agents [55-57].

| Oxidizing agent | Electrochemical Oxidation potential (EOP), V | EOP relative to chorine |
|---|---|---|
| Fluorine | 3.06 | 2.25 |
| Hydroxyl radical | 2.80 | 2.05 |
| Oxygen (atomic) | 2.42 | 1.78 |
| Ozone | 2.08 | 1.52 |
| Hydrogen peroxide | 1.78 | 1.30 |
| Hypochlorite | 1.49 | 1.10 |
| Chlorine | 1.36 | 1.00 |
| Chlorine dioxide | 1.27 | 0.93 |
| Oxygen (molecular) | 1.23 | 0.90 |

Many techniques exist for producing ˙OH. These comprise of both non-photochemical and photochemical procedures:

-Ozonation at elevated pH (>8.5)

-Ozone +hydrogen peroxide ($O_3/H_2O_2$)

-Ozone catalyst ($O_3$/CAT)

-Fenton system ($H_2O_2/Fe^{2+}$)

-$O_3$/UV

- $H_2O_2$/UV

- $O_3$/ $H_2O_2$/UV

-Photo-Fenton/Fenton-like Systems

-Photo catalytic oxidation (UV/$TiO_2$) [58].

## 2.4.1 Non-photochemical techniques

Few renowned techniques exist for producing hydroxyl radicals exclusive of using light power. Two of these techniques reside within the effects of ozone and one uses $Fe^{2+}$ ions as its method of operation. The latter techniques are considered ozonation at increased amounts of pH (>8.5), combining ozone with hydrogen, ozone+catalyst plus the Fenton scheme.

### 2.4.1.1 Ozonation at increased pH

The rate of disintegration rate of ozone in water rises as pH increases. For example, if we take pH10, the half-life of ozone in water can be less than one minute. As a result of the combination of reactions with molecular ozone and reactions with OH radicals, oxidation of pure species can take place. The reaction involving hydroxide ions and ozone lead to the creation of the super-oxide anion radical O2 and hydroperoxyl radical HO2. The reaction involving ozone and the super-oxide anion radical creates the ozonide anion radical O3.,The

radical instantly decays releasing OH radical. In short, the three ozone molecules generate two OH radicals [59].

$3O_3 + OH^- + H^+ \rightarrow 2\dot{O}\text{H}+4O_2$ (2)

### 2.4.1.2 Ozone + hydrogen peroxide ($O_3/_{H2O2}$) – (peroxone)

Combining hydrogen peroxide to ozone may instigate the composition sequence of ozone, which then results to the creation of OH radicals [60].

$H_2O_2 \rightarrow H_2O^- + H^+$ (2.1)

$HO_2^- + O_3 \rightarrow HO_2^{\cdot} + O_3^{\cdot -}$ (2.2)

The reaction carries all along the indirect passageway as mentioned in the latter process and the OH radicals are then formed [61]. This combination of the varying reaction steps illustrates that the two ozone molecules generate two OH radicals:

$2O_3 + H_2O_2 \rightarrow 2\dot{O}H + 3O_2$ (2.3)

### 2.4.1.3 Ozone + Catalyst ($O_3$/CAT)

Using diverse or homogenous catalysts is an additional opportunity to speed up ozonation reaction. Many metal oxides and metal ions ($Fe_2O_3$, $Al_2O_3$--Me, $MnO_2$, Ru/$CeO_2$, $TiO_2$-Me, $Fe_2$+, $Fe_3$+, $Mn_2$+, etc.) have been considered and at times, a considerable increase in the

decay of the main compound has been attained. This has occurred, even though the reaction device in the majority of the cases remained uncertain.

For example, the complex oxidation of chlorobenzenes in wastewater by means of iron and manganese ions as mixed catalyst resulted in the decrease of the overall organic carbon (TOC) and chemical oxygen demand (COD) from wastewater was more proficient with the ozone /catalyst method when compared to oxidation with ozone at elevated pH standards. The $O_3$/Mn(II) and $O_3$/Fe(II) methods were more efficient in the elimination of organochloride compounds compared to the $O_3$/Fe(III) and $O_3$/high pH methods[62].

#### 2.4.1.4 Fenton system ($H_2O_2/Fe^{2+}$)

More than a hundred years ago, Fenton explained the procedure for maleic acid oxidation [63].

$$Fe^{2+}+H_2HO_2 \rightarrow Fe^{3+}+ OH^{-}+\dot{O}\text{H} \qquad (2.4)$$

A stable space for feedback of ferrous ions with hydrogen peroxide is elevated Fe(II) oxidizes when compared to Fe(III) which ranges from a few seconds to minutes in the presence of surplus quantities of hydrogen peroxide. Hydrogen peroxide decays catalycally by Fe (III) and reproduces hydroxyl radicals with regard to the feedbacks:

$$Fe^{3+}+ H_2O_2 \rightleftarrows H^{+}+ \text{Fe}-\text{OO}H^{2+} \qquad (2.5)$$

$$\text{Fe}-\text{OO}H^{2+}+ HO_2^{\cdot} + Fe^{\dot{2}+}\dot{O}\text{H} \qquad (2.6)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \dot{O}\text{H} \qquad (2.7)$$

Because of this rationale, it is supposed that for the most part, waste devastation catalysed by Fenton's reagent is merely a Fe (III) _$H_2O_2$ method, catalysed devastation procedure. Additionally, Fenton's reagent with a surplus of hydrogen peroxide is fundamentally an Fe (III) __$H_2O_2$ procedure (referred to as a Fenton reagent). Therefore, we can substitute the ferrous ion in Fenton's reagent with a ferric ion [64]. Iron salt operates as a catalyst for the decay of hydrogen peroxide while producing additional feedback to redevelop Iron (II). It is proved Fenton's reagent is capable of wiping out various phenols, nitrobenzene and herbicides in water media along with reducing the COD in public wastewater [65].

The use of Fe (II)/$H_2O_2$ as an oxidant for wastewater treatment is attractive due to the facts that Iron is highly abundant and non-toxic element, and hydrogen peroxide is easy to handle and environmentally benign. But involves consumption of one molecule of $Fe^{2+}$ for each .OH radical produced, demanding a high concentration of Fe (II).

In a number of reactions, in-between corrosion of goods outstanding in the resolution may be oxidation reaction along with oxidative devastation of compounds' resistance to unaided ozone. $H_2O_2$ oxidation can simply be accomplished by increasing the reaction with UV emission.

### 2.4.2 Photochemical techniques:

In most instances, Inorganics such as $CO_2$ and $H_2O$ are not oxidised by Ozone, hydrogen peroxide or other organic compounds [66].

To have efficient ozone photolysis, UV lamps must have a maximum radiation output of 254 nm. Numerous contaminants absorb UV energy in the series of 200-300 nm and because of direct photocatalysis, decompose or become excited and are more reactive with chemical oxidants. Today, new excimer lamps, with radiation wave lengths have been developed at 172 and 222nm for direct photocatalysis of water. This produces ˙OH and H. Radicals which are very effective in the UV-oxidation processes [67] .

### 2.4.2.1 Ozone –UV radiation ($O_3$/UV)

Ozone for the production of H2O2 readily absorbs UV radiation at 245 nm wavelength as transitional, and the roots to .OH [68].

$$O_3 + \overset{hv}{\rightarrow} \; O_2 + O\,(^1D) \qquad (2.8)$$

$$O\,(^1D) + H2) \;\rightarrow\; H_2O_2 \rightarrow 2{\cdot}OH \qquad (2.9)$$

Surrounding components in the water can capture UV light. Because the transmission of Ozone can be achieved from UV by optically dynamic components like phenol, 5-methylresorcinol, xylenols, etc., UV radiation does not give any extra elements to ozone [58].

### *2.4.2.2* Hydrogen peroxide -UV radiation ($H_2O_2$/UV*)*

Photolysis of hydrogen peroxide in a direct method tends to the formation of ˙OH radicals [69,70].

$H_2O_2 \xrightarrow{h\nu} 2\,^{\cdot}OH$ (2.10)

In wavelength, 254nm $HO_2$ – as an acid – base equilibrium with $H_2O_2$, absorbs the UV radiation

$H_2O_2 \rightleftarrows HO_2^- + H^+$ (2.11)

$HO_2^- \rightarrow {}^{\cdot}OH + O^-$ (2.12)

For the destruction of chlorophenols, the $H_2O_2$/UV process has been successfully used, as have been chlorinated compounds [71].

### 2.4.2.3 Ozone – hydrogen peroxide-UV radiation ($O_3/H_2O_2$/UV)

The addition of hydrogen peroxide to the $O_3$/UV process, we see an acceleration in decomposition of ozone and a tendency towards an increased rate of ˙OH creation [72].

### 2.4.2.4 Photo-Fenton and Fenton –Like systems

Photo – Fenton – is a type of oxidation. At pH 3 this type of process occurs when Fe3+ ions are added to the H2O2/UV process. The method is regularly called, the $Fe(OH)^{2+}$ complex and is formed as the result of an acidic environment:

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H+ \quad (2.13)$$

$$Fe\ (OH)^{2+} \leftrightarrows Fe^{3+} + OH^{-} \quad (2.14)$$

This complex, when exposed to UV irradiation, is more subjected to decomposition and will produce $^{\cdot}OH$ and $F_2+$ ions:

$$Fe(OH)^{2+} \xrightarrow{hv} Fe^{2+} + {}^{\cdot}OH \quad (2.15)$$

It is obvious the photo-Fenton-type reaction relies heavily upon UV irradiation to initiate the generation of $^{\cdot}OH$. If required, organic pollutants can be mineralised completely with UV/visible irradiation. For example, a number of herbicides and pepticides can be totally mineralised by the hv-Fe (III)/$H_2O_2$ process, and the mineralisation of chlorophenol by the photo-Fenton process was demonstrated [73].

#### 2.4.2.5 Photocatalytic Oxidation (UV/$TiO_2$)

The source of photocatalysis is the photo-excitation of a semiconductor that becomes solid as a result of absorption of electromagnetic radiation, often, but not completely, in the near UV spectrum. Under near UV irradiation, an appropriate semiconductor material may be excited by photons possessing energies of adequate scale to produce conduction band electrons and valence band holes. These charge carriers are able to induce reduction or oxidation

correspondingly. At the surface of the $TiO_2$ particle, these may react with the absorbed group [74].

$$e^- + O_2 \rightarrow O_2^- \quad (2.16)$$

$$h+ + A- \rightarrow .A \quad (2.17)$$

$$h+ + OH- \rightarrow \cdot OH \quad (2.18)$$

$$\cdot OH + RH \rightarrow .RHOH \quad (2.19)$$

$$\cdot OH + RH \rightarrow .R + H2O \quad (2.20)$$

$$H^+ + + RH \rightarrow .RH^+ \quad (2.21)$$

## 2.5 Literature review of current study

Although there is no reasonable commercial process for decolourization by ozone, some interesting outcomes have been recorded in pilot plant studies. In general, it has been reported the reduction of COD and TOC colour via ozonation of dye wastewater results in increased BOD5 [75-76].

At present, no useful technology – at economical cost – has been created to accomplish colour deduction [43].

In wastewater, ozone can be used as a pre-treatment to increase biodegradability. However, ozone treatment still needs to be made cost effective. For example, the cost of ozone treatment of effluent is (1.57USD/t effluent for 100 tonnes of wastewater). While, compared to activated sludge (bio treatment), reclaiming dye wastewater the cost is only (0.72USD/t effluent) [31].

Oxidation methods such as ozonation,photo catalyst, and photo fenton are expensive and uneconomical.[77]

Due to the fact that ozone is very effective in removing colour from textile wastewaters, numerous published studies have emerged over the last decades and continue to grow significantly .In particular the ozonation of azo-dyes has gained considerable interest due to the facts that: azo-dyes form the largest group of dyes used in the textile industry (over 50% of all dyes) [78]

4-Ozonation can be applied to achieve pollutants complete oxidation (i.e. mineralization) or for biodegradability enhancement through chemical breakdown of refractory compounds into smaller and less recalcitrant molecules by partial oxidation [79].

The operational problems and costs of various methods are major unresolved problems in wastewater treatment. Developing better mechanisms and methods for the textile industry to reduce environmental impact of its activities and improve its environmental performance is a critical phase towards more sustainable practices. This is especially so in South Africa.

The main aim of this research is to investigate the use of ozone for decolouring of azo dye solutions in wastewater to a standard at which it may be reused in the process or to be safely discarded into the environment.

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# 3 Chapter Three: WASTEWATER TREATMENT OF REACTIVE DYESTUFFS BY OZONATION IN A SEMI-BATCH REACTOR

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**Abstract**

Water is quickly becoming both scarce and very expensive. Thus, it has become necessary for every industry to examine proposals for the purification and re-use of their wastewater and effluent streams. The Textile industry is one of the largest industrial consumers of water. Predominantly, wastewater from textile industry contains large amounts of dye and dyeing agents, as well as mordant and sizing agents. Current advanced oxidation processes (AOPs) which include ozone, photochemical and photo catalytic oxidation are techniques used for the treatment of such wastewater. Although AOPs are relatively expensive, they appear to be the most likely candidates for full-scale dye house effluent decolouration.

The ozonation of wastewater containing four different textile reactive dyestuffs in a semi-batch reactor have been studied. Various ozonation conditions – ozone dose, ozone

consumption efficiency, etc. – were explored and studied for these various types of dyestuffs. The mass transfer coefficient of ozone in water and its relationship to the ozone efficiency was studied. Pseudo-first order decolouration rate constants for all dyestuffs were determined experimentally.

Keywords: Advanced oxidation; ozonation; reactive dye; bath effluent; wastewater; semi-batch

## 3.1 Introduction

Water is considered as the most constructive and in terms of volume, the leading solvent in textile manufacturing. During the wet processing steps, large amounts of water have to be used in the textile manufacturing for methods such as sizing and desizing, bleaching, mercerising, dyeing, printing and finishing of fabrics and dyed yarns. The major industrial consumers of water are textile mills. To create 1 kg of finished goods in textile industry, normally 0.2-0.5$m^3$ of water is required. The chemical and mechanical action during processing is used to treat most impurities that are in the form of dirt, salts, oil, greases, and colours of natural fibres, used and dead dyestuffs, chemicals, polymers and fibres. Textile manufacturing as well as many other industries including pharmaceutical, food, paper and ink manufacturing use over 30 000 industrial dyes with 8000 varying chemical structures and more often than not they are released in waste water[1]. Approximately 10 to 20% of the dyes used in textile manufacturing do not adhere to the fibres during the dyeing process and are therefore discharged into the aquatic atmosphere [2]. These potentially toxic organic and mineral compounds form wastewater which is returned to the environment [3-5].

Due to water resources being very limited, costly and with many governments initiating more stringent governmental regulations, it is necessary for every industry to formulate and study

suggestions for purification of their wastewater treatment and effluent streams [6]. The advanced oxidation process (AOPs) is presently the most applicable technology for full-scale dye house sewage decolourisation [7]. Hydroxyl radicals are believed to be the most important oxidants for the degradation of these biological wastes in the AOPs [8]. Ozonation one of the advanced oxidation processes (AOPs) is considered by many as the most competent treatment application for effluent decolourisation [9-16].

It is also possible for dye formulas to include auxiliary ingredients for desizing, scouring, mercerizing and so-on. Colour and salts may remain virtually unaltered when typical organic treatment techniques are employed and these substances, along with heavy metals, can be lethal to aquatic life. [17,18]. Therefore, it must be recognised that manufacturing textile wastewater is an intricate combination of compounds and non-living salts which must be cleansed using cutting edge purification techniques [19].

In the present work, four representative reactive dyestuffs groupings were hydrolysed and ozonated to the point of complete colour removal. The mass transfer coefficient for the dissolution of the ozone in the water was also measured as was the stoichiometry for one dye.

The novelty of this research is to find out the relation between ozone and Azo dye in the semi-batch reactor with different dye and ozone concentration to enable us to design an industrial decolouration.

## 3.2 Materials and Methods

### 3.2.1 Reactive dye and synthetic dye effluent

Four reactive dyestuffs (Table 3.1) were provided as samples by Dye Star (Durban, South Africa).

According to the procedure followed by Gregory Knitting Mills PTY Limited, a domestic textile dye house in Johannesburg , the synthetic wastewater was arranged by dissolving each dye in various concentrations to replicate un-rinsed dye bathes and in the form of diluted factory wastewaters [20] .

Table 3.1 lists the physicochemical properties of the reactive dyes selected for the present study.

Table 3.1: Physicochemical prosperities of the reactive dyes used in the present study

| Dye number | Dye brand name | Color index reactive | Anchor group | Chromophore group | $\lambda_{max\ (nm)}$ | Dye or metal content(%) |
|---|---|---|---|---|---|---|
| 1 | Remazol Red RB | Red 198 | Vinylsulphone + Monochlorotriazinyl | Azo | 500 | -- |
| 2 | Remazol Turquoise Blue G133 | Blue 21 | Vinylsulphone | Phthalocyanine copper complex | 665 | 2.5% copper |
| 3 | Remazol Black RL | Black 31 | Vinylsulphone | Azo cooper complex | 570 | 43-45%dye |
| 4 | Remazol golden Yellow RNL | Orange107 | Vinylsulphone | Azo | 410 | 70-80%dye |

Abbreviation: Remazol Red RB (Red Dye), Remazol Turquoise Blue G133 (Blue Dye), Remazol Black RL (Black Dye) and Remazol golden Yellow RNL (Yellow Dye)

In order to achieve complete hydrolyzation of the reactive dye solution, 1000 mg /l water soluble stock emulsion of each dye was prepared by breaking up the dye in distilled de-ionized water. Following this, a 4.5 g /l from 48Bé NaOH solution was added under thermostatically controlled (60◦C) conditions and continuously stirred for a minimum of 4 hours. For the next 24 hours, the prepared "waste" dye solution was retained for an additional 24 hours at room temperature. This final step ensures complete hydrolysis and corresponds to processes utilised in other exhausted dye batch studies [21].

According to the reference information, synthetic reactive dye bath effluent was prepared in the manner given in Table 3.2. Typically 20% of the dye-stuffs, in their unchanged structure and 100% of all applied dye-assisting chemicals remain in the exhausted reactive dye-bath solution [22].

Table3.2 Elements of replicated textile wastewater.

| Elements | the reactive dye recipe concentration(g/l) | exhausted dye bath concentration (g/l) |
|---|---|---|
| Reactive dye | 1.25-5 | 0.25-1 |
| $Na_2CO_3$ | 5 | 5 |
| NaOH | 4.5-5 | 4.5-5 |
| NaCl | 40-50 | 40-50 |
| Acetic acid | 0.85 | |
| Anti-creasing agent | 0.9 | |
| Sequestering agent | 0.9 | |
| Detergent | 0.45 | |

For each dye, the UV-Vis absorption spectrum was measured and dye concentration was determined through a calibration curve by reading sample absorbance on a maximum wavelength . The values of these wavelengths are given as $\lambda_{max}$ in Table 3-1 and correspond to those recommended in the literature [6].

### 3.2.2 Ozone reactor and ozonation procedure

The reactive dye samples were ozonated in a 1L semi batch reactor as shown in Figure 3.1. Ozone was produced in an ozone generator (Model 502 Fisher Labor and Verfahernstechnik) with a maximum capacity of 8.5g/h ozone.

Ozone transfer efficiency was determined by measuring the input and off-gas concentration of each pre-ozonation experiment iodometrically. For mass transfer experiments the concentration of ozone in the semi-batch reactor was determined in pure water acidified with Phosphoric acid with a pH level of 3.2, as recommended by the IOA Standardisation Committee. This was achieved by employing a spectrophotometer (Model, Unico, 4802 UV/Vis Double Beam), using an indigo based analysis [23-24].

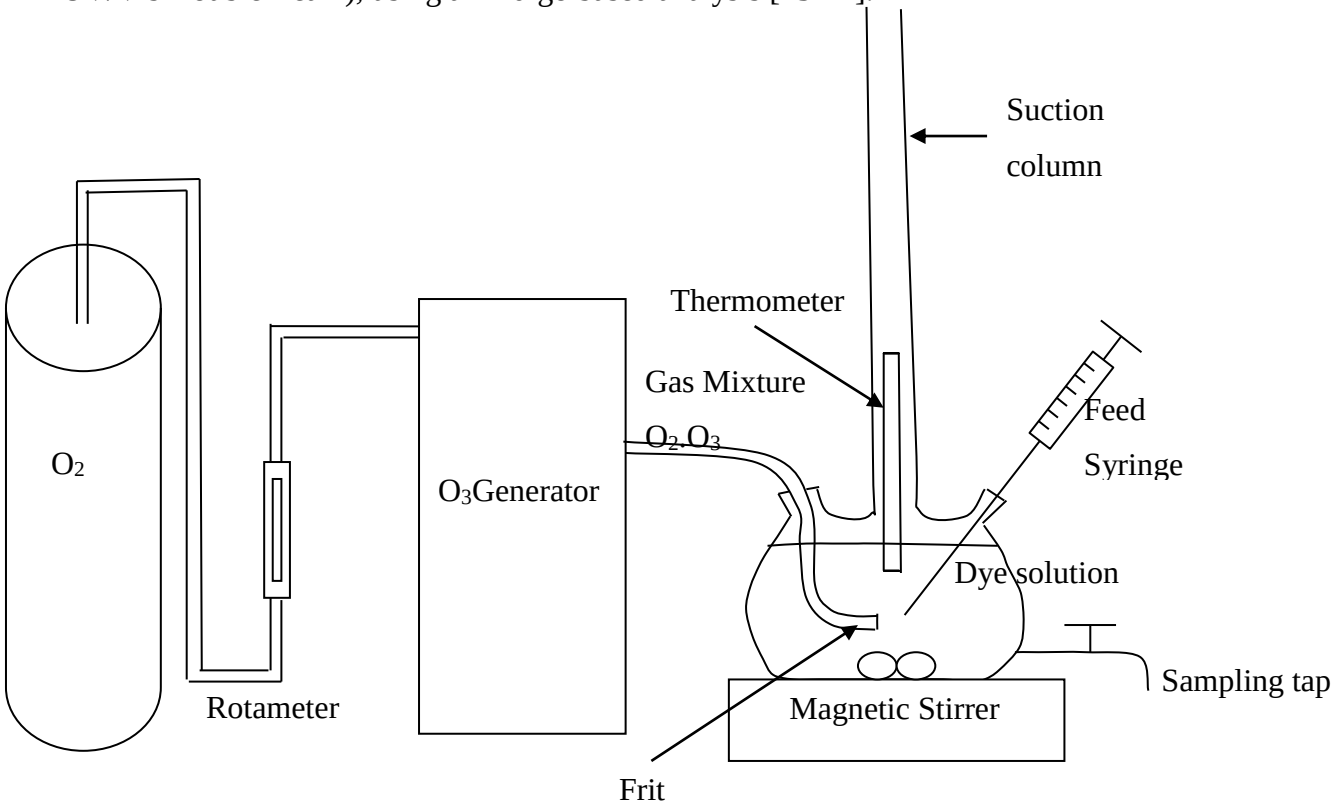



Figure 3.1: Diagram of ozonation system for decolouration of wastewater

Pure oxygen gas from a pressure cylinder was fed into the laboratory ozone generator, producing an ozone-oxygen mixture. A constant flow rate of oxygen generated approximately 5.8g/h of ozone. The concentration of ozone used was 52.5 mg/l. The decolouration experiments were conducted as a batch process in a 1000ml flat bottomed flask. The ozone/oxygen mixture was bubbled through a frit (with ISO 4793 designation of P160) as shown in Figure 1. Teflon tubing was used for all connections from the ozone generator to the reaction flask. Synthetic dye solution similar to textile wastewater was ozonated in the flask. Samples were taken at various times from the sampling tap and analysed using the spectrophotometer. Temperature was monitored with a thermometer. The magnetic stirrer was set at 500 rpm unless otherwise stated and the pH of the synthetic dye solution containing the alkali and acid as given in Table 3.2 was measured at 8.7.

In some cases, the synthetic dye solution was added to the flask and then the ozone flow was started. These are referred as normal experiments and are not labelled. When the ozone was allowed to bubble through the liquid for 30 minutes, and then the dye added, these are referred to as pre-ozonated experiments .The volume of pre-ozonated water reached to 990ml and in another 10ml of water dye solution was prepared. When the water in the flask reached to saturation status within 30 min ,then ready dye solution was added.

## 3.3 Theory

To oxidize and disinfect wastewater with ozone, ozone must be dissolved in the water and this can be accomplished in various ways. To bring about a proper disinfection and oxidation, the ozone concentration should be as high as possible. Prediction of ozone solubility is more complicated than for many others gases, because ozone solubility is influenced by several factors including temperature, pH and dissolved matter. This is a direct consequence of the instability of ozone in water. When matter is transferred from one phase to another across a gas-liquid interface, a concentration gradient will occur in each phase as a consequence of resistance. Phase transfer from gas to liquid is called mass-transfer and is often represented by Figure 3.2 (double–layer model) [25]. During the transfer of ozone from a gas to a liquid

state, the following three stages are observed: diffusion of ozone across the gas/liquid interface, dissolving into the liquid, diffusion into the liquid. The transfer rate is dependent upon the physical properties of the gas and the liquid and the difference in concentration across the interface and turbulence [26].

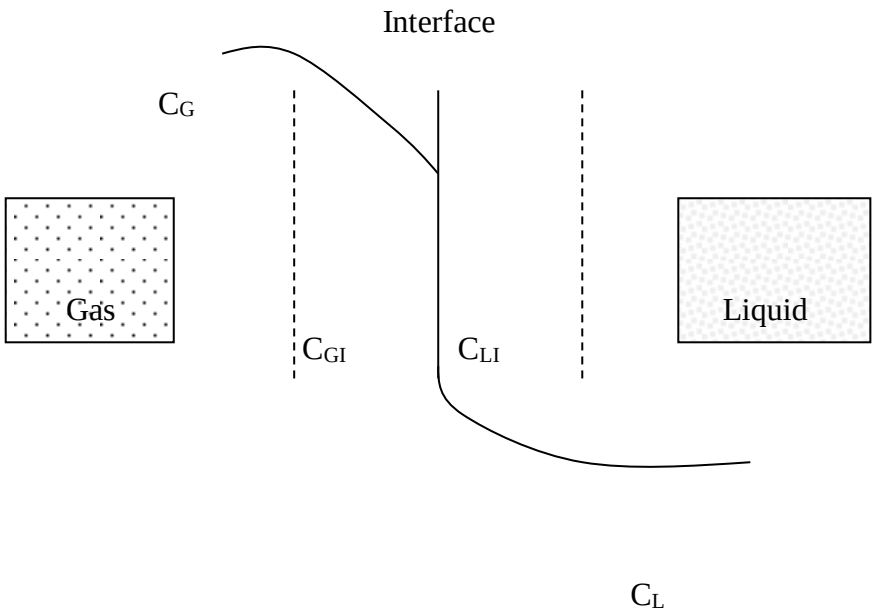



Figure 3.2: Model of ozone mass transfer

Where

$C_G$ = concentration of ozone in the gas phase

$C_L$ = concentration of ozone in the liquid phase

$C_{GI}$ = concentration of ozone in the gas phase at the interface

$C_{LI}$ = concentration of ozone in the liquid phase at the interface

The Existing assumptions on mass transfer such as penetration, surface renewal and film assume that the resistance to mass transfer in the fluid is insignificant and the main resistance takes place in the laminar films at the interface. Mass transfer coefficient in the film is

usually decrease by some of the molecular transfusion coefficient $D^{n,}$ when n differs from 0.5 to 1. The range of the value of n to foresee the mass transfer coefficient depends on the scale of turbulence in the system:

K= mass transfer coefficient of film

D=molecular diffusion coefficient

n=0.5 – 1; varying on system turbulence

Flux N in the mass transfer out of one of the segments is the creation of the film coefficient, multiplied by the concentration slope in the film, this is identical to the flux into the second phase:

$N=K_G(C_G-C_{Gi})=K_L(C_{Li}-C_L)$

The diffusing material concentration in the two stages placed instantly next to the interface

$c_{Li}$,$c_{Gi}$

are usually not equivalent however frequently believed to be associated by the rules of thermodynamic equilibrium. In order to give an estimate of the precise mass rate into the liquid, mass per unit t unit volume, the specific surface area, a, known as transfer surface area per volume is required in addition to $K_L$.

m=precise mass transfer rate

$m=K_La(C_{Li}-C_L)$

$V_L$ = liquid volume

$a=A/V_L$ =volumetric interfacial area

The transfer boundry created by the mass transfer apparatus presented in this paper is in the shape of bubbles. Calculating the surface area of swarms of irregular bubbles is extremely complicated. This complication in forming the interfacial area is defeated by swelling it together along with the mass transfer coefficient calculating $K_La$ as one limitation [27].

### 3.3.1 Model for prediction of mass transfer coefficient of ozone

In this situation, due to the fact that the ozone first has to be dissolved in the liquid before the decolouration takes place, it is important to establish whether mass-transfer is a rate limiting step.

In order to determine this, a mass transfer experiment was carried out. The experimental procedure was exactly the same as that used for the decolouration experiments but no dye was added to the liquid and the sample analysis was carried out as outlined in Section 2.1.

As previously shown, to model the mass transfer coefficient of a gas dissolving in a liquid, a first order model is frequently used in the literature [28-30].

The mass balance for ozone dissolution in a well-mixed batch container can be shown to be:

$$\frac{dC}{dt} = K_L a(C^* - C) \qquad (1)$$

Where

C= concentration of dissolved ozone

C*= the equilibrium ozone concentration in the liquid

$K_L a$= the volumetric liquid controlled mass transfer coefficient for ozone [31].

In the above experiments, the decomposition rate of ozone can be disregarded because the ozone was absorbed into pure water. This was checked by stopping the ozone when saturation was achieved by isolating the reactor and analysing for ozone again an hour later.

When combining equation (1) with the initial condition of C= 0 at t=0 one can solve equation (1) to get

$$Ln\frac{(C^*-C)}{C^*} = -K_L at \qquad (2)$$

The value of $K_L a$ is given by the slope of the straight line obtained by plotting the left hand side of equation (2) against the ozone water contact time.

### 3.3.2 Experimental determination of mass transfer coefficient

The value of C*, is a function of the experimental conditions (pH=8.7 and temperature 21°C in our experiments.). In view of the fact that ozone is only slightly soluble in water, it is likely that the process is controlled by the liquid phase resistance [32].

As the ozonation was achieved by vigorous bubbling of the ozonated oxygen through a glass sinter (frit) and the results were not significantly different using various frit sizes, $K_L a$was

usedin the model above. The value of C* was measured as the concentration of dissolved ozone at large gas-liquid contact times.

Figure 3.3 illustrates how the dissolved ozone concentration varied with time. It is clear from Figure 3.3 that saturation is reached (within about 15 minutes). Figure 3.3 also allows one to determine the saturated ozone concentration.

The results are then plotted in Figure 3.4 in line with equation (2) and a reasonably good straight line is obtained suggesting the model assumed in equation (1) is a good assumption. The value of $K_La$ obtained from this plot is $0.21min^{-1}$. The value determined is close to that reported in literature [6].

We note the time for nearly complete dissolution of the ozone is of the order of about 15 minutes while we will later see that for complete reaction it is about 30 minutes. This suggests the reaction rate is not solely controlled by mass transfer but still, it might be affected by mass transfer to some extent.

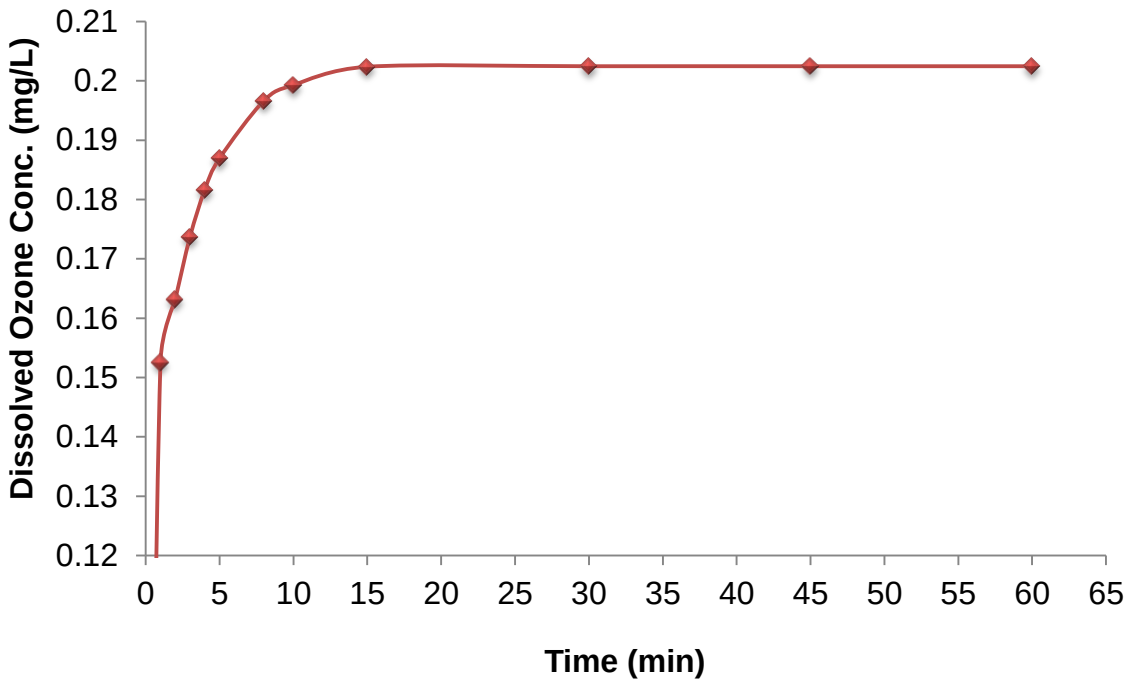



Figure 3.3: Concentration of dissolved ozone in water with time

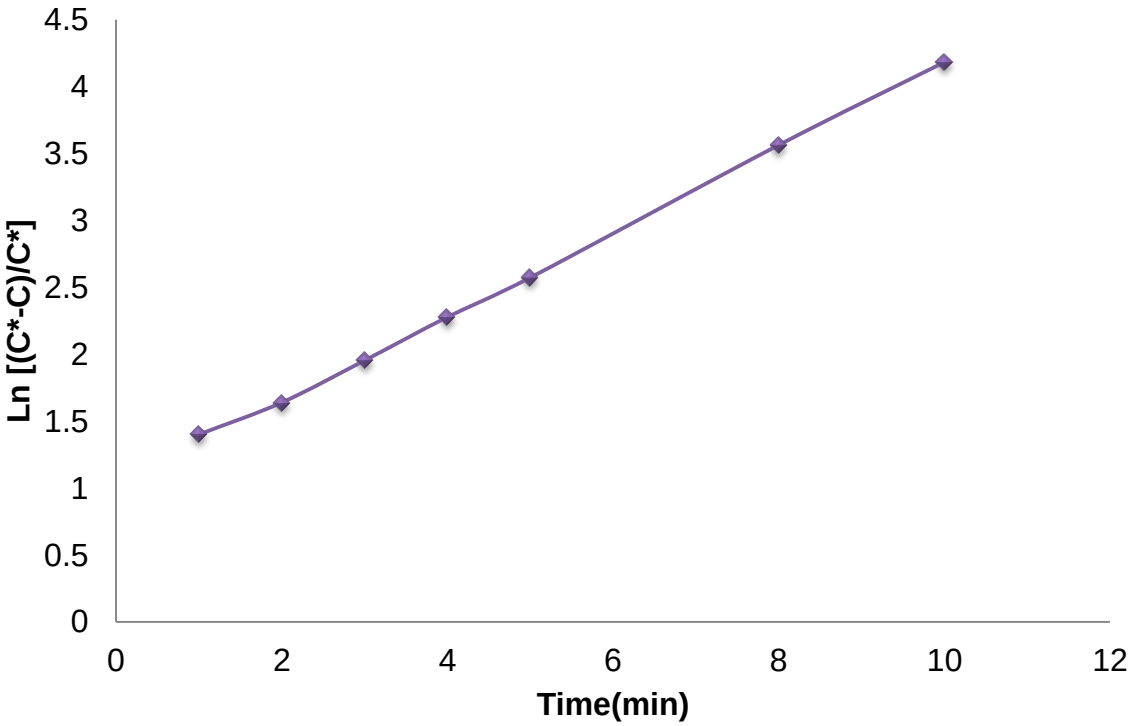



Figure 3.4: Log-linear plot of data from Figure 3.3 to estimate the mass transfer coefficient.

## 3.4 Preliminary Results and Discussion

Some preliminary experiments were done to determine the best conditions to do the more definitive final experiments. The first of these related to whether to add the dye and start the ozone flow at the same time or to pre-ozonated the liquid before adding the dye. The second was to determine whether the bubbling of the ozone into the liquid caused sufficient stirring on its own or whether a liquid stirrer was required.

### 3.4.1 Ozonation of reactive dyestuffs with 500 mg/l concentration of dye.

Originally dye was added to the water and then the ozone bubbling was begun. In this case, the initial ozone concentration in the liquid was zero. The results of these experiments are

shown in Figure 3.5. Once it was determined that the rate of dissolution of the ozone was of nearly the same order as the dye oxidation rate, the experimental procedure was changed to first saturate the liquid with ozone and then the dyestuffs were added. These results are shown in figure 3.6.

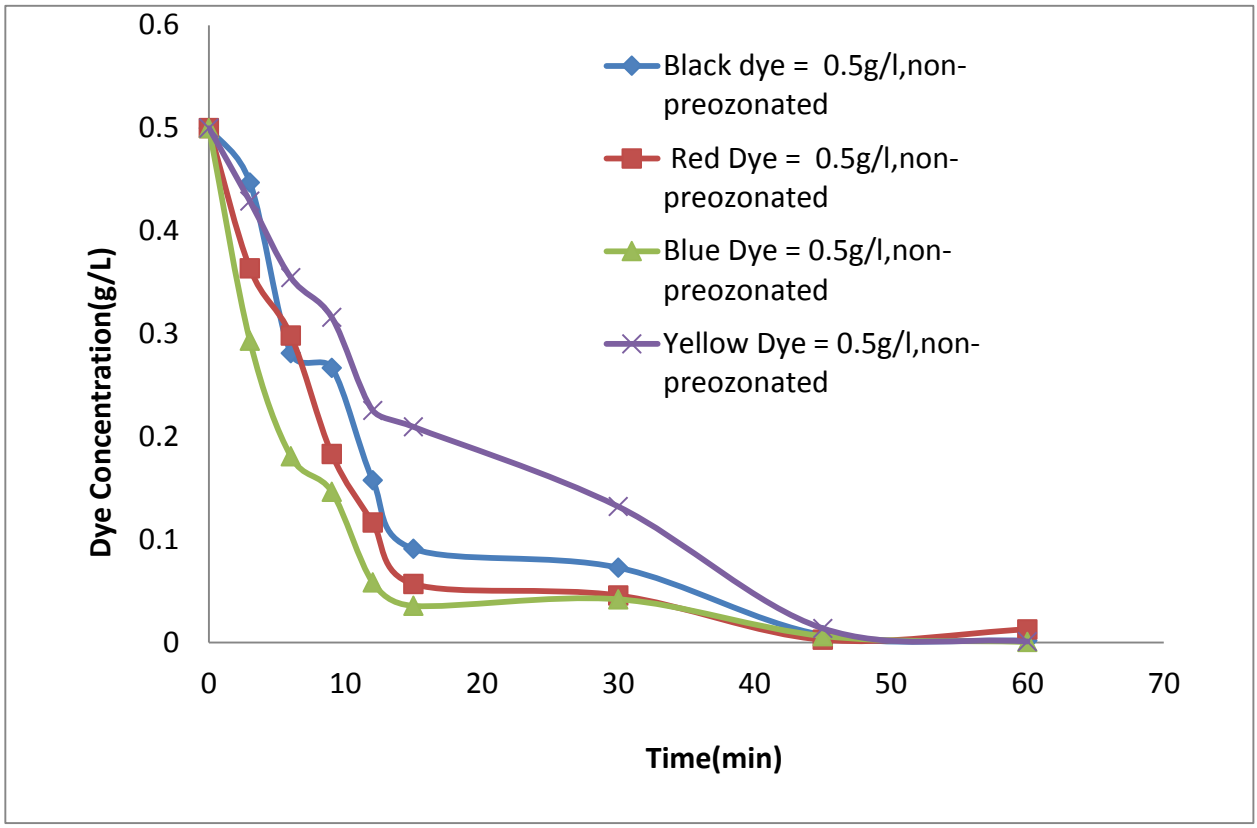



Figure 3.5: Decolouration of different dyestuffs without pre-saturation of ozone in the liquid. Experimental conditions: initial concentrations of synthetic dyes solution 0. 5 g/l, average $O_3$ input rate: 52.5mg/l, duration of ozonation: 60min, stirring speed: 500rpm.

One can see from the results for the liquid being pre-saturated with ozone, that there is not a slow initial period of decolouration, the decolouration goes to completion more rapidly and the results appear to be more consistent. As a result, it was decided to do all future experiments using liquid pre-saturated with ozone. Note also, as might be expected, that the time for complete decolouration varies with the different dyes with the order being Blue, Red, Black and Yellow taking the longest. All the curves however seem to have the same shape and so for all the remaining experiments the Red dye was used as representative.

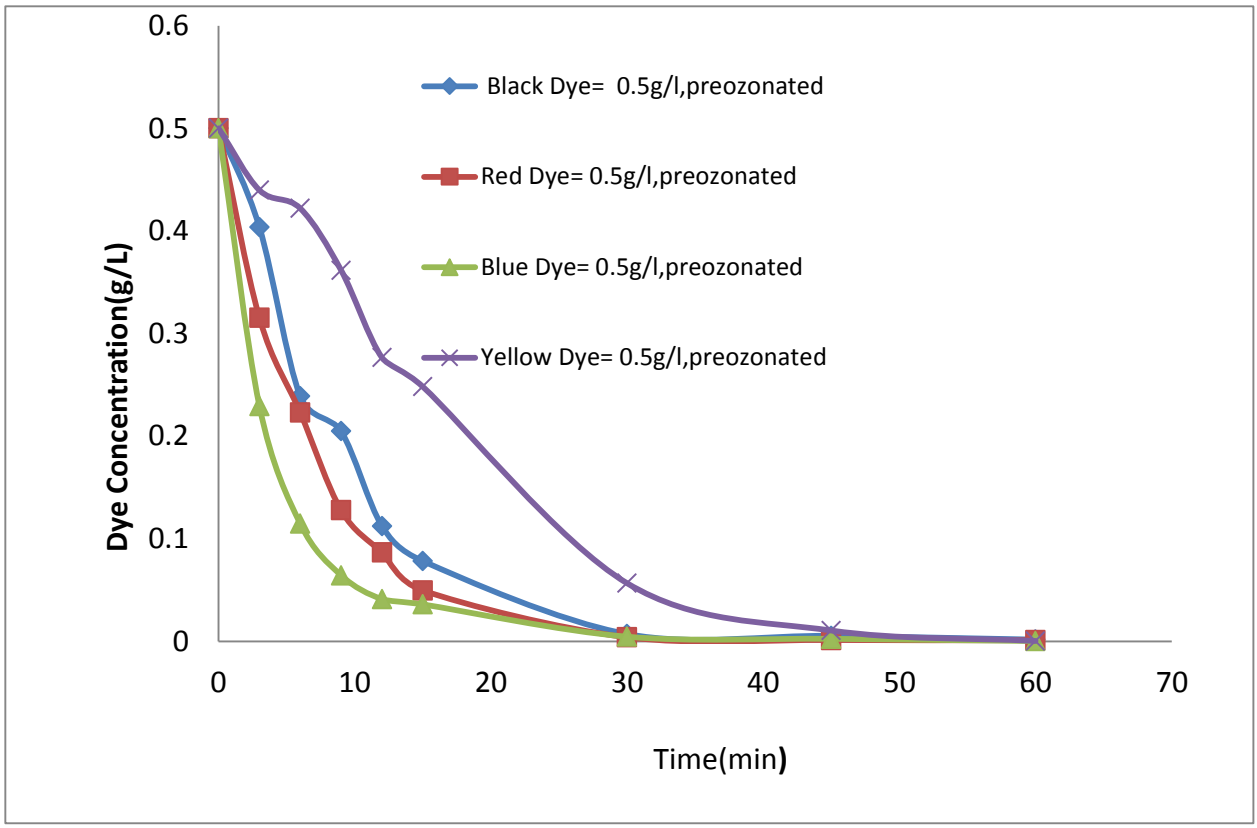



Figure 3.6: Decolouration of different dyestuffs with pre-saturation of ozone in the liquid. Experimental conditions: initial concentrations of synthetic dyes solution 0. 5 g/l, average $O_3$ input rate: 52.5mg/l, duration of ozonation: 60min, stirring speed: 500rpm.

### 3.4.2 The effect of stirrer speed on the decolouration of the dye

To test whether mixing was effective and important decolouration experiments were done on the Red dye with various stirrer speeds. This was done at three different stirrer speeds of 0 rpm, 250rpm and 500rpm respectively. The results are shown in Figure 3.7. It can be seen that the dye effectively decolourises within the first 30 minutes. The results for "no stirring" are slightly different, particularly at short times, from those at 250 rpm and 500 rpm, with the latter two readings being virtually identical. This suggests that mixing only due to the gas

being bubbled through the liquid was not sufficient enough to cause good mixing. It was thus decided to do all future experiments with a stirrer speed of 500 rpm.

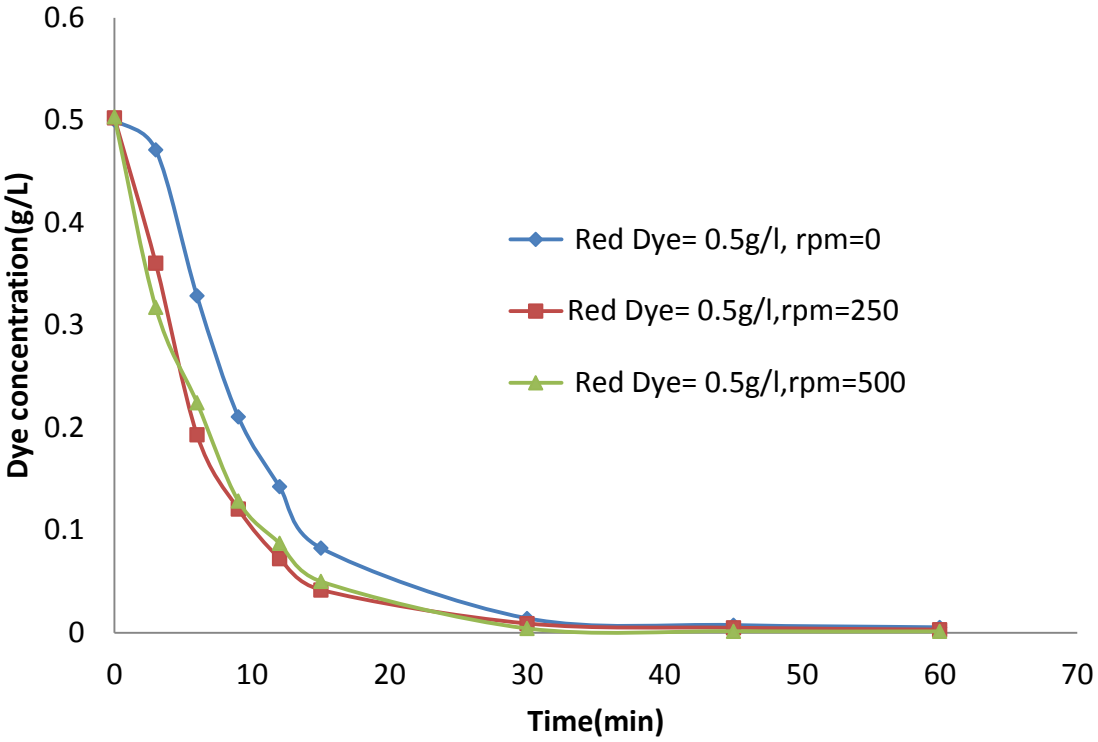



Figure 3.7: Decolouration of a reactive red dye solution of 500mg/l at different stirrer speeds Experimental conditions: initial concentrations of synthetic red dye solution 0. 5 g/l, average $O_3$ input rate:52.5mg/l, duration of ozonation: 60min, stirring speed varying from 0 to 500rpm, pre- ozonated .

## 3.5 Results

### 3.5.1 Dye concentration versus time

It was shown in Figure 3.7 that ozone is effective in decolourising the Red dye and it is obvious the dye colour is considerably reduced within 15 minutes and after 30 minutes, almost full decolouration is achieved. We now want to investigate the effect of different initial dye concentrations. The results of these experiments are shown in Figure 3.8.

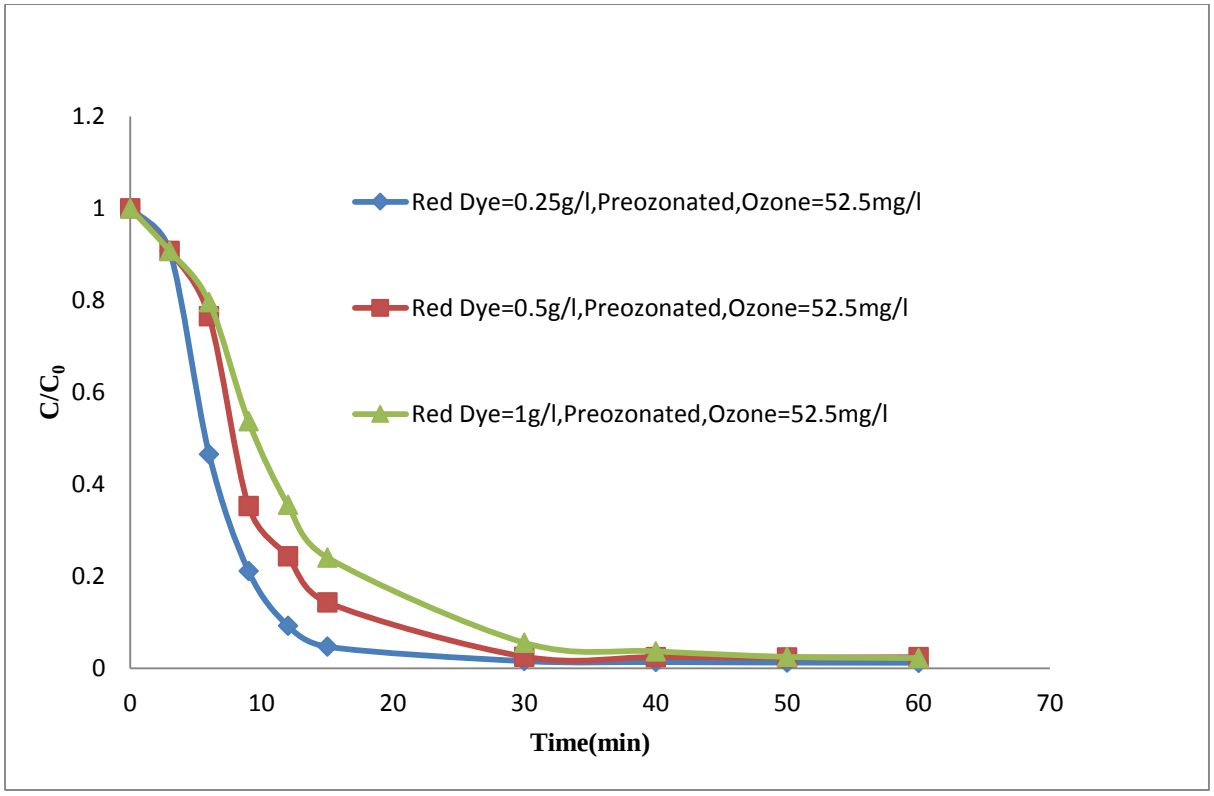



Figure 3.8: $C/C_0$ versus time for different initial concentrations. Experimental conditions: initial concentrations of synthetic red dye solution varying from 0.25 g/l to 1g/l, average $O_3$ input rate: 52.5mg/l, duration of ozonation: 60min, stirring speed: 500rpm, pre ozonated.

### 3.5.2 Different initial ozone concentrations

Experiments were also done to see the effect of the ozone concentration in the gas. Unfortunately the ozonation apparatus did not easily allow one to easily change the concentration without changing the flow-rate. Three initial ozone concentrations 52.5 mg/l, 68.7mg/l and 80mg/l at flow-rates 160 l/hr, 80 l/hr and 40 l/hr respectively were used to decolourise 0.25g/l of Red dye and the results are shown in Figure 3.9.

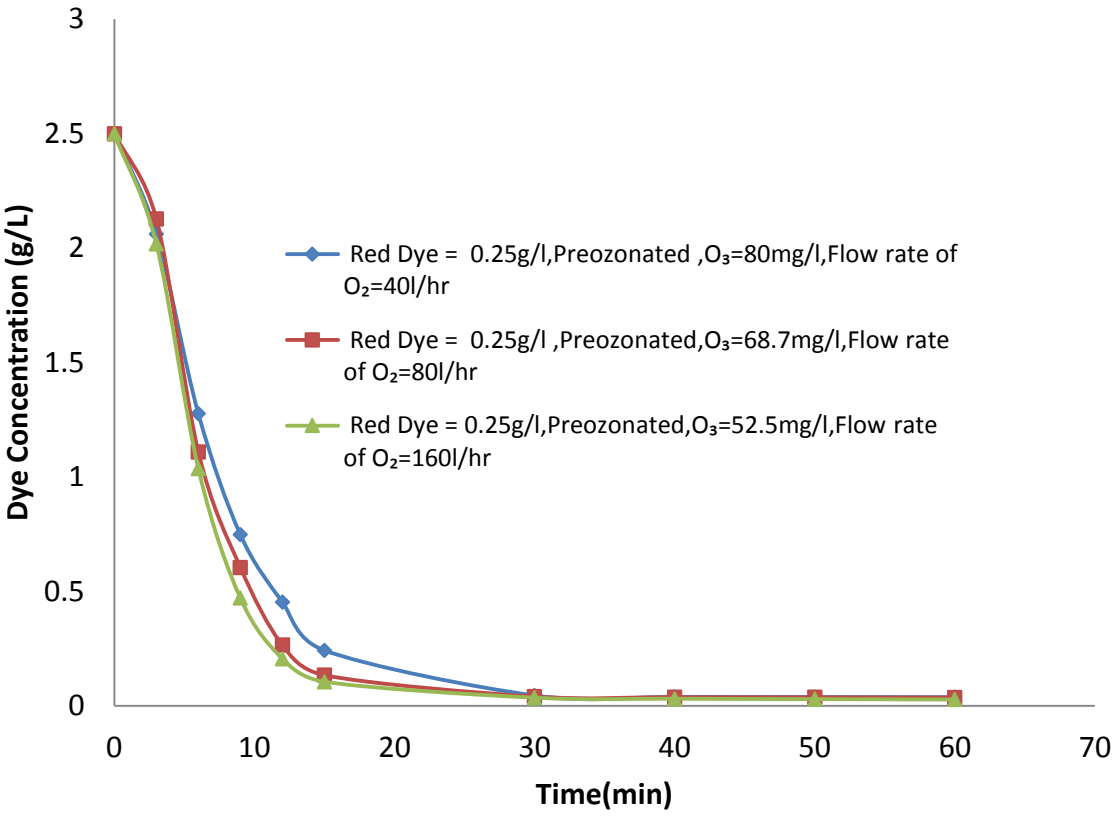


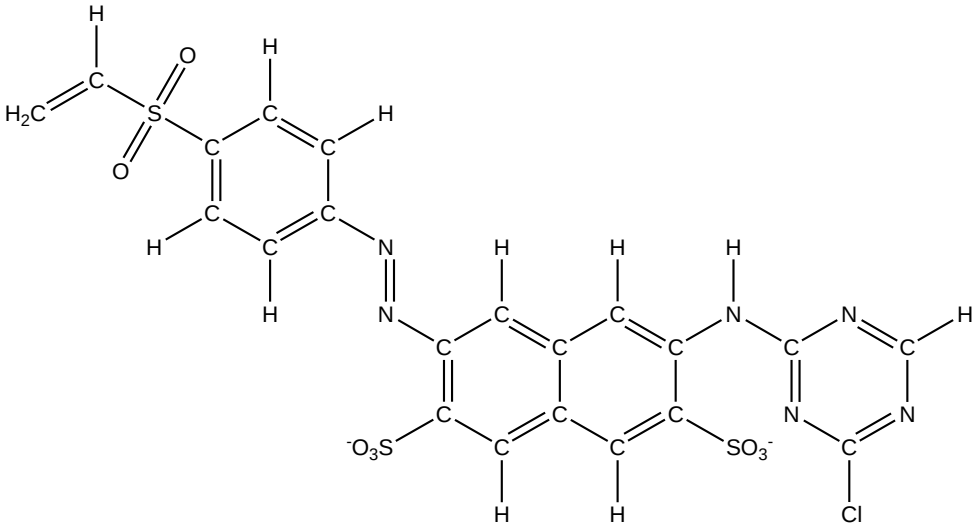

Figure 3.9: Red dye concentration versus time for different feed ozone concentrations and flowrates. Experimental conditions: initial concentrations of synthetic red dye solution 0.25 g/l, $O_3$ input rate varying from 52.5mg/l to 80mg/l, flow rate of $O_2$ varying from 40l/hr to 160l/hr, duration of ozonation: 60min, stirring speed: 500rpm, pre ozonated

A higher concentration of ozone decreases the rate of decolouration. This is a somewhat counter-intuitive result as one might expect higher ozone feed concentrations to lead to higher rates. However it should be noted that the higher concentrations occurred at lower flow rates. In any event the effects were not large and so it was decided it was not necessary to do any further experiments at different ozone conditions.

### 3.5.3 Calculation of Stoichiometric amount of ozone required to decolour dye

As the stoichiometry of the reaction of ozone with the Red dye was not known, it was decided we would measure this. This was to be accomplished by pre-saturating the liquid with ozone and then effectively titrating it with a solution of a dye. Because the ozone's reaction rate with the dye has been shown to be slow, this is a difficult experiment to perform accurately. However, it was regarded as important enough to attempt even if the results were not very accurate.

0.5 gram of Reactive Red 198 structure as shown in Figure 3.10, with a molecule weight of 968.21 grams was dissolved in 15 ml of water. This was gradually added to the liquid pre-saturated with ozone over a period of 45 minutes until the first sign of colour was seen. This occurred after 2.1ml of the dye solution had been added.



(*E*)-3-(4-chloro-1,3,5-triazin-2-ylamino)-6-((4-(vinylsulfonyl)phenyl)diazenyl)naphthalene-2,7-disulfonate

Rema:

Figure 3.10: Structural Formula of C.I. Reactive Red 198 [33].

Using these results, it was found that each ozone molecule de-colourises 58 molecules of dye (Appendix 1). Such a large amount of dye decolouration by such a small quantity of ozone strongly suggests a radical-based chain reaction is taking place. Because of the potential of dye fragments to further decompose or react with ozone and the extended time the experiment took to perform, the probability is that if there is an error in these results, the true stoichiometric coefficient would be even greater.

## 3.6 Discussion

### 3.6.1 Reaction kinetics during ozonation

Given that the rate at which ozone is fed to the reactor is constant and mass transfer is faster than reaction (limited by reaction) it might be the ozone concentration in the solution remains constant at its saturation level. In this case, the simplest model for the dyestuffs decolouration might be that the rate is first order with respect to the dye concentration. This has been suggested previously in the literature [34].

Figure 3.11 shows a plot of ln $((c-c_\infty) / (c_0-c_\infty))$ versus time. This shows the latter part of each curve yields an approximate straight line. It can also be seen that the initial rates (slopes) are lower but generally all about the same. The other result to be clearly seen is the most surprising – the rates are lower for the higher initial concentrations (1 gr/L) of dye after about 5 minutes.

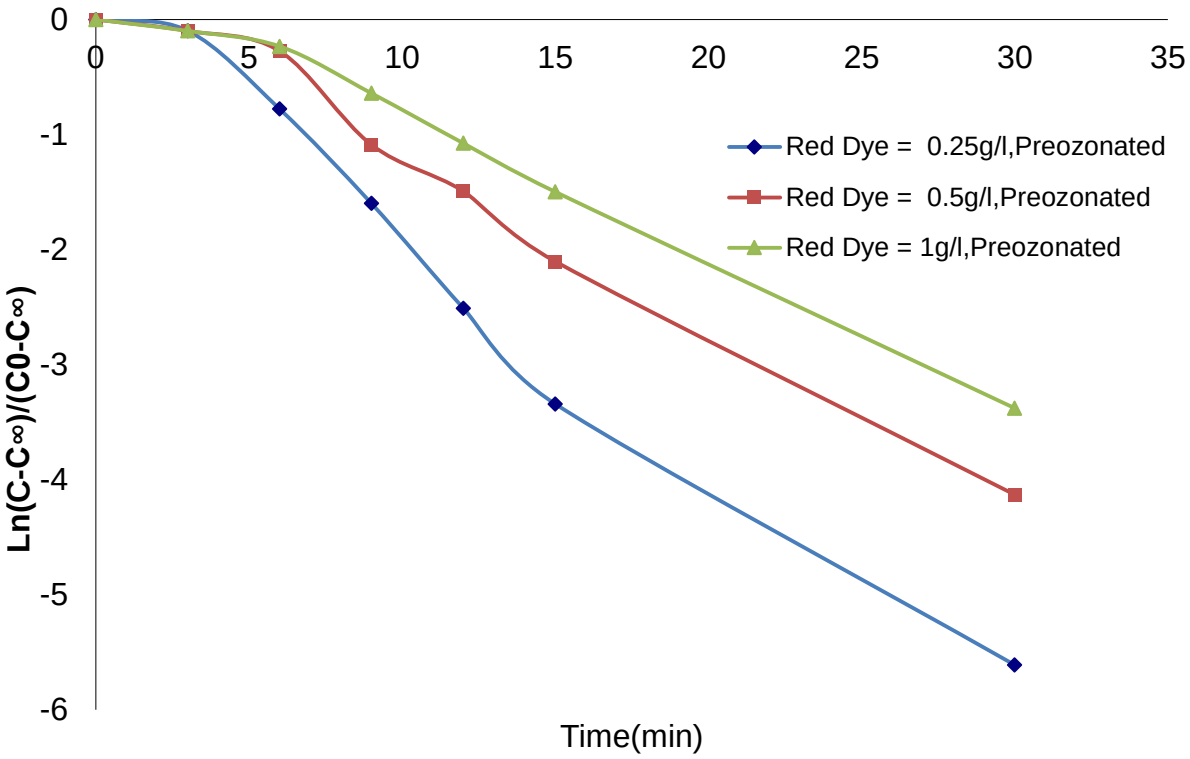



Figure 3.11: Log of dye concentration versus time (first order test) for Red Dye decolouration for different initial dye concentrations (pre-ozonated) using the results from Figure 3.8

### 3.6.2 Rate versus concentration

In order to better understand factors affecting the rate, it is convenient to plot the rate of reaction versus the concentration of dye. The rate is estimated by taking two successive points from the dye versus the concentration curve, subtracting them and dividing by the time interval.

Figure 3.12 shows how the rate of dye decolouration varies with dye concentration at different initial dye concentrations. The results found do not follow what one might at first expect. The rate for each initial concentration starts low and builds up to a maximum. Then, it follows roughly a straight line through to the origin. This latter part of the curve one might attribute to a first order reaction for each of the curves as shown in Figure 3.11. We note that

on this plot, taking the logarithm of the dye concentration emphasises the latter part of the curve (low concentrations), while the plot in Figure 3.12 emphasises the high concentrations.

The other very important point we discovered is: while for each of the separate initial concentration experiments, we get something approaching linear kinetics for the latter parts of the curves, the higher initial concentration curves give lower rates. Whatever models one produces to explain the results would need to address this apparently anomalous behaviour.

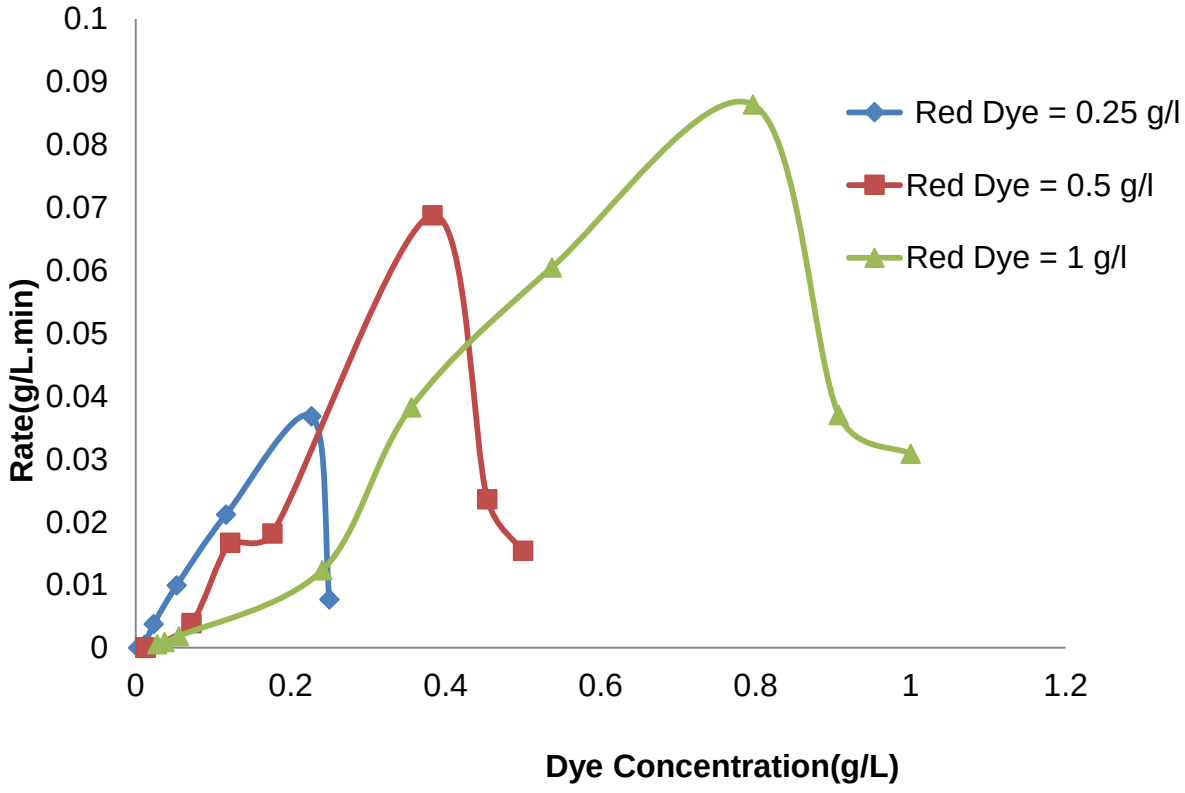



Figure 3.12: The rate of dye decolouration versus dye concentration (pre-ozonated) for different initial dye concentrations. Results from Figure 3.8

## 3.7 Summary and conclusions

The ozonation at alkaline pH of reactive dye hydrolysates was observed to be effective in partially oxidizing and completely decolourizing textile dyes at relatively high concentrations. In order to better understand the process of decolouration, further experiments were conducted. This was done with the view to eventually model the process. It is clear from the results found that the process is complex. A summary of the important points is listed below in bullet form. A successful model would need to incorporate the phenomena listed here.

- Stoichiometry shows many dye molecules are expended per ozone molecule. This suggests a radical chain reaction.
- There was a difference between the results of experiments where the solution was pre-ozonated and those where it was not. The former gave more consistent results and showed slightly higher initial rates.
- Different coloured dyes had different rates of decolouration. This suggests the rates are not totally mass transfer controlled.
- The rate of ozone dissolution is relatively slow but faster than the reaction rate. This suggests that in doing the modelling, both phenomena may need to be taken into account.
- Mass transfer rate could be modelled using a standard mass transfer model.
- It was found with faster stirrer speeds the results were independent of stirrer speed, thus one could regard the vessel as well mixed.
- Different ozone concentrations in the gas phase gave rise to different rates of decolouration. However, in order to achieve the higher concentration, lower flow rates of gas were used. The effects were however quite small
- The latter part of each decolouration experiment could be described by first order kinetics in the remaining dye concentration.

- The higher the initial dye concentration, the lower this first order rate. Again, this is a very surprising result needing to be explained by the model.

It is clear from the above that the system's model will need to be quite complex. In order to design an industrial decolouration plant such understanding is necessary. In order to gain more information about the system, the same apparatus was used for experiments where the dye was flowed continuously through the apparatus. These results are described in a subsequent paper. If we can then produce such a model, then we will be in a position to effectively design systems for use in decolourising dye waste utilising ozone.

**NOMENCLATURE**

| | |
|---|---|
| a=A/VL | volumetric interfacial area |
| AOPs | advanced oxidation process |
| Bé | bohme |
| C | concentration of dissolved ozone |
| C* | the equilibrium ozone concentration in the liquid |
| CG | concentration of ozone in the gas phase |
| CGI | concentration of ozone in the gas phase at the interface |
| CL | concentration of ozone in the liquid phase |
| CLI | concentration of ozone in the liquid phase at the interface |
| COD | chemical oxygen demand |
| D | molecular diffusion coefficient |
| K | mass transfer coefficient of film |
| $K_{La}$ | the volumetric liquid controlled mass transfer coefficient for ozone |
| N (0.5 – 1) | varying on system turbulence |
| M | precise mass transfer rate |
| V | volume of the liquid contents of the vessel |
| VL | liquid volume |
| λ max | maximum wavelength |

## 3.8 Appendix 1

### Calculation of Stoichiometric amount of ozone required to decolour dye

In a 1000ml of water was added to the reactor .Ozone was started to bubble in the water for 30 minute to be sure which has reached to saturated status .

According to the Fig 3.3 concentration of dissolved ozone in water is show as 0.2mg.

In a 15 ml of water 0.5gr of Reactive Red 198 was added .Gradually within 45 min 2.1 ml of dye solution was added to the reactor to titrate with ozone and the colour of water changed.

15 ml water 0.5 g of dye

0.2 X=0.07g of dye

0.07/968.21=0.0000723 mol dye

2mg ozone 48g/mol

$2x10^{-3}$ g = 0.00417 mol ozone

0.000417/0.0000723=57.67

Each mol of ozone decolorizes 58 mol of dye.

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# 4 Chapter Four: OZONATION OF TEXTILE REACTIVE RED 198 DYE IN A CSTR

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**Abstract**

The decolouration effect of ozone on the reactive dye Reactive Red 198 in a CSTR was the subject of a series of experiments. The results showed that ozonation is capable of reducing the colour remaining in the water after using reactive dyes rapidly and effectively of around 15 minutes. The effect of the frit was analysed to check that it was not a factor limiting oxidation. The effect of flow rate and of the initial concentration of dye on the dye concentration as a function of time and at steady state were measured, and the rate of decolouration was calculated under both steady and unsteady state conditions. The flow rate was adjusted for various initial dye concentrations as well as at various flow rates of dye solutions. The apparent first order rate constant is about 0.10 $min^{-1}$.

Though first-order kinetics in dye concentration fitted the individual sets of results, the rate constants were significantly different from those expected, suggesting that any model that aims to predict the results in general would need to be more complex, and probably include modelling the effective ozone concentration.

Key words: Ozonation; Reactive dyes; De-colouration; Advanced oxidation; Wastewater; CSTR

## 4.1 Introduction

In the treatment of textile dyeing wastewater and dye production wastewater, the major issue is the elimination of dye colour [1-4].

In the textile manufacturing industry, huge amounts of organised dyestuffs of various kinds are used, and these affect the chemical properties of the resultant effluent. The most common dye molecules to be found in textile wastewater are elevated organised polymers. These consist of two main elements: the chromophore, which carries the colour, and a functional group of chemicals that assist bonding between the dye and the fibres. Azo dyes, which are very widely used (and which form the focus of this paper), usually include between one and three azo linkages (—N=N—). These connect phenyl and naphthyl radicals, which in turn are generally replaced with, for example, amino (—$NH_2$), chloro (—Cl), hydroxyl (—OH), methyl (—$CH_3$), nitro (—$NO_2$) functional groups [5]. Azo dyes are most commonly used nowadays to colour fabrics, especially cotton goods (which account for about 50% of the money spent on textiles worldwide).

During the last decade, the increasing use of reactive dyes has presented a serious problem because these dyes (and especially those containing azo-groups) are not readily biodegradable under aerobic conditions, which is the traditional, environmentally friendly, means of treating dye-house effluent. The resistance of azo-dyes to conventional treatment became a source of concern when some of the precursors of azo-reactive dyes were found to be toxic and carcinogenic. Researchers had to devise means to separate the recalcitrant elements in dye-bath effluent and subject them to advanced treatment before they could be discharged into conventional purification systems or publicly-owned wastewater works [6].

Another contributor to the challenge of treating textile effluent, in particular from dyeing and processing units, is the large quantities of water they consume, which when discharged contain not only the chemicals for the acid, basic, direct, vat, sulphur, and reactive dyes, but others belonging to the processes that occur before dyeing takes place — sizing, desizing, scouring, bleaching and mercerization. All of these accumulate in wastewater which cannot safely be released into the environment or recycled, unless an effective treatment regime is carried out first. Also, the reactive dyes have a lower percentage of the dye up-take, which

suggests that the amount of dye retained in the effluent is greater than that found with any other type of dye, which is conventionally estimated at 10–15% [7-9].

Various treatment methods have been used to degrade azo dye effluent [10]. Among these are oxidation processes (AOPs), which provide up-to-date methods for decolorizing dye effluent and reducing the proportion of recalcitrant wastewater in the textile dyeing industry. Among the various AOP methods, treatment with ozone has been particularly successful [11-14]. The research described in this paper investigates the use of ozonation to decolour dye effluent.

Ozone may either react directly with organic compounds or decompose into highly reactive species such as hydroxyl radicals. The latter have a probability for decomposition which goes beyond that of ozone and $H_2O_2$ —2.80V for hydroxyl radicals, 2.07V for ozone and 1.78Vfor $H_2O_2$. It also offers various other advantages:

(1) there is no residual sludge;

(2) there is very little danger to the operator;

(3) de-colouration and degradation occur in one step;

4) the process is easily performed;

(5) little space is required, and

(6) all residual ozone can be easily decomposed to oxygen and water.

All of the above make ozone-based systems feasible for decolouring azo dyes [11].

The treatment of industrial or domestic wastewater by ozone, which depends on both kinetic reactions and the mass transfer between phases, can be carried out in diffusion ozone contactors or mechanically agitated reactors. The kinetic reaction is a complex mechanism because the consumption of ozone by water depends on parameters relating to water quality, such as temperature, pH, alkalinity and organic matter content. On the other hand, the efficiency of ozone mass transfer depends on the hydrodynamic behaviour of the fluid, solubility ratio (m), and mass transfer coefficient ($K_La$) [15].

Depending on the molecular selectivity and decay stage of the dye effluent, ozone can oxidize inorganic and organic components to their uppermost oxidation stages. The decomposition level of ozone is affected by pH, temperature and the existence of inorganic/organic genera in the reaction medium. Ozone reacts with organic compounds dissolved in water through either direct ozone attack or indirect free radical attack. Hydroxyl radicals are generated by ozone decomposition in aqueous solutions and catalyzed by hydroxide ions [1].

Various researchers, such as Wu, Doan and Konsawa[16-17], have reported that the rate-limiting step in the ozonation of dye-containing wastewater is the mass transfer of ozone from the gas to the liquid phase. Nevertheless, the main reason for ozone mass transfer (that is, the variation between the absorption of the softened ozone and the equilibrium ozone absorption of the gas–liquid boundary) differs with the different degrees of water quality and operating situations. [16-17]

Consequently, the efficiency of ozone treatment for textile wastewater depends on both: in the first case, the character and concentration of the residual dye and secondly on operational decisions like the ozone dose and temperature [16-17].

In this paper the experimental investigation of ozone as a de-colouration agent was carried out on Reactive Red 198 dye in a CSTR. After reporting the results, we will interpret them in terms of a number of parameters, such as the initial dye concentration, the flow rate, and the effect of frit, and reach an assessment of the effectiveness of ozonation as a means of treating dye effluent.

## 4.2 Experimental Procedures

### 4.2.1 Reactive dye and synthetic dye effluent

All of the experiments described in this paper were carried out on a sample of Remazol Red RB (Reactive Red 198) from Dye Star (Durban, South Africa). (See Table 4.1 below for the specific properties of this dye.). In accordance with the procedure followed by Gregory Knitting Mills PTY Limited, a domestic textile dye house in Johannesburg, we prepared the synthetic wastewater by dissolving each dye in various concentrations of water, to replicate un-rinsed dye baths and diluted dye factory wastewaters [18].

Table 4.1: Lists of the physicochemical properties of the reactive dyes selected for the present study.

| dye brand name | colour index | anchor group | chromophore | $\lambda_{max}$ (nm) |
|---|---|---|---|---|
| reactive | | group | | |
| Remazol Red RB | Red 198 | Vinylsulphone + Monochlorotriazinyl | Azo | 500 |

Abbreviation: Remazol Red RB (Red Dye)

In order to achieve complete hydrolyzation of the reactive dye solution, we broke up the dye in distilled de-ionized water in the ratio1000 mg/l water, after which we added 4.5 g/l of 48Bé NaOH solution at a temperature controlled thermostatically at 60°Cwhile the solution was continuously stirred for a minimum of four hours. It was then left for an additional 24 hours at room temperature. This final step, which ensured complete hydrolysis, corresponds with the processes used in other exhausted dye batch studies carried out by researchers in previous studies [19].

Synthetic reactive dye bath effluent typically retains 20% of the dye stuffs, with their structure unchanged, and 100% of all applied dye-assisting chemicals remain in the exhausted reactive dye-bath solution [20].

Table 4.2: Elements of replicated textile wastewater.

| elements | the reactive dye recipe concentration($gL^{-1}$) | exhausted dye bath concentration ($gL^{-1}$) |
|---|---|---|
| Reactive dye | 1.25-5 | 0.25-1 |
| $Na_2CO_3$ | 5 | 5 |
| NaOH | 4.5-5 | 4.5-5 |
| NaCl | 40-50 | 40-50 |
| Acetic acid | 0.85 | |
| Anti-creasing agent | 0.9 | |
| Sequestering agent | 0.9 | |
| Detergent | 0.45 | |

For the sample of dye, the UV-Vis absorption spectrum was measured and a place in the spectrum identified where the absorbance could be measured without interference from other species. The value of this wavelength is given as $\lambda_{max}$ and in nm.

In Table 4.1 and corresponds to that recommended in the literature [21].

### 4.2.2 The ozonation and decoloration procedure

The experiments were carried out in a 1L CSTR, as shown in Figure 1below.

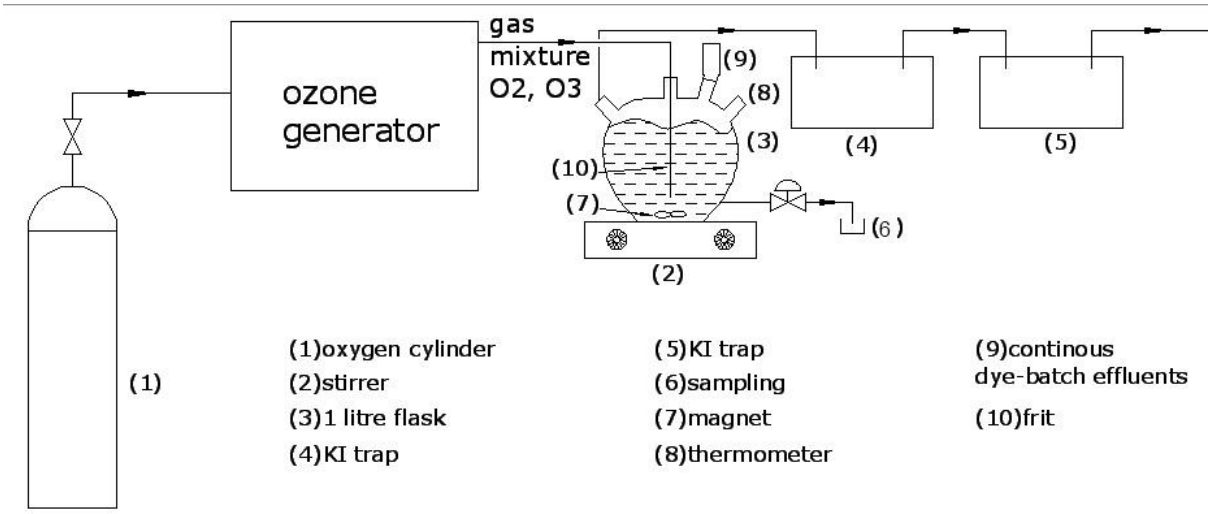



Figure 4.1: CSTR experimental set-up

The reactive dye sample was ozonated in the following manner. Ozone was produced in an ozone generator (Model 502 Fisher Labor and Verfahernstechnik) with a maximum capacity of 8.5g/h ozone. Pure oxygen gas from a cylinder was then fed into the laboratory ozone generator, producing an ozone–oxygen mixture. A constant flow rate of oxygen generated approximately 8.5g $O_3$/h, and the concentration of ozone used was 52.5 mg/l [22].

The decolouration experiments were conducted as a continuous process in a 1000ml flat-bottomed flask as it is shown in Fig4.1. The dye solution was continuously added to the reactor from a 1.5L reserve tank above it. In general, the ozone/oxygen mixture was bubbled through a frit with an ISO 4793 designation of P160, although we conducted controlled variations on occasion. Teflon tubing was used for all connections from the ozone generator to the reaction flask. The magnetic stirrer was set at 500 rpm (unless otherwise stated) and the pH of the synthetic dye solution was established as 8.7. The ozone flow was initiated only after the dye was flowing at a steady rate through the CSTR: the moment ozonation began was designated as time zero. The synthetic dye solution was ozonated in the flask for 60 minutes. Samples were taken from the sampling tap at various times, and analysed using the spectrophotometer. The temperature was monitored with a thermometer.

### 4.2.3 UV/Vis Double Beam spectrophotometer

A Unico 4802 UV/Vis Double Beam spectrophotometer was used for absorbance measurements in all experiments. This was calibrated using standard solutions. Dye concentration was determined through a calibration curve by reading sample absorbance on a maximum wavelength. By measuring the amount of the substrate remaining overtime, we can obtain the concentration versus time plot.

## 4.3 Theory

### 4.3.1 Ozone dissolution

We can write an unsteady state mass balance equation for the ozone in the CSTR thus:

$$\frac{dC_{ozone}}{dt} = K_L a(C^*_{ozone} - C_{ozone}) - \frac{Q}{V} C_{ozone} - \frac{R_{ozone}}{V} \qquad (1)\ [23, 24]$$

where

$C_{ozone}$= the concentration of ozone in the liquid

$C^*_{ozone}$= the equilibrium concentration of ozone in the liquid

t = time

$K_L a$ = the mass transfer coefficient for ozone dissolution (0.21min$^{-1}$) (25).

Q = the volumetric flow-rate of the liquid

V = the volume of the reactor

$R_{ozone}$= the rate of consumption of ozone.

Now if we first look at the steady-state ozone concentration when no reaction is occurring ($R_{ozone}$ = 0), we can show that:

$$F = \frac{C_{ozone}}{C^*_{ozone}} = \frac{1}{\left(1+\frac{\frac{Q}{V}}{KLa}\right)} \qquad (2)$$

Thus for the cases of flow-rate of liquid of 40, 65, 92,110,180 and 230 ml/min, the steady state values of F (the fraction of the ozone dissolved in the CSTR relative to the batch with no reaction) will be 0.84, 0.76 , 0.70, 0.66, 0.54 and 0.48 respectively. This indicates that the steady state F is significantly reduced as the flow rate is increased.

We also note that ($K_L a + \frac{Q}{V}$) is the time constant for dissolution, so the higher the flow rate of the solution, the more slowly the ozone concentration in the solution without reaction will reach steady state.

### 4.3.2 Dye mass balance

Let us now express an unsteady state mass balance on the dye concentration:

$$\frac{dC_{dye}}{dt} = +\frac{Q}{V}\left(\left(C^{*}_{dye} - C_{dye}\right) - \frac{R_{dye}}{V}\right) \qquad (3) \qquad [26]$$

Where

$C_{dye}$ = the concentration of dye in the vessel

$C^{\circ}_{dye}$ = the concentration of dye in the feed stream

$R_{dye}$ = the rate of consumption (decolouration) of the dye.

## 4.4 Results and Discussion

### 4.4.1 The effect of the frit on the decolouration of the dyestuff

In the experiments, we used three different types of frit (No1: coarse; No2: medium; and No3: fine) with three standard specifications. The aim of using these frits, which are shown in Figure 4.2, along with the stirrer, was to check to what degree the frit constituted a factor that limited the ozone dissolution. The results shown in the figure make it clear that in general the

frit size does not have a major effect on the decolouration of the dye solutions. Only one frit, No 1, was recorded as having a slightly slower decolouration effect during the first 15 minutes, but it did not significantly affect the final steady state. As Frit No 1 had been used in the research that formed the subject of the previous chapter/paper [25], it was retained in all the subsequent experiments so that the results could be compared. The only exception was the 1g/L run, which was done with Frit 3 only.

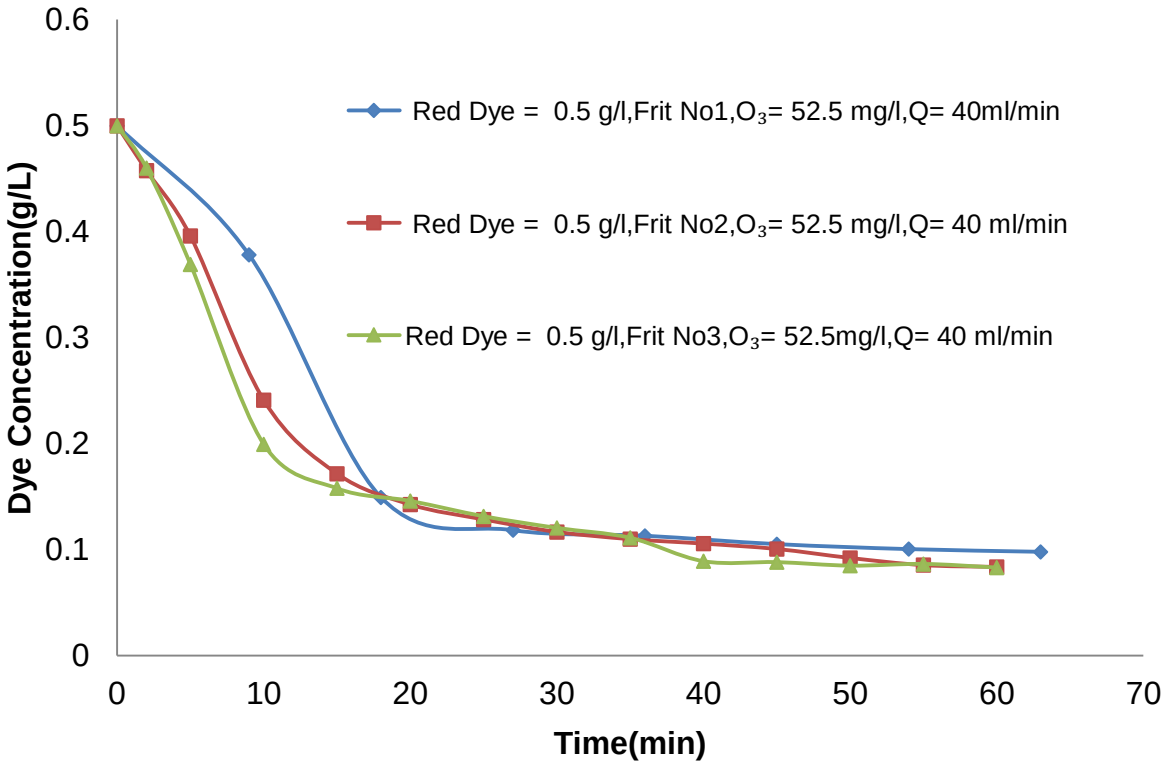



Figure 4.2: Effect of the frit on the decolouration of the dye solution.

Experimental conditions: Initial concentrations of synthetic red dye solution, 0. 5 g/l; average $O_3$ input rate, 52.5mg/l; duration of ozonation, 60min; stirring speed, 500rpm; flow rate of synthetic red dye, 40ml/min. Frit No1: coarse, ISO 4793 designation P160; frit No 2: medium, ISO 4793 designation P100; and frit No 3: fine, used for analytical work, ISO 4793 designation P40.

### 4.4.2 Dye concentration versus time

In the experiments we used four different synthetic dye solutions (0.25, 0.375, 0.5 and 1g/L), with a standard flow rate of 40ml/min of dye and fixed flow rate of ozone. It is clear from the results shown in Figure 4.3 that most of the dye was decolourised within the first 15 minutes, and that steady state had been achieved effectively after less than 60 minutes. As expected, the results show that the higher the initial dye concentration, the higher the final steady-state dye concentration. We see very similar behaviour in dye decolouration in both semi-batch and CSTR experiments in the reports published by other researchers in the field [20, 24].

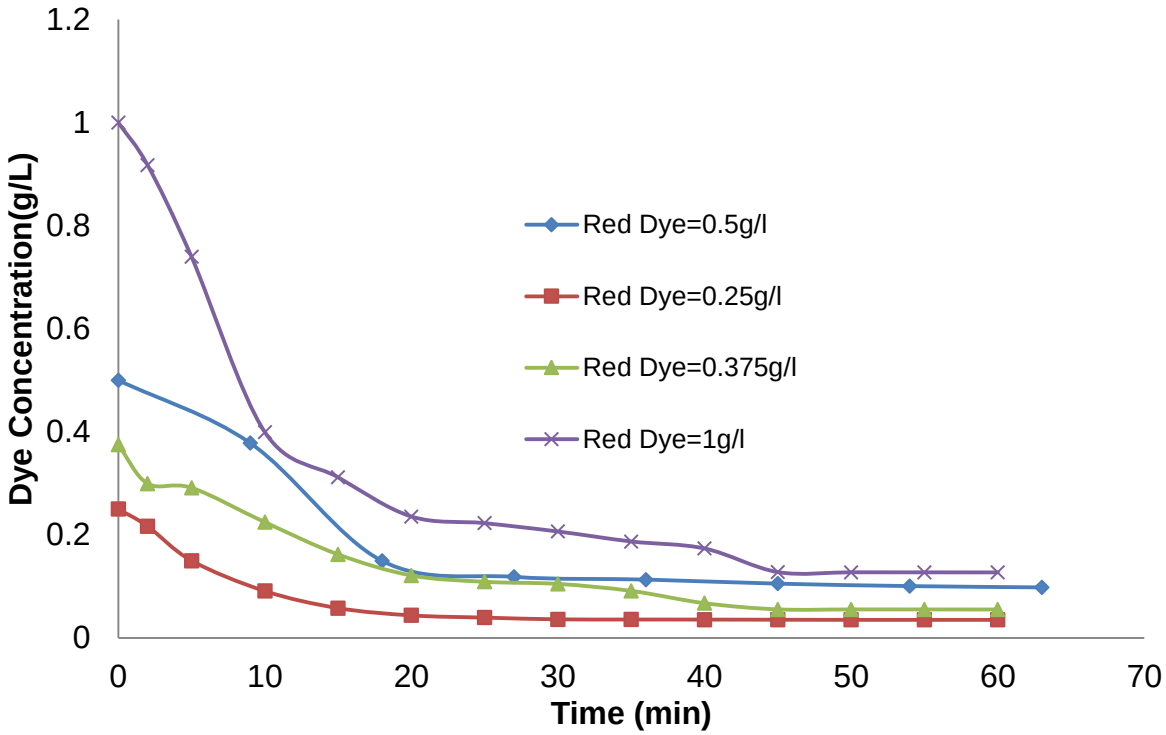
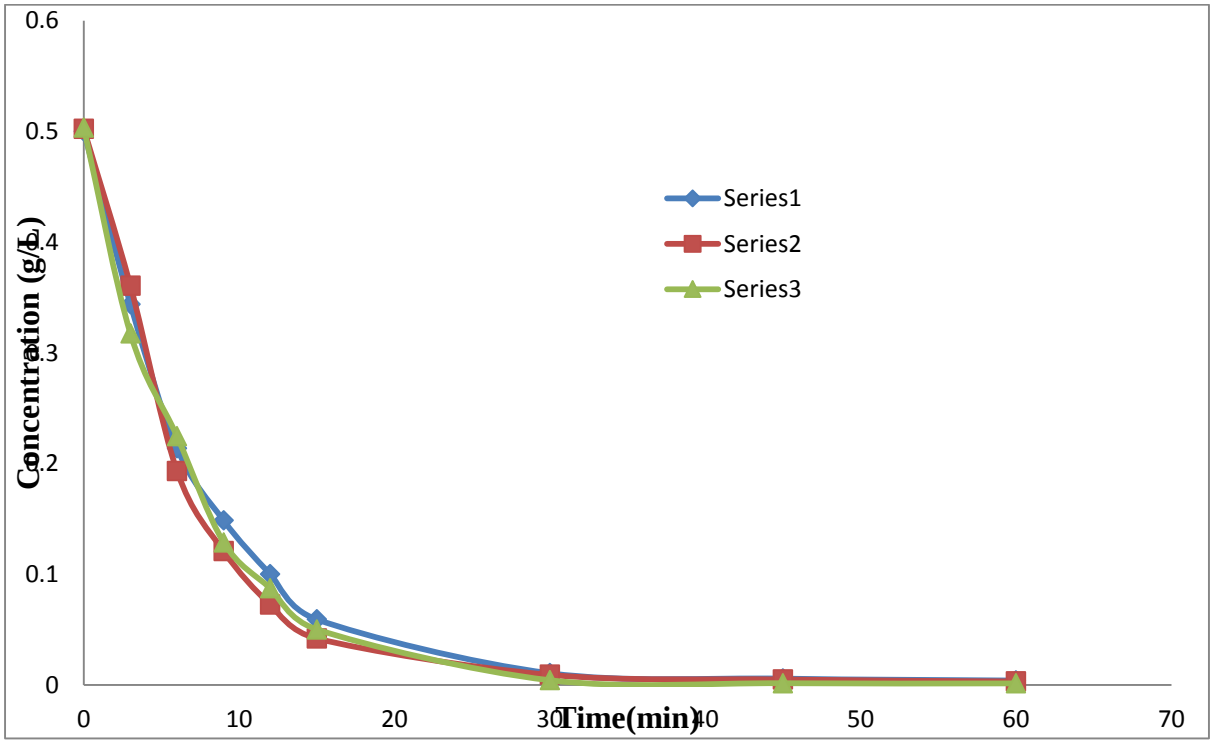



Figure 4.3: Different dye concentrations over time.

Experimental conditions: Initial concentrations of synthetic red dye solution, varying from 0.25 g/l to 1g/l; average $O_3$ input rate,52.5mg/l; duration of ozonation,60min;stirring speed,500rpm; flow rate of synthetic red dye, 40ml/min.

To ensure that the experimental time courses were reproducible, we conducted the experiments using the initial concentration of 0.5 g/L dye in triplicate. As Figure 4.4 illustrates, all three in the series have almost similar dye colouration plots.

Figure 4.4: Comparison of experimental series with initial concentration of 0.5g/L dye




### 4.4.3 The effect of different flow rates

We ozonated the synthetic dye solution of 0.5 g/L with 52.5 mg/L of ozone at various flow rates in these experiments, the results of which are shown in Figure 4.5. As expected, the results indicate that the lower the flow rate, the greater the reduction of dye colour. Because the liquid was not pre-ozonated there is an initial slower portion as the ozone concentration in the solution increases.

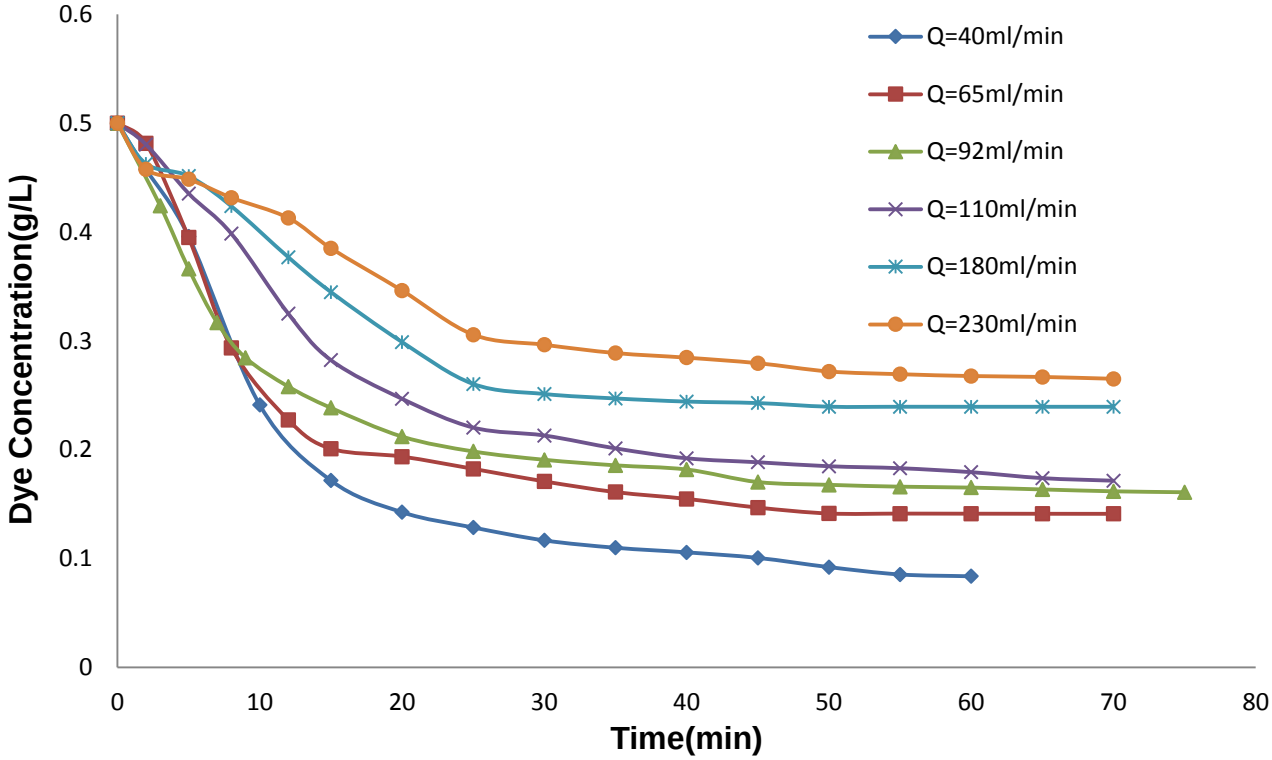



Figure 4.5:Effect of different flow rates on the decolouration of dye solution.

Experimental conditions: Initial concentrations of synthetic red dye solution, 0.5 g/l; average $O_3$ input rate:52.5mg/l; duration of ozonation,60 to 70 min; stirring speed,500rpm;flow rate of synthetic red dye varied from 40ml/min–230ml/min.

### 4.4.4 First order rate

If we assume $R_{dye} = kC_{dye}$(that is, the rate) is first order with respect to dye concentration, as has been suggested by many other authors [16, 27], and then equation (26) can be interpreted and the plot of $\log(C_{dye} - C_{dye}^{final})$ versus time should be a straight sloping line — $(\frac{Q}{V}+\frac{k}{V})$. The results delineated in Figure 4.5 are shown in plot form in Figure 4.6. It is clearly observable that the earlier results (up to about 40 minutes) can be reasonably fitted to a straight line. Another interesting result is that the slopes do not seem to depend on the value of Q (the volumetric flow rate of the liquid). This is surprising, as certainly the final

values,$C_{dye}^{final}$ are dependent on Q, as Figure 4.6 shows. It is worth noting that these results show us the way the results reach steady state, but do not take into account what the steady state is. The apparent first order rate constant is about 0.10 $min^{-1}$.

We can do the same analysis on the results for the different initial dye concentrations. See Figure 4.7. Here the graph shows approximately straight lines, but what is interesting is that the slopes seem to differ from each other, with the lowest slope obtained for the intermediate initial concentrations.

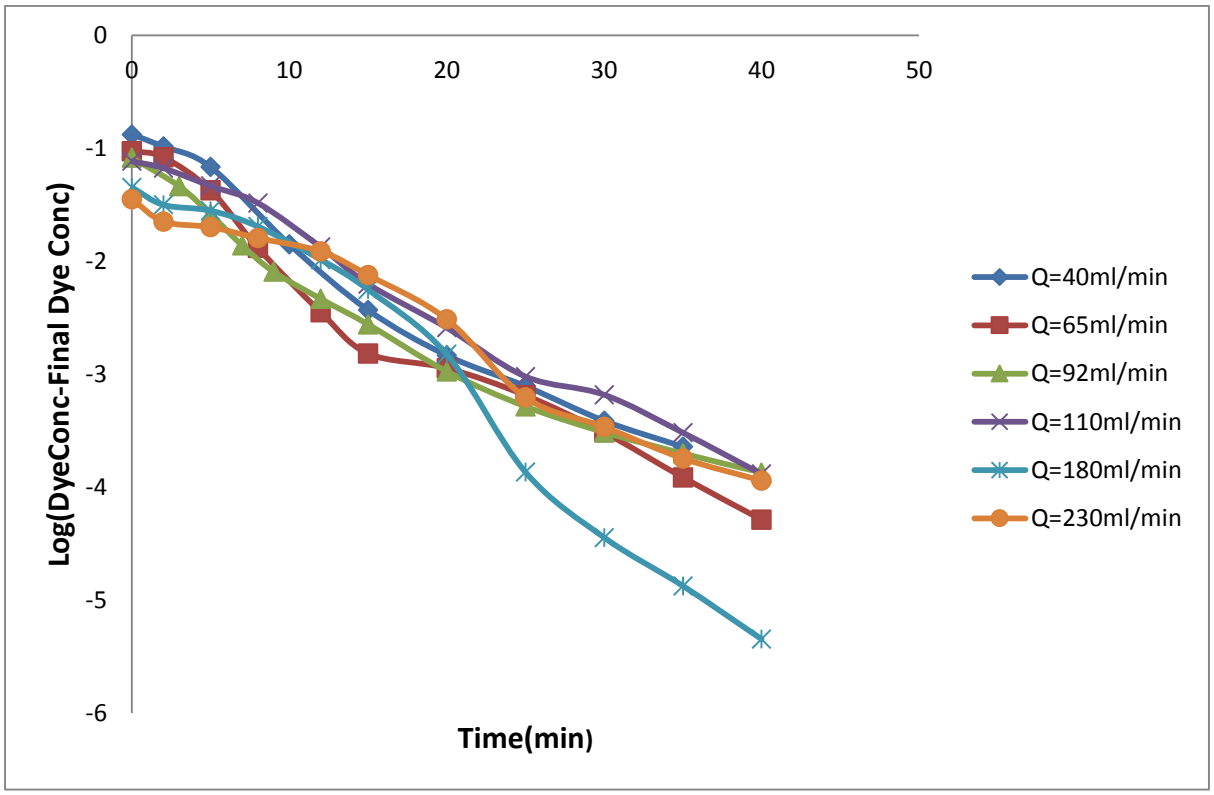



Figure 4.6: Graph of log($C_{dye} - C_{dye}^{final}$)versus time to test the first-order reaction mechanism

Conditions: Initial concentration of synthetic red dye solution, 0. 5g /l; average $O_3$ input rate,52.5mg/l; duration of ozonation,60 min; stirring speed,500rpm;flow rate of synthetic red dye varying from 40ml/min–230ml/min.

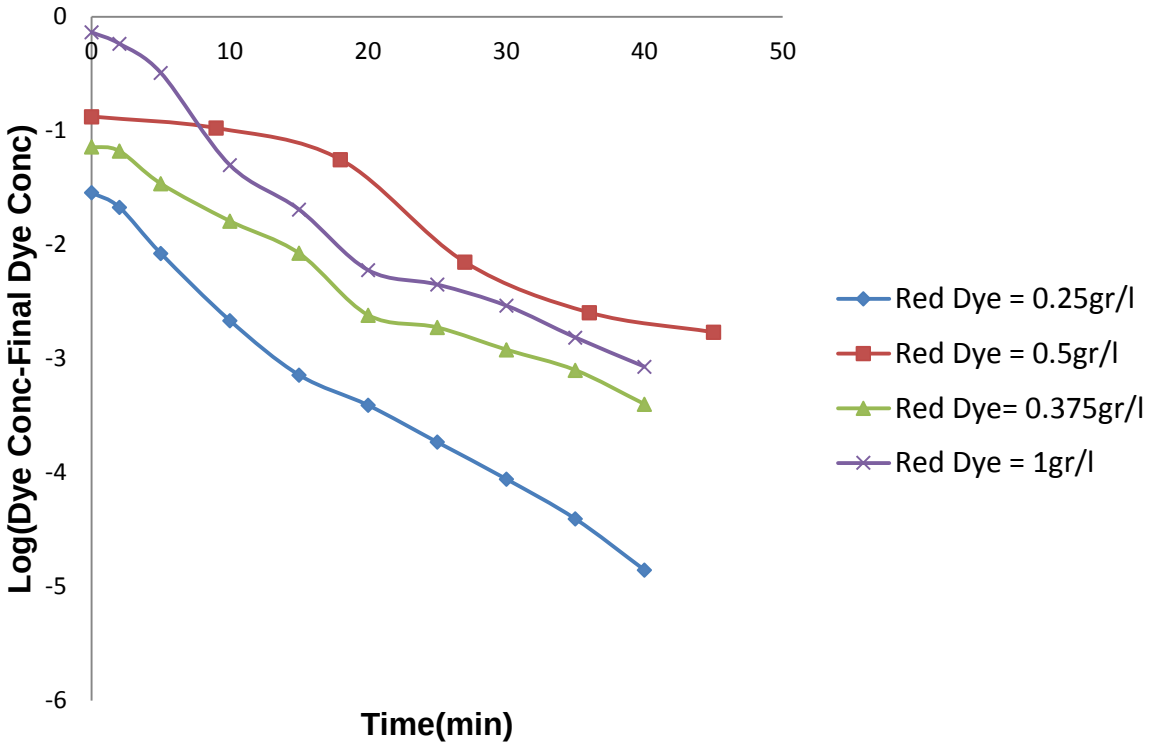



Figure 4.7: Graph of log ($C_{dye}$- $C_{dyefinal}$) versus time to test first-order reaction mechanism.

Conditions: Initial concentrations of synthetic red dye solution vary from 0.25–1g/l; average $O_3$ input rate, 52.5mg/l; duration of ozonation, 60 min; stirring speed, 500rpm; flow rate of synthetic red dye, 40ml/min for all experiments.

### 4.4.5 Rate versus concentration (different initial concentrations and constant flow rate)

An alternative way of analysing the data is to use equation (3) to calculate the rate of reaction from the concentration over time data given in Figures 4.3 and 4.5. The estimation of the value of the derivative is arrived at by subtracting the concentrations of neighbouring points and dividing the result by the time difference.

The rate of decolouration in a CSTR of the dye solutions (0.25, 0.375, 0.5and 1 g/L) was determined as a function of concentration at a fixed dye flow rate of 40 ml/min. The results are shown in Figure 4.8, which indicates that initially the rates increase as the dye concentration falls. This corresponds with the period during which the ozone concentration is low, as is proved by the slow dissolution rate we have already established. However, in the latter part of each curve, the rate of reaction hardly alters as the concentration varies. Although this would be taken as characteristic of a zero order reaction rate, these zero order rates seem to depend on the initial concentrations. The rate then falls with the reduction in concentration. All of the end points of the curves (steady state values) seem to lie on a straight line that goes through the origin. This is a characteristic of a first order reaction. The apparent rate constant is 0.35 $min^{-1}$.

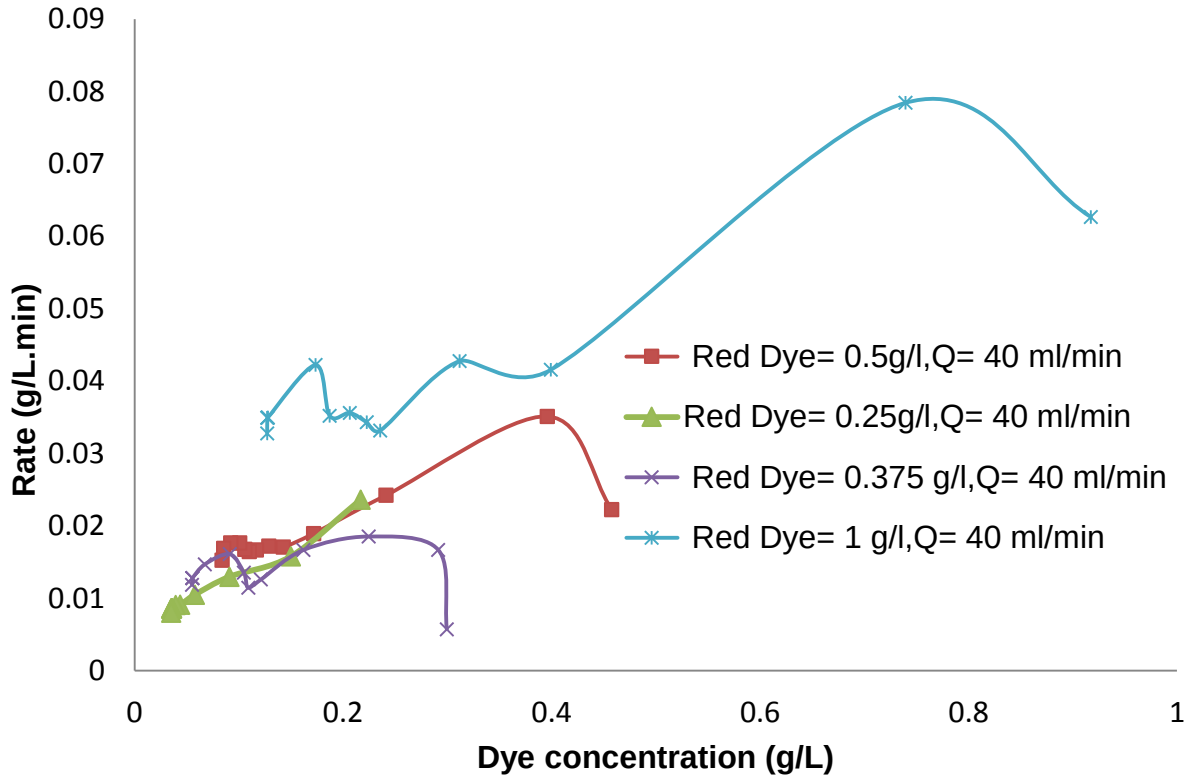



Figure 4.8: Rate of decolouration versus dye concentration with equal flow rate.

Conditions: Initial concentrations of synthetic red dye solution vary from 0.25–1g/l; average O3 input rate, 52.5mg/l; duration of ozonation, 60 min; stirring speed, 500rpm; flow rate of synthetic red dye, 40ml/min for all experiments.

### 4.4.6 Rates of decolouration at different flow rates

The rate of decolouration was determined for different flow rates of dye solution (40, 65, 92, 110, 180 and 230 ml/min) for a fixed initial concentration of dye (0.5 g/L). The results are shown in Figure 4.9 as a function of dye concentration.

What this figure demonstrates is that, as the flow rate (Q) decreases, the steady-state rate of decolouration decreases. This is to be expected, as the concentration is lower at the outlet. As before, these final values lie on a good straight line going through the origin. The apparent

first-order rate constant is 0.21min$^{-1}$. Interestingly, this is the same value as the measured mass transfer coefficient, but it is very different from the other two values.

In the unsteady-state region we see very similar pattern to that in Figure 4.8 for the lower flow rates, namely an early increase in reaction rate with concentration, followed by a flat section that is different for each of the flow rates. The two higher flow rates show only the early rising part of the curves. Now, as mentioned earlier it is to be expected that with the higher dye flow-rates it would take longer for the ozone concentration to reach its steady state. Therefore it is perhaps not surprising that in these two cases the dye de-colouration rates rise as the dye concentration falls, because this reaction rate is probably determined more by the increasing ozone concentration than the decreasing dye concentration.

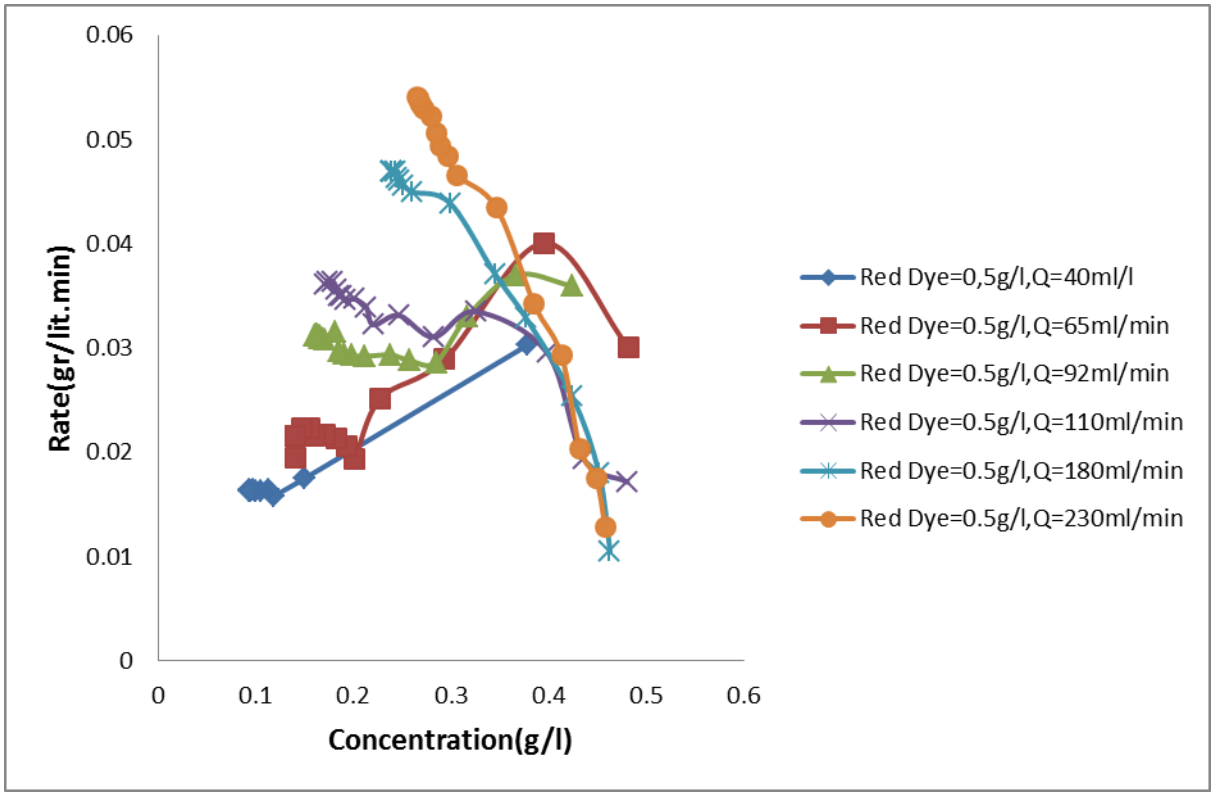



Figure 4.9: The rate of decolouration versus dye concentration at various flow rates.

Conditions: Initial concentrations of synthetic red dye solution 0.5g/l; average $O_3$ input rate,52.5mg/l; duration of ozonation, 60 min; stirring speed,500rpm;flow rate of synthetic red dye varying from 40ml/min–230ml/min.

## 4.5 Summary and Conclusion

The experiments recorded in this paper were intended to investigate the decolouration effect of ozone on a reactive dye in a CSTR.The results obtained during the course of this series of experiments demonstrate that the dye studied can be decoloured effectively by the ozonation process. We measured the decolouration of the dye by ozone by determining the dye concentration as a function of time up to steady state for various initial dye concentrations and at various dye flow-rates.

The first stage of our investigation established that with a low dye flow rate, the frit size did not have a significant impact on the rate of dye decolouration. However, as the ozone dissolution rate is probably lower at higher dye flow-rates, this may not be true for the higher dye flow rates.

We analysed the experimental data were analysed in two rather different ways: the rate at which the final steady state was reached; and the rate of the steady state versus the final steady-state dye concentration. Both were reasonably well fitted by first-order rates in terms of the dye concentration alone, but the values of the rate constants were significantly different in the two cases. As the ozone concentration starts at zero, it would be surprising if the ozone concentration did not influence the reaction rate of the dye decolouration, at least in the early stages (the transient results).

Thus, even though simple first-order analysis of the kinetics of dye concentration seems to fit the individual results, we require more than this to obtain a model that fits the entire range of results.

It is clear from the above that a model for the above decolouration system will need to be quite complex, but it is needed if we intend to use this research to design an industrial decolouration plant. In a previous publication we described our use of the same apparatus as that set out in the early part of this paper, for experiments in a semi-batch system [25]. If we can produce a model that can in effect correctly predict the results from both the earlier experiments and those reported here, then we will be in a position to design such a system for use in decolouring dye wastewater.

Summary of major CSTR results

- The major benefit of using the CSTR rather than a semi-batch reactor is that one can explore different regions of the reaction space.
- There are a range of steady states as a function of residence time that enable the researcher to explore short and long residence times.
- When we modelled the progression to the steady state, the rate from rate of approach showed a first-order dependence that was not affected by the flow rate.
- The rate as a function of initial dye concentration showed a maximum at an intermediate value.
- The rate as a function of flow rate showed an increase, with a decrease in concentration at high flow rates and the reverse effect at low flow rates.

**Nomenclature**

| | |
|---|---|
| AOPs | advanced oxidation process |
| Bé | Bohme |
| $C_{dye}$ | the concentration of dye in the vessel |
| $C_{dye}^{\circ}$ | the concentration of dye in the feed stream |
| COD | chemical oxygen demand |
| $C_{ozone}$ | the concentration of ozone in the liquid |
| $K_{La}$ | the mass transfer coefficient for ozone dissolution (0.21min-1) |
| nm | nanometre |
| Q | the volumetric flow-rate of the liquid |
| $R_{ozone}$ | the rate of consumption of ozone |
| $R_{dye}$ | the rate of consumption (decolouration) of the dye. |
| t | time |
| V | the volume of the reactor |
| λ max | maximum wavelength |

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# 5 Chapter Five: A SIMPLE KINETIC MODEL FOR THE DECOLOURATION OF REACTIVE RED 198 DYE USING OZONE

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**Abstract**

A kinetic model has been developed to simulate the dye decolourisation of Reactive Red 198 using Ozone. Several experiments at different initial dye concentrations and different flow rates were performed in both a continuous stirred tank reactor (CSTR) and semi-batch reactor as a function of time. Based on the qualitative results observed [1,2], it was established the reaction was a radical chain reaction and towards the end of the decolouration, it was first order in dye concentration but showed complex behaviour with respect to initial dye concentration.

Using these results as a mass action based kinetic model with three constants representing the rate of ozone decomposition to form radicals, the rate of radical termination and the rate of

decolouration has been proposed. For the semi-batch tests,the values of the three constants were regressed by comparing the model results with the experimental results. Using these constants, it was shown the CSTR results could be accurately predicted indicating that the model was appropriate.

Keywords: Kinetics, Ozonation, Reactive dye, Wastewater, Modelling

## 5.1 Introduction

Textile wastewaters are a mix of many types of dyestuffs and textile auxiliaries. These include detergents, levelling agents, pesticides, acids, grease, oils, solvents, heavy metals, inorganic salts and fibres which are added in the three sections of spinning, weaving and finishing. It is crucial to remove the effluent colour from the textile dyeing and finishing process to alleviate environmental problems [3].

Textile industry wet process effluents – combinations of those from de-sizing, bleaching, dyeing, printing and finally finishing may contain chemicals with toxic effects upon microbial populations. Conventional methods for the removal of dyes in wastewater include physical, chemical, and biological processes. The majority of azo dye compounds, unfortunately, inhibit bacterial activity and biological processes are very slow. Hence, several methods must be developed to overcome the problem [4].

In the textile industry, dyes and auxiliaries are essentially toxic and if they remain untreated could create long-term health concerns. It is estimated some of the man-made textile dyes used, remain in effluent streams during developing or processing procedures. Indeed, textile dyes have appeared as a spotlight of environmental remediation efforts. Among the many categories of textile dyestuffs, reactive azo dyes contribute a considerable portion of dye pollutants and possibly have the most severe consequences for the environment [5].

In conventional treatment systems, some of the more environmentally challenging dye auxiliaries may be completely removed from wastewater. However, they cannot completely

decolour the solutions as the textile dyes are purposely engineered to oppose biological, photolytic and chemical degradation. Textile wastewater frequently needs pre-treatment of separate process streams (e.g. dye bath effluent) [6]. There are also ecological problems around potential toxicity and carcinogenicity of some organic dyes. Reactive dyes are mostly used for cotton dyeing and typically an estimated 30% of dyes are not absorbed by the yarn and fabrics and remain in the wastewater. In view of the fact these types of dyestuffs were deliberately planned to resist degradation, old conventional organic wastewater treatment processes are unsuccessful in eliminating the colour [7].

In many industries such as textile, plastic, food, leather, cosmetics, printing and pharmaceutical, dyes are widely used. In the $20^{th}$ century, numerous synthetic dyes have come into production. These "new" classes include acidic, direct, azo, disperse, basic, cationic, anthraquinone, reactive, phthalocyanine, neutral and metal complex. The majority of these dyes react with nucleophilic groups and form covalent bonds between the dye and fibre which can establish a very strong bond.

Popular dye groups are azo, phthalocyanine, and anthraquinone while 60% of reactive dyes are azo dyestuffs [3, 8]. The easy application of reactive dyes as well as their excellent colour fastness and brightness have made them very popular. They demonstrate a broad variety of diverse chemical constructions mainly based on alternative aromatic and heterocyclic groups. Unfortunately many of the reactive dyes, due to their toxicity, can kill creatures in the water. We need to appreciate that reactive dyes are highly soluble in water and it is difficult to remove them using conventional physicochemical and organic treatment processes [9].

To re-iterate, in an aqueous system of the textile process, many auxiliaries are added in the dye bath such as levelling and wetting agents, anionic, cationic and non-ionic surfactants, softeners, fixing agents. In addition, many other additives are also used in these wet processes – bleaching, de-sizing, dyeing and finishing. The end result is a complex and highly polluting effluent containing wide variations of pH, high temperatures, high COD and high concentrations of dissolved salts in textile dyeing effluents. The most serious problem of textile waste effluent is the strong colour remaining in the wastewater. For the cotton industry particularly, treating wastewater with reactive dyes, is an extremely difficult problem [10].

Ozonation is possibly the best method used for decolourisation of textile effluents. It is very well known ozone is a powerful oxidant and its oxidizing potential compared to chlorine is

nearly twofold. Because of its high oxidation potential most organic compounds can easily be degraded [11-17].Ozone ($O_3$) is thus very useful in the decolouring of textile effluents. Bio noncompliant dyes in the effluent can be converted by ozone into environmentally acceptable groups and the usual efficient organic processes then can be utilised. It is presumed that advanced oxidation processes (AOPs) which includes ozonation, usually involve a particular non-selective oxidizing agent, namely the hydroxyl radical ($^{\cdot}OH$) to destroy harmful contaminants [18]. Many studies on dye degradation by Ozone have been published [19 -22].

In principle, one can describe the kinetics of a reaction system by mathematical modeling. The most important point is to derive a model equation with the capacity to approximate the value of the reaction rate close to that of the experimentally measured one. The proposed reaction system model must take into account all important phenomena and parameters observed in the experimental results. Once created, it can be solved and the predicted performance can be compared with the experimental data. Any major differences between the system performance and the performance predicted by the model means there may well be some important effects not considered. By fitting the model equations to the experimental data, kinetic constants may be obtained. The model can then be used for calculating the system performance under different working conditions, reactor design, optimization, upgrading, and control of the system [23-25].

In this paper, a kinetic model has been developed to simulate the dye decolourisation of Reactive Red 198 using Ozone. The values for the three kinetic constants were obtained by regressing the model with the semi-batch experimental data. The effectiveness of the model was then determined by comparing the concentration time results obtained experimentally for the CSTR experiments with those obtained from the model.

## 5.2 Materials and Methods

### 5.2.1 Reactive dye

The reactive dyestuff was obtained from Dye Star (Durban, South Africa).In order to achieve complete hydrolysation of the reactive dye solution; 1000 mg/l water soluble stock emulsion of the dye was prepared by breaking up the dye in distilled de-ionized water. Following this, a 4.5 g/l from 48Bé NaOH and 5g/l of $Na_2CO_3$ and some other additives as mentioned in reference[1]solutions was added under thermostatically controlled (60 ◦C) conditions and continuously stirred for a minimum of 4 h. The prepared "waste" dye solution was retained for an additional 24 h at room temperature. This final step ensures complete hydrolysis and corresponds to processes utilized in exhausted dye batch studies. Adding sodium bi carbonate as buffer kept pH at 8.2 for the experiments [26].The reactive dyestuff concentration was selected between 250mg/l up to 1000 mg/l for the ozonation experiments. Table 5.1 lists the physicochemical properties of the reactive dye selected for the present study.

Table 5.1 Physicochemical properties of the reactive dyes used in the present study.

| Dye Brand Name | CI reactive | Anchor group | Chromophore group | λ max (nm) |
|---|---|---|---|---|
| Remazol red RB | Red198 | Vinylsulphone + Monochlorotriazine | Azo | 500 |

For the ozonation experiment, a UV-Vis absorption spectrum was measured and a place in the spectrum identified where the absorbance could be measured without interference from other species. The value of this wavelength is given as $\lambda_{\max}$ in Table 5.1 and corresponds to that recommended in the literature [27].

### 5.2.2 Ozone reactor

The experimental set-up used in this study is shown in Fig 5.1. Pure oxygen gas from a pressure cylinder was fed into a laboratory ozone generator which produced an ozone-oxygen mixture. A constant flow of oxygen generates about 52.5 mg $O_3$ /h.Ozone transfer efficiency was determined by measuring the input and off-gas concentration of each experiment iodometrically [28, 29]. Ozone is sent to a stirred reactor with a capacity of 1000 mL via a frit as shown in Fig 5.1. For the CSTR experiments, dye solution is continuously added to the reactor from a 1.5L reserve tank and the inlet and outlet flow of the dye solution is controlled via valves. The details for these experiments can be found in references [1, 2].

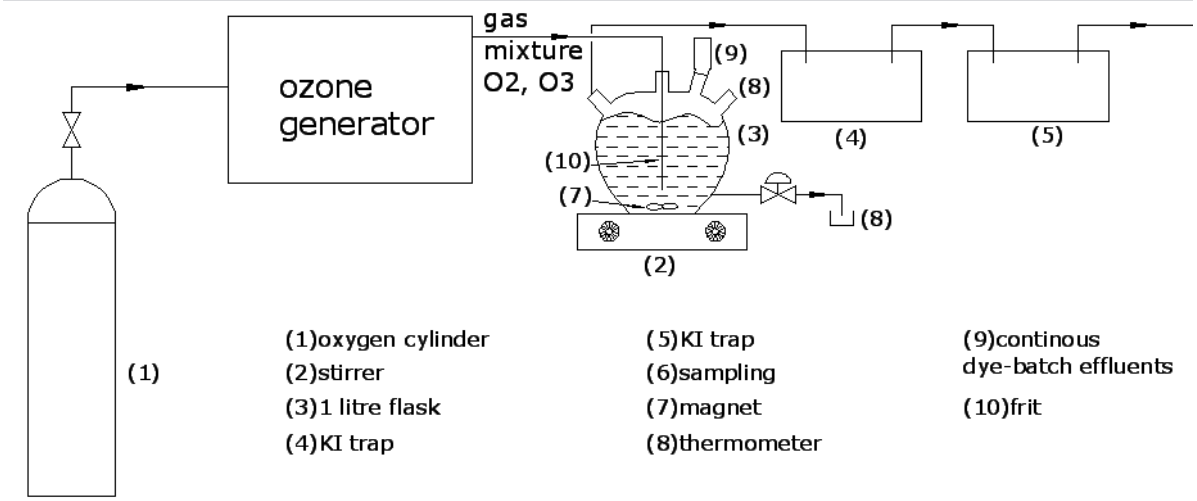



Figure 5.1: Experimental set-up.

## 5.3 Modelling the Decolouration Kinetic

Some important results have arisen from the previous work [1, 2]. These are as follows:

- The reaction is a chain reaction in that many dye molecules are decoloured by the decomposition of one ozone molecule decomposition. In the light of this, one thinks of a radical reaction for the decolouration of the dye.
- The reaction rate to colour remaining towards the end of the decolouration, appears to be first order with respect to the colour remaining.
- These first order rate constants appear to have a complex relationship in relation to the initial dye concentration. In particular, the rate constant at higher initial dye concentration appears to be smaller than those at lower initial dye concentration.
- Experiments have been conducted on an ozone semi-batch reactor and a CSTR (both steady and unsteady state) and the kinetic model needs to be able to explain both sets of results.

There are then essentially three things needed to be modelled – namely the ozone concentration, the colour and the radical concentration.

From our initial experiments, we already have the ozone dissolution rate, a first order mass transfer model, with a rate constant and the solubility of the ozone in the aqueous phase for this apparatus – the rate of ozone flow, the ozone concentration in the gas and the frit used. We can use this information in our ozone model to cut down the number of constants needing to be estimated.

The purpose of the exercise is to keep the model as simple as possible while reasonably accurately describing the experimental results as the model is intended for use in designing such systems.

For reasons which will become apparent later, we will use the semi-batch results to estimate the parameters in the model and then verify them by testing the model on both the steady state and unsteady state CSTR results.

In this paper we propose a simple kinetic model based on the formation of radical species..

### 5.3.1 Model

As mentioned before, there are three rates needed to be modelled. The first is the decomposition of the ozone to form the active radical. Now the dye molecule is very complex but it really has only one colour centre (Chromophore). Ozone is a very strong oxidant and is likely to attack the dye molecules in many places. Thus the model we are proposing is the ozone reacting with the initial dye concentration on the assumption that it effectively does not get used up even if it has lost its colour.

$$\text{Ozone} + Dye^{\circ} \longrightarrow \text{Radical} \qquad \text{(a)}$$

When we come to decolouration of the dye, we assume the radical reacts with the coloured dye to decolour it so we get:

$$\text{Radical} + \text{Dye} \longrightarrow \text{DDye} + \text{Radical} \qquad \text{(b)}$$

We use $Dye^{\circ}$ to refer to the initial dye concentration while Dye refers to the coloured dye and DDye refers to decoloured dye.

Finally, we assume the radical itself can also react with all the dye components, not only colour centres, to get deactivated. This gives:

Radical + $Dye^{\circ}$ ⟶Termination (c)

We further assume all these reactions are second order – namely first order in each of the components on the left hand side – and are irreversible.

Using the above assumptions, we can now write rate expressions for the rate of ozone formation ($R_{ozone}$), the rate of radical formation ($R_{radical}$), the rate of dye decolouration ($R_{dec}$) and the rate of radical termination ($R_{term}$).

$$R_{ozone} = -k_1 C_{dye}^{\circ} C_{ozone} = -R_{radical} \quad (1)$$

The rate of dye decolouration:

$$R_{dec} = k_2 C_{dye} C_{radical} \quad (2)$$

While the rate of the radical termination reaction is given by:

$$R_{term} = k_3 C_{radical} C_{dye}^{\circ} \quad (3)$$

We note: we have made the termination rate proportional to the total initial dye concentration because of our assumption that the radicals can react with the dye even if the colour centre has been removed.

We are now in a position to write mass balances for all the species involved in the model.

#### 5.3.1.1 Ozone mass balance

We can write an unsteady-state mass balance equation for the ozone in the CSTR

$$\frac{dC_{ozone}}{dt} = K_{La}(C_{ozone}^{*} - C_{ozone}) - \frac{Q}{V} C_{ozone} - \frac{R_{ozone}}{V} \quad (4) \quad [30]$$

Where $C_{ozone}$= the concentration of ozone in the liquid

$C^*_{ozone}$= the equilibrium concentration of ozone in the liquid (0.0002g/L) [1]

t = time

$K_{La}$= the mass transfer coefficient for ozone dissolution ($0.21min^{-1}$) [1]

Q = the volumetric flow-rate of the liquid

V = the volume of the reactor

$R_{ozone}$= the rate of consumption of ozone

For the CSTR experiments the initial condition is $C_{ozone}$=0 at t=0

For the semi-batch experiments Q=0 and $C_{ozone} = C^*_{ozone}$ at t=0 0 as the reactor was saturated with ozone first and the dye solution was added to the reactor [1].

#### 5.3.1.2 Dye mass balance

Let us now do an unsteady-state mass balance on the dye colour concentration in the CSTR:

$$\frac{dC_{dye}}{dt} = \frac{Q}{V}\left(C^{\circ}_{dye} - C_{dye}\right) - \frac{R_{dye}}{V} \qquad (5) \quad [31]$$

Where $C_{dye}$ is the concentration of dye in the vessel

$C^{\circ}_{dye}$is the concentration of dye in the feed stream

$R_{dye}$is the rate of consumption (decolouration) of the dye

Here the initial condition is that: at t=0 $C_{dye} = 0$

For the semi-batch reactor the mass balance has Q=0

with initial condition $C_{dye} = C^{\circ}_{dye}$ at t=0

## 5.3.2 Radical balance

$$\frac{dC_{rad}}{dt} = R_{radical} - R_{termination} - \frac{Q}{V}C_{rad} \qquad (6) \qquad \text{for the CSTR}$$

at t=0 ,$C_{rad} = 0$ for both CSTR and semi-batch while as before for semi-batch Q=0

### 5.3.2.1 CSTR steady – state

From all the three mass balances for the CSTR we can get the steady-state values by setting the time derivatives equal at zero.

In order to understand qualitative unsteady behaviour of the CSTR model, we can set the ozone and radical derivatives to zero (a pesudo-steady state assumption) and get an expression for the rate of decolouration.

$$R_{dec} = k_2\left(\frac{k_1}{k_3}\right)K_{La}C^*_{ozone}/(K_{La} + \frac{Q}{V} + \frac{k_1 C^{\circ}_{dye}}{V})C_{dye} \qquad (7)$$

This gives a first order in dye concentration rate expression as found experimentally and shows inverse behaviour with respect to the initial dye concentration as also found experimentally. This gives us confidence that we are on the right track with the model.

## 5.3.3 Solutions of the semi-batch model equations

If it so happens that the semi-batch equations have an analytical solution, this is very convenient as it can be used for a regression on the experimental results to obtain values of the unknown constants ($k_1, k_2, k_3$). Once these constants are known, the CSTR equations can

be integrated to prove how well the results fit the CSTR experimental data. The derivations of the analytical solutions are given in appendix A.

## 5.4 Results and Discussion

### 5.4.1 Regression and comparison with semi-batch results

Experimental results from reference [1] were used in conjunction with equation A12 to determine the constants $k_1, k_2\ and\ k_3$ by minimising the sum of squared errors between the experimental and the model value of $C_{dye}$, using all the experimental results given in Fig 5.2, Fig 5.3 and Fig 5.4. The values of the constants found are given in Table 5.2.

Table 5.2 Regressed value of constants from semi-batch experiments given in Fig 5.2, Fig 5.3 and Fig 5.4.

| Constant | Value L /gr.min | Nature of constant |
|---|---|---|
| $k_1$ | 0.010123 | Initiation (Radical) |
| $k_2$ | 57200 | Propagation (Decolour) |
| $k_3$ | 0.384 | Termination (Radical) |

The goodness of fit of the model to the data was also assessed.. The R Square value was calculated to be 0.987 and the standard error is less than 2%.

In Fig 5.2, we show the accuracy of the fits for different initial concentrations. It can be seen the fit is reasonably good. These results are shown for only single experiments at each of the initial concentrations. However, from the 0.25 g/l and 1 g/l initial dye concentration replicates were conducted and the results are shown in Fig 5.3 and Fig 5.4.

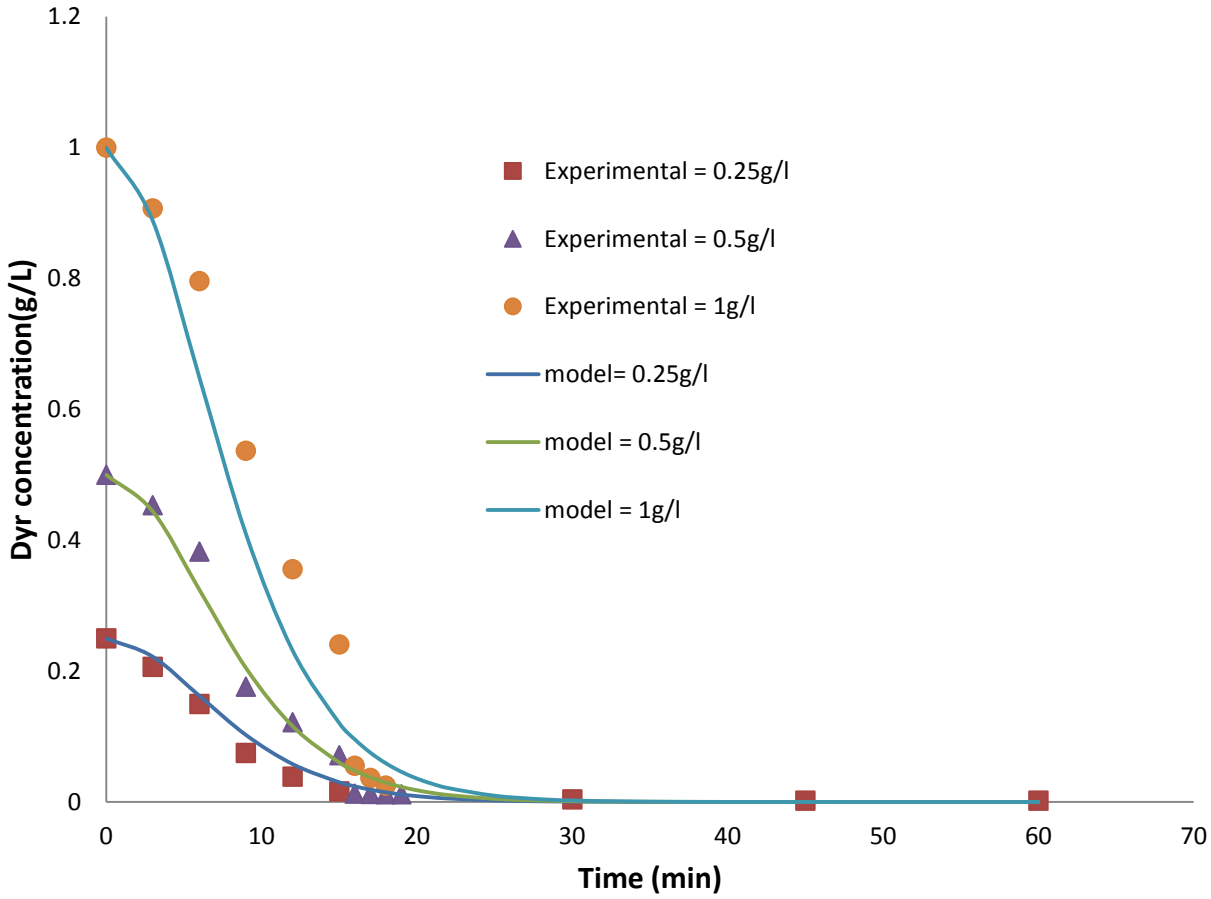



Figure 5.2: Comparison of experimental and predicted dye concentration in semi-batch with different initial dye concentrations. Experimental results from reference [1].

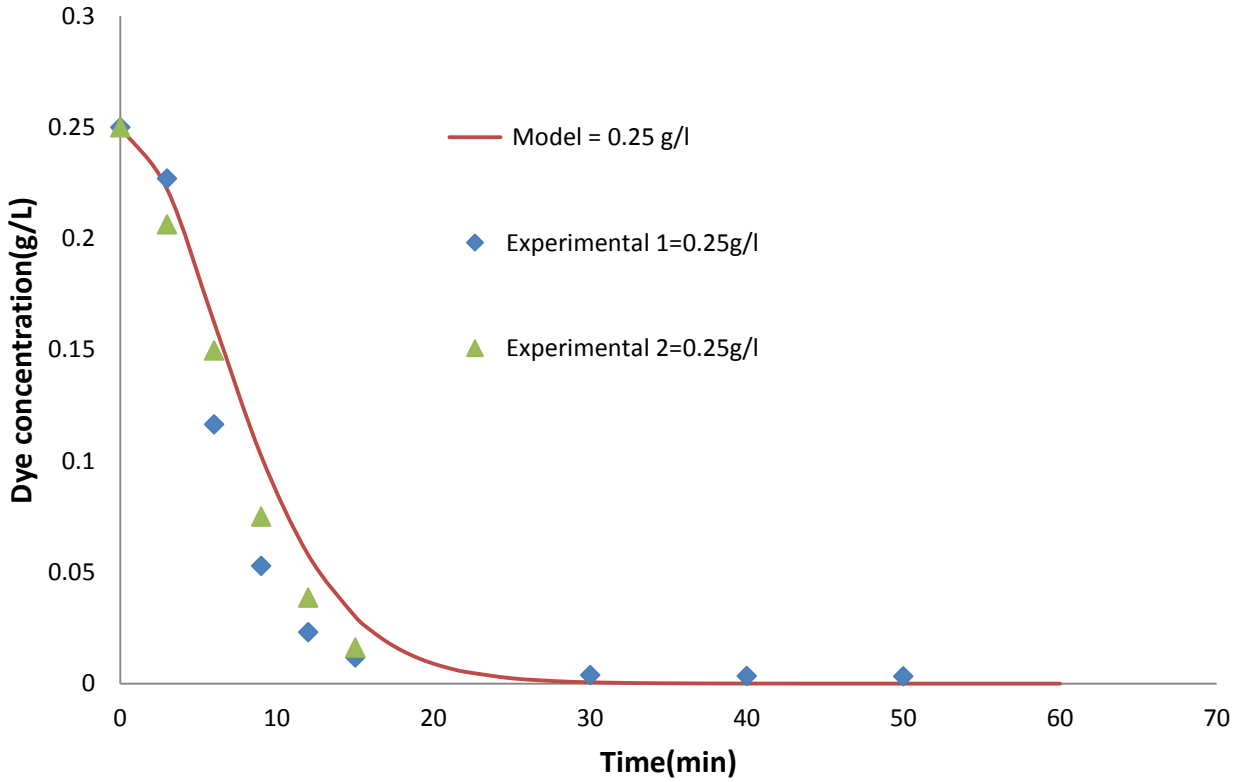



Figure 5.3: Comparison of experimental and predicted dye initial concentration versus time with two experimental runs for 0.25g/L of initial dye concentration. Experimental results from reference [1].

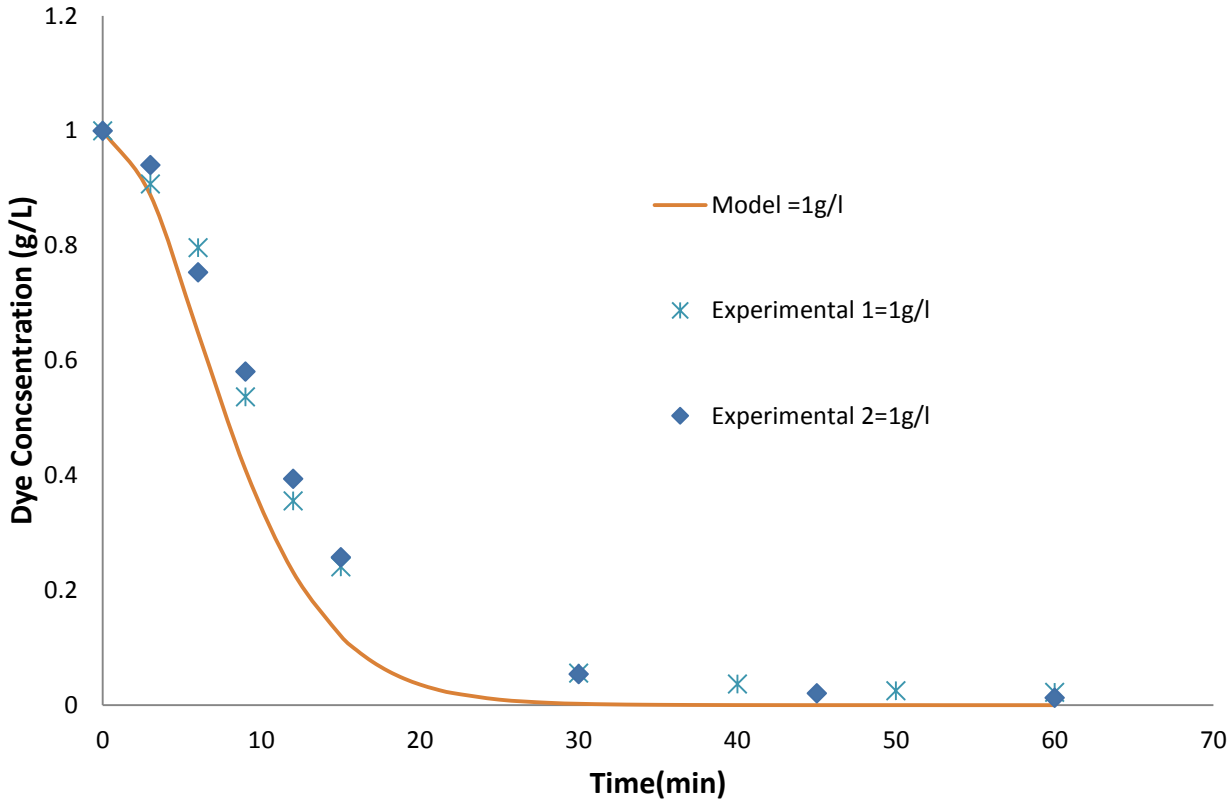



Figure 5.4:Comparison of experimental and predicted dye initial concentration versus time with two experimental runs for 1 g/L of initial dye concentration. Experimental results from reference [1].

### 5.4.2 Comparison of model results with those for the steady-state CSTR results.

The results from the model for the steady-state CSTR are given in appendix A in equation A19. The comparison with all the steady-state experimental results from reference [2] is given in Fig 5.5. The fit is seen to be excellent.

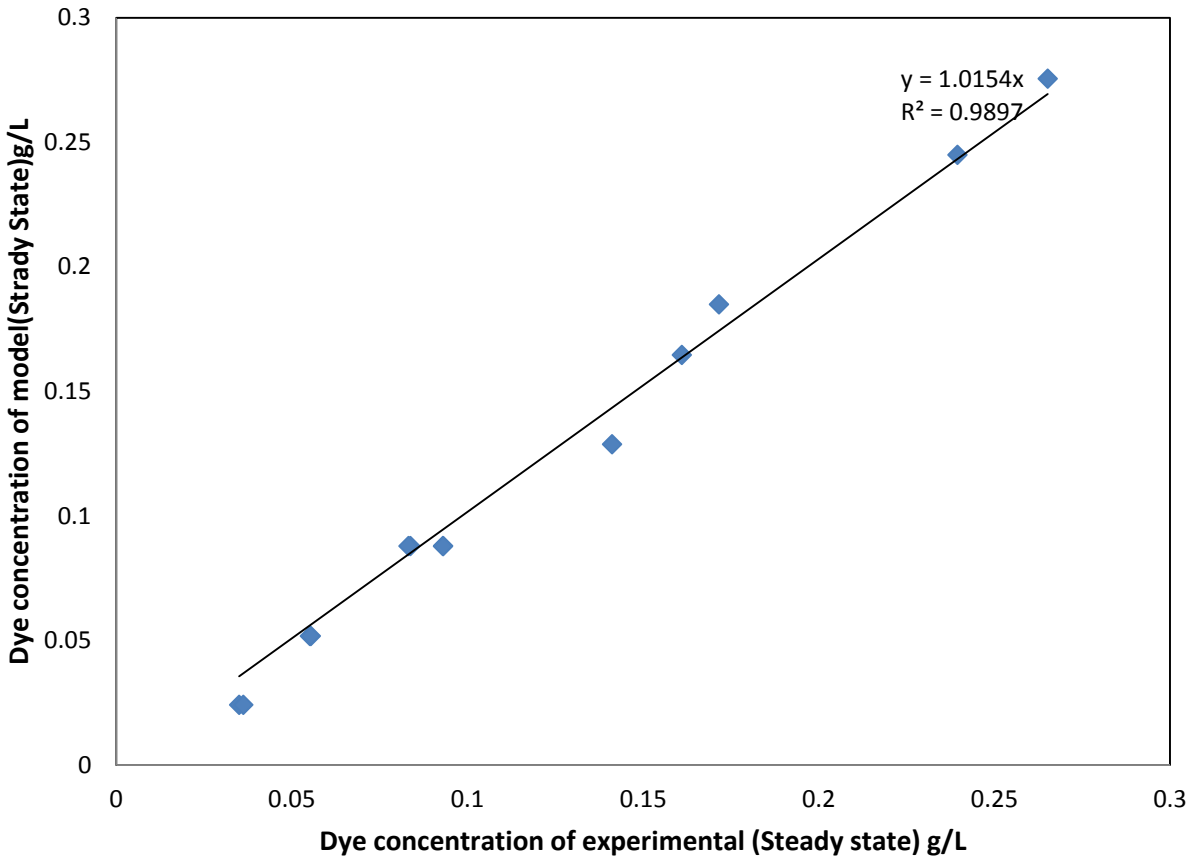



Figure 5.5: Model vs. experimental of dye concentration for steady-state CSTR experiments from reference [2].

### 5.4.3 Comparison of model with unsteady-state (USS) CSTR experimental results.

Unfortunately, there does not seem to be a simple analytical solution to the USS CSTR model. Thus, the differential equations (a) (b) and (c) using the regressed constants were integrated numerically using the Runge-Kutta method using Matlab. The results for three initial concentrations are shown in Fig 5.6. Again, the results are reasonably good. As before, duplicate results were taken for 0.5 g/L and 0.25 g/L initial dye constants and these results are shown in Fig 5.7 and Fig 5.8 respectively.

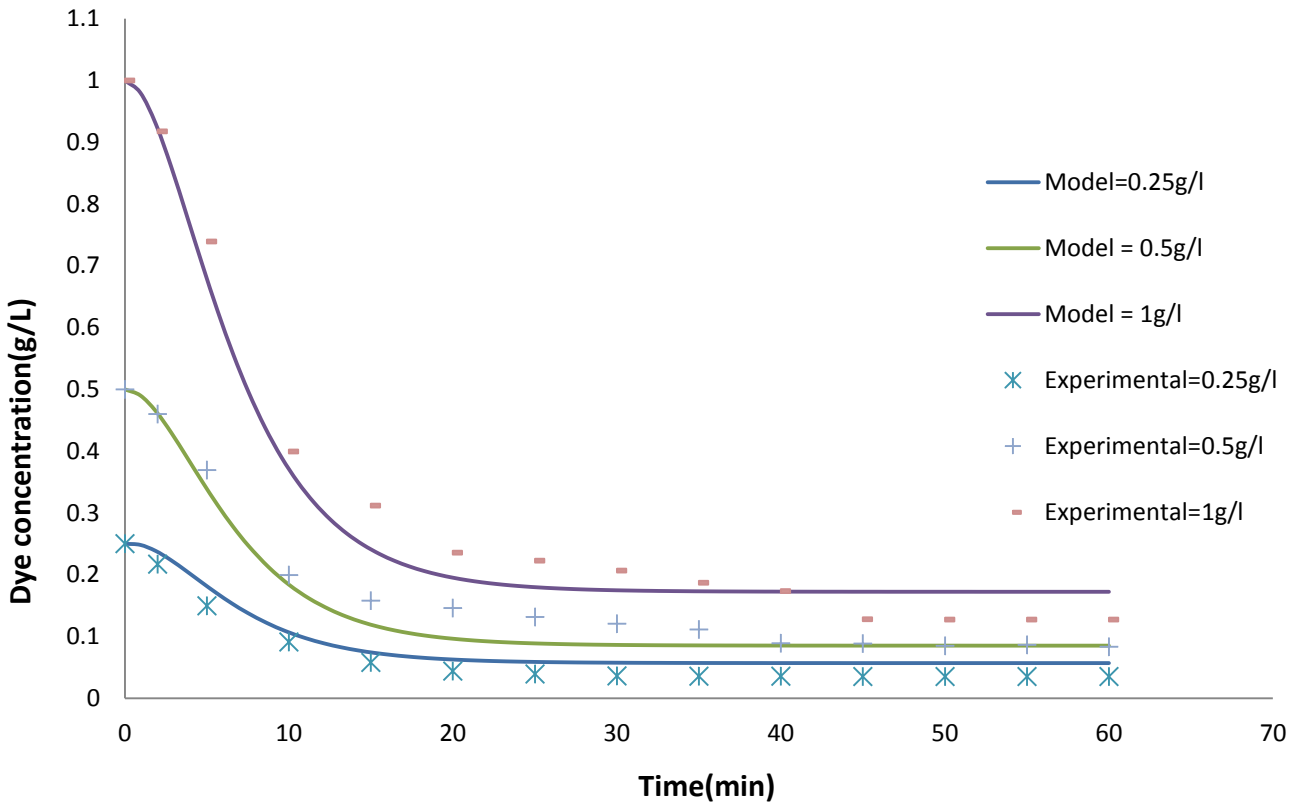



Figure 5.6: Comparison of experimental and predicted dye concentration in a CSTR with different initial dye concentrations versus time. Experimental results from reference [2].

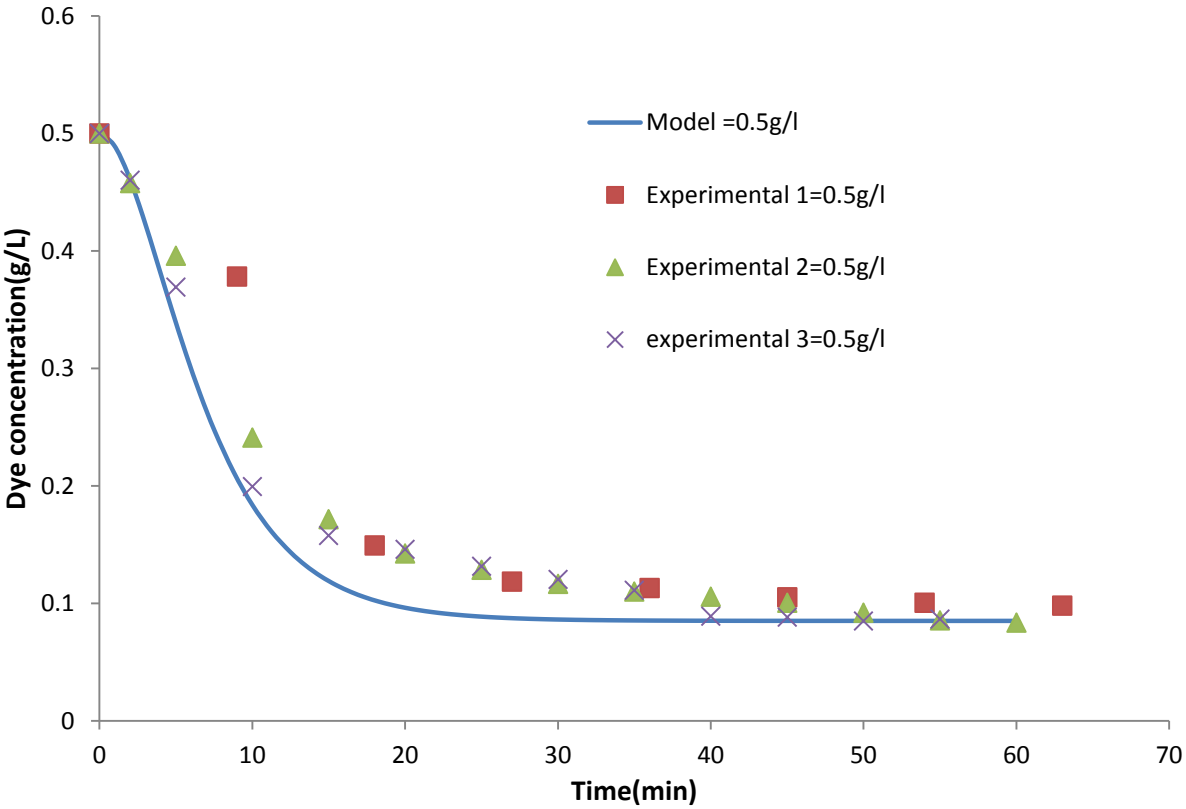



Figure 5.7: Comparison of experimental reference [2] and predicted dye concentration versus time in a CSTR with three repeat experimental run for 0.5 g/L initial dye concentration.

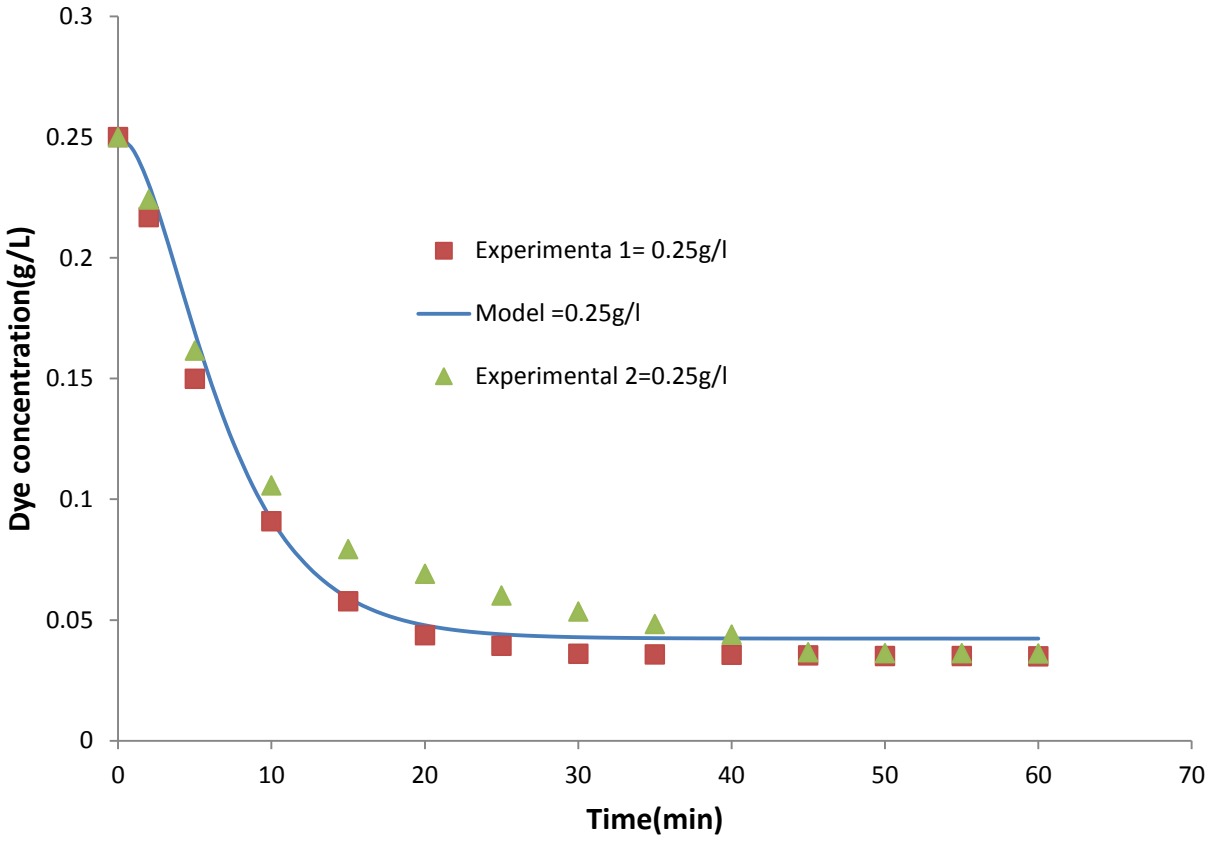



Figure 5.8: Comparison of experimental results from reference [2] and predicted dye concentration versus time in a CSTR for two experimental runs for 0.25 g/L initial dye concentration

## 5.5 Summary and Conclusions

A reasonably simple model for the kinetics of the dye decolouration by ozone has been proposed. This model was based on a number of experimental observations from references 1 and 2. The most significant being:

- The reaction was a radical chain reaction
- The latter stages of decolouration were first order with respect to dye concentration
- There was a complex relationship between the first order rate constant and the initial dye concentrations.

As a consequence of these results, mass action models for the rates of reaction for ozone decomposition, radical formation and termination and decolouration were proposed. These models, among them, had three rate constants. Using the experimental results for the semi-batch results [1], these constants were regressed for using the analytical solutions of the model equations. The model was then used to predict the CSTR results. The fit between the experiment and the model was in all cases found to be very good ($R^2$ =0.9897 Model versus experimental), garnering us a great deal of confidence in the model. This model should prove to be very useful in the design of commercial systems.

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## 5.6 Appendix A:

1. Analytical solution for the semi-batch equations and steady-state modelling for the semi-batch reactor

For ozone concentration we have:

$$\frac{dc_{ozone}}{dt} = K_{La}(C^{*}_{0z0ne} - C_{ozone}) - (k_{1/\mathrm{v}})C^{\circ}_{dye}C_{Ozone} \quad \text{(A1)}$$

With boundary condition $C_{ozone} = C^{*}_{0z0ne}$ at t=0

This is a first order differential equation that can be integrated to give:

$$C_{Ozone} = \frac{C^{*}_{ozone}}{K_{La}+K_1\frac{C^{\circ}_{dye}}{V}}(K_{La} + \frac{K_1}{V}C^{\circ}_{dye}exp - (K_{La} + K_1\frac{C^{\circ}_{dye}}{V})\mathrm{t}) \quad \text{(A2)}$$

Let $K_1\frac{C^{\circ}_{dye}}{V} = a$

$$C_{Ozone} = \frac{C^{*}_{ozone}}{K_{La}+a}(K_{La} + a(exp - (K_{La} + a)\mathrm{t}) \quad \text{(A3)}$$

If $\mathrm{b} = \frac{K_3}{V}C^{\circ}_{dye}$ then we have

$$\frac{dC_{rad}}{dt} = aC_{Ozone} - bC_{rad} \quad \text{(A4)}$$

$$\frac{dC_{rad}}{dt} + bC_{rad} = a\frac{C^{*}_{ozone}}{K_{La}+a}[K_{La} + aexp - (K_{La} + a)\mathrm{t}] \quad \text{(A5)}$$

$$\frac{d[C_{rad}expbt]}{dt} = a\frac{C^{*}_{ozone}}{K_{La}+a}[K_{La}expbt + aexp(b - K_{La} - a)\mathrm{t}] \quad \text{(A6)}$$

$$C_{rad}\exp(bt) = a\frac{C^{*}_{ozone}}{K_{La}+a}\left[\frac{K_{La}}{\mathrm{b}}\exp(bt) + \frac{a}{b-K_{La}-a}exp(b - K_{La} + a)\mathrm{t}\right] + \mathrm{d} \quad \text{(A7)}$$

At t=0 we have $C_{rad} = 0$

$$d = -a\frac{C^{*}_{ozone}}{K_{La}+a}(\frac{K_{La}}{\mathrm{b}} + \frac{a}{b-K_{La}-a}) \quad \text{(A8)}$$

$$C_{rad} = a\frac{C^{*}_{ozone}}{K_{La}+a}[\frac{K_{La}}{\mathrm{b}} + \frac{a}{b-K_{La}-a}exp - (K_{La} + a)t] \quad \text{(A9)}$$

$= -a\frac{C^*_{ozone}}{K_{La}+a}\left(\frac{K_{La}}{\mathrm{b}} + \frac{a}{b-K_{La}-a}\exp(-bt)\right)$

$= a\frac{C^*_{ozone}}{K_{La}+a}\left(\frac{K_{La}}{\mathrm{b}}(1 - exp - bt\right) + \frac{a}{b-K_{La}-a}(exp-(K_{La}+a)\mathrm{t}) - \exp\ -\mathrm{b\ t}$ (A10)

Now

$\frac{dC^{\circ}_{dye}}{dt} = -\frac{K_2}{V}C_{dye}C_{rad}$ And $\frac{dlnC_{dye}}{dt} = -\frac{K_2}{V}C_{rad}$

$$= -\frac{K_2}{V}a\frac{C^*_{ozone}}{K_{La}+a}[+\frac{a}{b-K_{La}-a}(exp-(K_{La}+a)\mathrm{t}) - \exp\ -\mathrm{b\ t}]$$

$lnC_{dye} = -\frac{K_2}{V}a\frac{C^*_{ozone}}{K_{La}+a}[\frac{K_{La}}{\mathrm{b}}(\mathrm{t} + \frac{1}{\mathrm{b}}exp - bt) + \frac{a}{b-K_{La}-a}\left(\frac{1}{-(K_{La}+a)}exp-(K_{La}+a)\right)t + \frac{1}{b}\exp -bt + e$ (A11)

At t=0 $C_{dye}$=$C^{\circ}_{dye}$

$$\mathrm{e} = \ln C^{\circ}_{dye} + \frac{K_2}{V}a\frac{C^*_{ozone}}{K_{La}+a}[\frac{K_{La}}{\mathrm{b}^2} + \frac{a}{b-K_{La}-a}\left(\frac{1}{-(K_{La}+a)} + \frac{1}{b}\right)]$$

$\ln\left(\frac{c_{dye}}{c^{\circ}_{dye}}\right) = -\frac{K_2}{V}a\frac{C^*_{ozone}}{K_{La}+a}\left[\frac{K_{La}}{\mathrm{b}^2}\left(t + \frac{1}{b}(\exp(-bt)-1)\right) + \frac{a}{b-K_{La}-a}\left(\frac{1}{-(K_{La}+a)}[exp-(K_{La}+a)t - 1\right] + \frac{1}{b}\exp(-bt)+1))\right]$ (22)

$c_{dye} = c^{\circ}_{dye}\exp[-\frac{K_2}{V}a\frac{C^*_{ozone}}{K_{La}+a}\frac{K_{La}}{\mathrm{b}}\left(t + \frac{1}{b}(\exp(-bt)-1) + \frac{a}{b-K_{La}-a}\left(\frac{1}{-(K_{La}+a)}[exp-(K_{La}+a)t - 1\right] + \frac{1}{b}\exp(-bt)-1])\right]$ **(A12)**

2. <u>Steady state modelling For CSTR</u>

We can write for the concentration of ozone:

$$\frac{dc_{ozone}}{dt} = k_{La}(c^{*}_{ozone} - c_{ozone}) - \frac{Q}{V}c_{ozone} - R_{ozone}/V \qquad \text{(A13)}$$

But $R_{ozone} = k_1 C^{\circ}_{dye} c_{ozone}$/V

$$\frac{dc_{ozone}}{dt} = k_{La}(c^{*}_{ozone} - c_{ozone}) - \frac{Q}{V}c_{ozone} - \frac{K_1}{V}C^{\circ}_{dye}c_{ozone}$$

At Steady state we have

$$k_{La}(c^{*}_{ozone} - c^{SS}_{ozone}) - \frac{Q}{V}c^{SS}_{ozone} - \frac{K_1}{V}C^{\circ}_{dye}c^{SS}_{ozone}=0$$

$$C^{SS}_{Ozone} = \frac{K_{La}C^{*}_{ozone}}{K_{La}+\frac{Q}{V}+K_1\frac{C^{\circ}_{dye}}{V}} \qquad \text{(A14)}$$

Now for Dye in CSTR we can write

$$\frac{dC_{rad}}{dt} = -\frac{Q}{V}C_{rad} + \frac{K_1}{V}C^{\circ}_{dye}C_{Ozone} - \frac{K_3}{V}C^{\circ}_{dye}C_{rad} \qquad \text{(A15)}$$

At SS $C^{SS}_{rad} = \frac{\frac{K_1}{V}C^{\circ}_{dye}C^{SS}_{Ozone}}{\frac{Q}{V}+\frac{K_3}{V}C^{\circ}_{dye}}$ (A16)

$$\frac{dC_{dye}}{dt} = \frac{Q}{V}\left(C^{\circ}_{dye} - C_{dye}\right) - \frac{K_2}{V}C_{dye}C_{rad} \qquad \text{(A17)}$$

At SS $C^{SS}_{dye} = \frac{-\frac{Q}{V}C^{\circ}_{dye}}{\frac{Q}{V}+\frac{K_2}{V}C_{rad}}$ (A18)

$$C^{SS}_{dye} = \frac{QC^{\circ}_{dye}}{Q + \frac{K_2K_1C^{\circ}_{dye}C^{SS}_{Ozone}}{Q+K_3C^{\circ}_{dye}}}$$

$$C^{SS}_{dye} = \frac{QC^{\circ}_{dye}}{Q+(\frac{K_2K_1C^{\circ}_{dye}}{Q+K_3C^{\circ}_{dye}})(\frac{K_{La}C^{*}_{ozone}}{K_{La}+\frac{Q}{V}+K_1\frac{C^{\circ}_{dye}}{V}})} \textbf{(A19)}$$

**Nomenclature**

| | |
|---|---|
| AOP | advanced oxidation process |
| Bé | Bohme |
| $C_{dye}$ | the concentration of dye in the liquid |
| $C_{dye}^{\circ}$ | the concentration of dye in the feed stream |
| $C_{dye}^{ss}$ | the dye concentration in steady-state |
| COD | chemical oxygen demand |
| $C_{ozone}$ | the concentration of ozone in the liquid |
| $C_{ozone}^{*}$ | the equilibrium concentration of ozone in the liquid |
| $C_{ozone}^{ss}$ | the ozone concentration in steady-state |
| $C_{radical}$ | the concentration of dye decolouration |
| CSTR | continually stirred reactor |
| DDye | decoloured dye |
| $K_{La}$ | the mass transfer coefficient for ozone dissolution |
| nm | nanometre |
| Q | the volumetric flow-rate of the liquid |
| $R_{dec}$ | the rate of dye decolouration |
| $R_{dye}$ | the rate of consumption (decolouration) of the dye |
| $R_{ozone}$ | the rate of ozone formation |
| $R_{radical}$ | the rate of radical formation |

| | |
|---|---|
| $R_{term}$ | the rate of radical termination |
| SS | steady-state |
| t | time |
| USS | unsteady-state |
| UV/Vis | ultra violet/visible |
| V | the volume of the reactor |
| $\lambda_{max}$ | maximum wavelength |

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# 6 ChapterSix:CONCLUDING REMARKS

## 6.1 Introduction

Advanced oxidizing methods (AOPs) with ozone have been particularly successful in decolourising azo dye effluent. The aim of this thesis was to measure experimentally, the behaviour and performance of the de-ozonation in two types of reactors i.e. semi-batch (SBR) and continuous stirred tank reactor (CSTR). It also aimed to develop a kinetic model which identifies the rate-controlling processes in the system.

## 6.2 Wastewater in textile industry

This research is a contribution to the understanding of advanced oxidation processes (AOPs) for textile wastewater treatment. Wastewater decolouration is one of the major problems facing industries discharging wastewaters containing a wide variety of dyes. Ozonation as an advanced oxidation process (AOPs) represents an especially efficient treatment for effluent decolourization. In this report, we have shown AOPs – specifically ozone – can garner appropriate and positive results for wastewater treatment.

## 6.3 Wastewater treatment of reactive dye in a semi-batch reactor

The simplest mechanism for dye effluent decolouration is a semi-batch reactor. Ozonation of wastewater containing several textile reactive dyestuffs in a semi-batch reactor was studied. Ozonation at an alkaline pH of reactive dye hydrolysates was observed to be effective in partially oxidizing and completely decolouring textile dyes at relatively high concentrations.

Stoichiometry shows many dye molecules are expended per ozone molecule consumed. This suggests a radical chain reaction. There was a difference between the results of experiments where the solution was pre-ozonated and those where it was not. The former gave more consistent results and showed slightly higher initial rates.

Different dye concentrations had different rates of decolouration. This suggests rates are not totally mass-transfer controlled.

The rate of ozone dissolution is relatively slow but still faster than the reaction rate. This suggests that in doing the modelling, both phenomena may need to be taken into account.

Mass transfer rate could be modelled using a standard mass-transfer model.

It was found with faster stir speeds, results proved to be independent of stirrer speed. Thus, one can regard the vessel as well mixed.

Different ozone concentrations in the gas phase gave rise to different rates of decolouration. However, because of the apparatus used to achieve higher concentration, lower gas flow rates were used. The effects were, however, quite small

The latter part of each decolouration experiment can be explained by first order kinetics in the remaining dye concentration.

The result was – the higher the initial dye concentration; the lower the first order rate. Again, this is a very surprising result needing to be explained by the model.

## 6.4 Ozonation of textile reactive dye in CSTR

The major benefit of using CSTR over a semi-batch reactor is that one can explore different areas of the reaction space.

A range of steady states as a function of residence time enabled the researcher to explore short and long residence times.

When the progression to the steady state was modelled, the rate of approach showed a first-order dependence not affected by the flow rate.

Rate as a function of initial dye concentration showed a maximum at an intermediate value.

Rate as a function of flow showed an increase with a decrease in concentration at high flow rates and the reverse effect at low flow rates.

## 6.5 Simple kinetic modelling

A kinetic model for reaction rate was developed to simulate the dye decolourisation of Reactive Red 198 using Ozone. The model was based on a chain reaction mechanism and contained three unknown constants – a rate of radical formation, propagation rate and termination rate. Concentration time results obtained from the model were regressed against experimentally obtained results to estimate kinetic constants that minimized the sum of squared errors. The close correlation between the predicted and the experimental results seems to establish the reliability of the model.

In order to validate the kinetic model, it was applied to predict the experimental results from the CSTR. A good fit was shown, giving further evidence for the validity of the assumptions leading to the model.

This model can now be used as a basis for predicting of the behaviour of decolouration units in the industry. In particular, it can be used for designing such units to ensure adequate decolouration of textile industry wastewater streams.

## 6.6 Future work and recommendations

Removal of colour is just one step in the treatment of textile industry wastewater, If these methods are to be widely used, they may need to be combined with other physical , chemical and biological methods. This will ensure the purity of decoloured wastewater to make it safe for re-use and/or disposal. This work still needs to be done and could form the basis for future work in this area.