A Comparative study to analyse efficacy of O_3, O_3/UV, O_3/UV/PS for the degradation of reactive dyes in wastewater

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Mr. Sandip Sharma (10EXTPHDE47)

Institute of Technology

Nirma University

Ahmedabad-382481

Gujarat, India

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Certificate

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This is to certify that the thesis entitled **A Comparative study to analyse efficacy of O_3, O_3/UV, O_3/UV/PS for the degradation of reactive dyes in wastewater** has been prepared by **Mr. Sandip P. Sharma** under my supervision and guidance. The thesis is his / her own original work completed after careful research and investigation. The work of the thesis is of the standard expected of a candidate for **Ph.D. Programme in Chemical Engineering** and I recommend that it be sent for evaluation.

Date: 06/4/2018

Signature of the Guide

Forwarded Through:

(i) Dr. J. P. Ruparelia
Head of the Department

(ii)Dr.Alka Mahajan
Dean Faculty of Technology

(iii) Dean Faculty of Doctoral Studies and Research

To:
Executive Registrar
Nirma University

Abstract

The aim of present work was to investigate the performance assessment of reactor configurations for mineralization of synthetic wastewater by ozonation and ozone based Advanced Oxidation Processes (AOPs), i.e., O_3, O_3/UV, O_3/UV/PS. Preliminary studies were carried out in Bubble column reactor with RB5 dye and efforts have been made to determine effects of various operating parameters such as, ozone flowrate, pH, UV intensity and TOC: PS ratio on selected processes i.e. O_3, O_3/UV and O_3/UV/PS at constant parameters such as, initial concentration of RB5 at 500 mg/L, 12 pH, 60 LPH flow of O_3, UV intensity 66 W (if applicable) and TOC:PS ratio 1:40 (if applicable). It was observed that O_3/UV/PS is more efficient in removal of TOC. Further, experiments were conducted in the bubble column with recirculation and in Venturi reactor, the result exhibited better performance of Venturi reactor in terms of %TOC removal. Further, the design of experiments was planned with parameters such as types of dye, water recirculation flow, pH, ozone flow, UV intensity, TOC:PS ratio and initial dye concentration, for both the reactor configuration. The study revealed that in Bubble column with recirculation reactor, water recirculation had a significant effect on overall treatment performance, i.e. %TOC removal, whereas, for Venturi reactor dye had a significant effect on overall treatment performance. In design of experiments excluding dye as parameter and remaining set of parameters as it is, with three different dyes, i.e., RB5, RY145 and RR 120 for both the reactor configuration, confirmed superior performance of Venturi reactor. The better performance of Venturi reactor may be attributed to proper contact of ozone, persulfate, and pollutant. Based on design of experiments best operating parameters were chosen to be 1.86 g hr^{-1} ozone flowrate, 12 pH, 66W UV intensity and 1:40 TOC:PS ratio. It was also investigated that %TOC removal of synthetic dye solution of selected reactive dyes follows pseudo first order kinetics with respect to the dye. Compared to Bubble column with recirculation, degradation rate was higher in Bubble column and Venturi reactor. In addition, kinetic studies were conducted for O_3/UV/PS process in three different reactor configurations. The kinetic rate constants obtained were, 0.0122 min^{-1}, 0.0115 min^{-1} and 0.0205 min^{-1} for Bubble column, Bubble column with recirculation and Venturi, respectively. Thus, O_3/UV/PS was found to be a most efficient process with Venturi reactor amongst the above-mentioned processes. Further, studies were carried out with the optimized parameters for O_3/UV/PS in Venturi reactor for an individual dye to identify some important parameters such as kinetic rate constant, EE/O and TOC/OCC. Studies revealed TOC removal 86.34%, 82.14% and 59.47% for RB5, RR120, and RY145 respectively. In addition, the result of EE/O which is used to analyze the effectiveness of selected AOPs on the basis of electrical energy consumption, was 125.35, 144.88 and 276.40 for RB5, RR120, and RY145 respectively, reflects higher energy consumption per order reaction for RY145. Similarly, TOC/OCC results were 0.053, 0.043 and 0.039 for RB5, RR120, and RY145 respectively, reflects recalcitrant nature of RY145. Thus, the research concluded that O_3/UV/PS process provides efficient removal of TOC. However, its performance depends on reactor configuration. Venturi reactor is more efficient than bubble column reactor with recirculation.

Key words: Ozonation, Reactive dyes, Reactor comparison, Persulfate

Declaration

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I, **Mr. Sandip P. Sharma**, registered as Research Scholar, bearing Registration No. **10EXTPHDE47** for Doctoral Programme under the **Faculty of Technology** of Nirma University do hereby declare that I have completed the course work, pre-synopsis seminar and my research work as prescribed under R. Ph.D. 3.5.

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(Dr. J P Ruparelia)

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Sandip P. Sharma

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Nomenclature

List of Abbreviations

AOPs	Advanced oxidation processes
BOD	Biological oxygen demand
CAGR	Compound Annual Growth Rate
COD	Chemical oxygen demand
Dia	Diameter
DOC	Dissolved organic carbon
DOE	Design of Experiment
EE/O	Electrical Energy per Order
FICCI	Federation of Indian Commerce and Industry
h/d	Height to diameter ratio
KI	Potassium iodide
KWh	Kilo watt hour
LPH	Litre per hour
nm	Nano meter
NPOC	Non-purgable organic carbon
O_3	Ozonation
OCC	Oxygen-equivalent chemical-oxidation capacity
pH	Potential of hydrogen
ppm	Parts per million
PS	Persulfate
RB5	Reactive Black 5
RR120	Reactive Red120
RY145	Reactive Yellow 145
TOC	Total Organic Compound
UV	Ultraviolet
V	Volts
W	Watt

1 Introduction

Rapid industrialization and increased population is one of the major issue related to environmental degradation worldwide (Pokhrel, et al., 2004; Allegre, et al., 2006; Anwar Hossain, et al., 2010). Among the industrial effluents, textile effluents are considered to be very problematic to treat not only due to its volume but also due to its varying composition (Anwar Hossain, et al., 2010; Pereira, et al., 2012). The government has made strict legislation regarding treatment of industrial effluent, and therefore it is mandatory to treat textile effluents before its final disposal. So, as to overcome this issue several techniques are being employed (Pereira, et al., 2012; Arslan-Alaton, et al., 2012).

1.1. Background and Motivation

The textile industry in India including both domestic and export market is expected to grow at 9% compound annual growth rate (CAGR) with estimation to achieve around USD 210 billion by 2012 (Sardana, 2013). Textile and dyeing industries are among one of the major consumers of water as well as the generator of wastewater (Wang, et al., 2011). There are various kinds of dyes which are being used in textile and dyeing industries like, reactive dyes, direct dyes, naphthol dyes, indigo dyes, dispersed dyes, basic dyes and direct dyes (Ghaly, et al., 2014).

However, the majority of synthetic dyes which are being used in industries are azo derivatives (Forgacs, et al., 2004). Ghaly et al., 2014, reported that reactive dyes are among most commonly used dyes in the textile sector and its worldwide consumption was 178,000 tonnes in 2004 which was approximately double to that of consumption in 1988. Amount of dye in wastewater is highly dependent on the class of dye used (Pereira, et al., 2012). Dyes, chemical compounds, and additives are required during various processes of dyeing and finishing (De Souza, et al., 2010). Azo dyes are most widely used among different types of dyes (Ramdan, et al., 2014). It is further stated that presence of azo dyes in wastewater has an adverse effect on aquatic life, mutagenic and carcinogenic in nature. Azo dyes are mostly recalcitrant in nature and cannot be treated by conventional treatment methods (Weng, et al., 2013). Reactive dyes are typically azo-based chromophores combined with different reactive groups (Bilinska, et al., 2015; Bouraie, et al., 2016). Bilinska, et al., 2015, further mentioned that Reactive Black 5 (RB5) is widely used in dyeing processes. Reactive dyes are extremely soluble in water and have reactive groups which can form covalent bonds between chromophoric groups of dyes and fiber. RB5 is the most commonly used to dye cotton and other cellulosic fibers, wool and nylon (Bouraie, et al., 2016). Losses of dye in wastewater can vary from 2% for basic dyes to around 50% for reactive dyes (Pereira, et al., 2012). Textile effluents are very tricky to treat due to its varying composition (De Souza, et al., 2010). Due to various dyes and intermediates, textile effluents are highly colored, toxic recalcitrant organic compounds and also it shows high resistance towards treatment by conventional treatment methods (Gokcen, et al., 2006).

Therefore, advanced oxidation processes are emerged as a proficient alternative to treat colored effluents of dyeing and textile industries. It has been well reported in the literature that among AOPs, ozonation (O_3) is emerging as one of the potential technique for treating wastewater containing dyes. Ozonation is a powerful technique which effectively removes color from textile and dyeing effluents due to the fact that oxidation potential of ozone is high (2.07V) and it can react with a wide range of organic compounds through direct or indirect reactions (Oguz, et al., 2005; Gokcen, et al., 2006).

The foremost aim of present study is to degrade and treat synthetic wastewater containing three different dyes namely, Reactive Black 5 (RB5), Reactive Red 120 (RR120) and Reactive Yellow 145 (RY145) as model pollutants. Literature reveals that chromophores group present in dye are responsible for imparting color (Sarayu, et al., 2007).

Ozone molecule is very selective in nature and it rapidly attacks unsaturated bonds of chromophores resulting in decolorization (Soares, et al., 2006; Sarayu, et al., 2007). However, it is worth mentioning that ozonation alone is not capable of 100% degradation of pollutants in wastewater (Oguz, et al., 2005; Shu, 2006; Pirgalıoglu, et al., 2009). This can be due to the fact that during ozonation of dye molecule some by-products are generated such as organic compounds, aldehydes and ketones which cannot be further oxidized with ozone molecule because of high selectivity of ozone molecules (Sundrarajan, et al., 2007; Pirgalıoglu, et al., 2009). Furthermore, low solubility and low stability of ozone molecule may also contribute resistance to by-products for further oxidation (Pirgalıoglu, et al., 2009).

Thus, to overcome above mentioned limitations, combination of O_3 with UV and combination of O_3 with UV and Persulfate has been employed to achieve better mineralization efficiency in the present work. It was reported in the literature that hydroxyl radical or secondary oxidants so produced due to dissociation of ozone molecules are more powerful oxidizing agent as compared to molecular ozone. Additionally, hydroxyl radical or secondary oxidants are non-selective in nature and they react rapidly with a wide range of organic pollutants and convert them or degrade them into carbon-di-oxide (CO_2) and water (H_2O) (Taseidifar, et al., 2015).

1.2. Scope of the work

The focus of present research work is on removal of recalcitrant organic pollutant (RB5) from wastewater without generation of by-products/sludge employing ozonation, O_3/UV, O_3/UV/Persulfate (PS) processes respectively. Although, it is in literature that for removal of RB5, various processes were adopted but they were not found effective for complete degradation of dye from wastewater and generation of sludge or secondary pollutants was major issue of concern. Moreover, it was observed from literature and work compiled by various researchers that ozonation process alone was not so effective in removal of dyes in terms of TOC removal. The modification was made by combining ozonation process with UV and persulfate(PS) process which further enhances process effectiveness and improves TOC removal. In addition, efforts were made to select most effective reactor configuration for selected treatment process through design of experiments. Finally, kinetic studies performed for selected treatment process and reactor configuration.

1.3. Objectives

Present work is focused on decolorization and degradation of synthetic wastewater containing RB5 as a model pollutant, by utilizing O_3, O_3/UV, O_3/UV/PS processes respectively. Reactor configuration and its effect on degradation efficacy of dye wastewater were also analyzed. The effectiveness of all three process is analyzed in terms of decolorization and TOC removal. Further Kinetics, OCC, and cost-effectiveness, EE/O has also been evaluated. Three different dyes namely RB5, RR120, and RY145 were compared for to analyze the effectiveness of process and reactor selected based present study. The objectives of the studies are:

1 To identify appropriate reactive dyes, AOPs and reactor configuration for comparative study.

The aim of conducting the current investigation is to analyze various AOPs based on literature review and to select most suitable process for degradation of dye wastewater containing reactive dyes. Then the selected AOPs from literature which are analyzed during present study are O_3, O_3/UV and O_3/UV/PS. For comparing above chosen processes various assessment parameters were analyzed and examined such TOC removal, kinetics of process, the effectiveness of process under various reactor configuration and cost-effectiveness.

2. To study effect of various operating parameters on treatment of wastewater

To analyze most appropriate method study begins with the effect of operating parameters on all the selected process namely O_3, O_3/UV and O_3/UV/PS. For this effect of ozone concentration was varied from 30 to 60 LPH and its effect on degradation of wastewater containing RB5. Effect of pH was also determined by altering in the range of 4 to 12 pH. UV light intensity was varied from 11W to 66W and its effect on degradation was identified by conducting series of experimental study. Effect of Persulfate dosage (TOC:PS) was also a key parameter which needs to optimized to increase the effectiveness of the process.

3. Comparison of different configuration of reactor for ozonation and integrated ozonation process

   Bubble Column, Bubble Column with recirculation and Venturi reactors were compared for all three selected processes. The aim was to evaluate best reactor and process combination to maximize removal efficiency of dye from dye wastewater.

4. To investigate the kinetics of the degradation of reactive dyes.

   Further, under a selected process of O_3/UV/PS, reactor configurations were analyzed on the basis of the kinetics of degradation of RB5. This step will provide the best process among all three selected processes.

5. Identification of most appropriate method in terms of degradation efficiency.

   The last objective of present study was to analyze best selected reactor and process which is obtained from present research for varying concentration of dye for 500, 1000 and 1500 mgL^{-1} for RB5 and also for two different dyes namely- RR120 and RY145.

1.4. Organization of thesis

A thesis on **"A Comparative study to analyse efficacy of O_3, O_3/UV, O_3/UV/PS for the degradation of reactive dyes in wastewater"** is presented on number of chapters.

Chapter 1: Introduction

It emphasizes on the recent scenario of textile and dyeing industry worldwide in general and in India particular. It also includes adverse effects of wastewater from textile and dyes industries on the environment. It provides a general introduction to ozonation process and its limitations. The motivation for present work and general introduction of combined O_3/ UV and O_3/UV/PS has also been included in this chapter. Scope and objectives of present work are part of this chapter.

Chapter 2: Literature Review

It highlights recent scenario of water and wastewater worldwide. Further, classification of dyes and comparison of various treatment technologies for decolorization and mineralization of wastewater containing dyes are incorporated in this chapter. It also includes mechanism of O_3, O_3/UV and O_3/UV/PS processes. Summary of effect of various operating parameters such as, ozone flow rate, liquid flow rate, initial dye concentration, initial pH, intensity of UV light and Persulfate dosage were also discussed in this Chapter.

Chapter 3: Material and Method

This chapter of the thesis contains various materials, chemicals, and reagents which were utilized for conducting present study. The protocols used in the research and various characterization techniques used are also elaborated in this chapter. Finally, reactor setup and sequence of the experimental study are also discussed in this chapter.

Chapter 4: Results and Discussion

In this chapter the results obtained after all the experiments were discussed and compared with literature. This chapter discusses the effect of various operating parameters on removal efficiency of model pollutant (RB5) from synthetic wastewater for comparing all three processes. The performances of all three processes were analyzed in terms of %TOC removal, EE/O and OCC consumption, etc.

Chapter 5: Conclusion

This chapter provides final outcome of the study. Efficiency of ozone based AOPs and importance of effects of process parameters for degradation of reactive dyes are presented including scope for possible future work.

The thesis ends with references, includes literature referred for experimental, application and discussion part, while appendices, presents calculative part for experimental work as well as Design of Experiments (DOE) studies. List of publications related to Thesis are shown at the end of the report.

2 Literature Review

Literature survey serves as a backbone of any research work. It provides a wide glance about the present and past work carried out by various researchers and provide guidance to carry out investigation in a proper direction.

In recent past, stringent government rules and increased public concern has drawn tremendous attention for treatment of wastewater before its final disposal (Lackey, et al., 2006; Palit, 2010). Various physical, chemical, and biological methods are available for treatment of textile wastewater. However, these conventional methods of wastewater treatment are insufficient to treat textile effluent due to presence of strong color, high toxicity imparted by various chemicals such as surfactants, wetting agents, fixing agents, softeners, etc and also high content of organic compounds which are recalcitrant in nature (Arslan, et al., 1999; Arslan, et al., 2000; Hessel, et al., 2007). Therefore, the requirement of suitable and reliable treatment to degrade wastewater from textile industries need to be developed.

2.1. Water Availability and Use

Water is an essential element of life and it is needed for all aspects of life (Asiwal, et al., 2016). Amount of fresh water available for use is approximately 0.03% of earth’s available water resource (Allegre, et al., 2006). Arnell, et al., 1999, reported that in 1997 the United Nations represented a comprehensive review of “Freshwater Resources of World” (WMO, 1997). It was approximated that almost one-third of total world's population was facing modest or severe water stress and it was also anticipated that by 2025 almost two-thirds of the world population will be facing water stress due to increased population and improper usage of water (Arnell, 1999). In addition, by 2025, 5 billion people out of total population of 8 billion people will be living in countries experiencing water stress (Arnell, 1999). However, water stress is increasing globally due to increased population and industrialization which in turn decreases the fresh water available per person (Allegre, et al., 2006; Abu Amr, et al., 2013). According to literature, it is estimated that per capita annual fresh water availability will reduce to 1341 m^3 in 2025 and which will further reduce to 1140 m^3 in 2050 (Kaur, et al., 2012).

Water resources represents as one of most essential assets of any country (Kumar, et al., 2005). India consists of 2.45% of the total available land area of the world and 4% of total world's water resources; however, it contributes to 16% of the world population (Kaur, et al., 2012). Chawan 2005, reported similar findings to that of Kaur, et al., 2012, and stated that India has 5% of total world's available water resource to support 15% of world's total population. It was further reported that nearly 900 million people suffers a severe scarcity of water in India. Kaur, et al., 2012, further reported that with population in India is increasing with growth rate of 1.9% and the population is expected to cross 1.5 billion by 2050. Owing to the fact of increasing population and overall development in all sectors of a country the per capita freshwater availability has been reducing from 5177 m^3 in 1951 to 1869 m^3 in 2001 and 1588 m^3 in 2010. In India, available water resource for consumption consists of 690 km^3 of surface water and 396 km^3 of groundwater (Kumar, et al., 2005).

According to the Federation of Indian Chambers of Commerce and Industry (FICCI) survey on "Water Risk in Indian Industry Survey", water usage has tremendously increased among various sectors of industries in India. It was further reported in the survey report that requirement of water in the industrial sector is raised by 8.5 and 10.1 percent of total freshwater in 2025 and 2050 respectively. However, above said consumption represents 4% increment from that of water requirement in 2011 and that of 6% increment from freshwater requirement in 2010 respectively. Zou, et al., 2008, has reported that water has become a limited resource in most of the countries and owing to this fact need to treat wastewater for reuse has become a foremost priority.

2.2. Wastewater and Types of Pollutants

Wastewater may be defined as water containing waterborne solids and liquids. It is a combination of liquid or water-carried waste discharged from various activities carried out at domestic, industrial, institution or commercial, along with groundwater, surface water and stormwater (Metcalf & Eddy, 2004).

The principal constituents of concern in wastewater treatment are suspended solids, biodegradable organics, pathogens, nutrients, organic and inorganic pollutants, refractory organics, heavy metals and dissolved inorganic such as calcium, sodium, sulfate, etc (Metcalf & Eddy, 2004).

Increased industrialization has led to increased usage of freshwater along with generation of a massive amount of wastewater (Shi, 2009). Shi, 2009, further reported that industrial wastewater varies in composition and depends upon sector from which it is generated. It is reported in the literature that Iron and steel, Textiles, leather, Pulp and paper¸ Petrochemicals and Refineries, Chemicals, Non-ferrous metals, Microelectronics, and Mining are various sectors which generates wastewater with varying composition (Liu, et al., 2015). Types of pollutant generated from various industrial sector are as shown in Table 2.1. Among all above sector of industries, textile industries are considered to be a significant consumer of freshwater as well as producer of wastewater (Turgay, et al., 2011).

Table 2.1 Types of pollutants generated by various industrial sectors (Shi, 2009)

Industrial Sector	Pollutants
Iron and steel	BOD, COD, oil, metals, acids, phenols, and Cyanide
Textiles and leather	BOD, solids, sulfates and chromium
Pulp and paper	BOD, COD, solids, Chlorinated organic Compounds
Petrochemicals and Refineries	BOD, COD, mineral oils, phenols, and chromium
Chemicals	COD, organic chemicals, heavy metals, SS, and Cyanide
Non-ferrous metals	Fluorine and SS
Microelectronics	COD and organic chemicals
Mining	SS, metals, acids, and salts

The leather industry is considered to be among one of the major sources of water pollution due to the intricacy of effluents discharged (Preethi, et al., 2009). Typical characteristics of effluents from leather industry mainly consist of high organic and inorganic loadings, strong color, dissolved and suspended solids, salinity with specific pollutant such as chromium, etc. and chemicals such as sodium sulphite, basic chromium sulfate, wetting agents, bactericides, soda ash, CaO, sodium sulphide, ammonium chloride, NaCl, H_2SO_4, formic acid, enzymes, vegetable tannins, syntans, resins, poly urethane, dyes, fats and proteins, pigments, binders, waxes, lacquers, formaldehyde and variety of solvents and auxiliaries which is treated by conventional physiochemical techniques leading to generation of solid sludge as secondary pollutants (Preethi, et al., 2009; Vijayalakshmi, et al., 2011).

Pharmaceuticals compounds are noticed to enter freshwater due to improper disposal or leakage in landfill, further it was noteworthy to mention that expired medicines are directly discarded into sewage or solid waste disposal sites which create potential threat to freshwater as pharmaceutically active compounds can easily enter freshwater as well as wastewater treatment facility (Gao, et al., 2012). It is further mentioned that the adverse effect of pharmaceutically active compounds includes abnormal physiological effects, reproductive impairment, increasing cancer incidences, development of antibiotic-resistant bacteria and potential enhanced toxicity of chemical mixtures (Gao, et al., 2012).

Micro-Electronics and electronic manufacturing industry consume variety of organic solvents for carrying out various processes such as photolithography, stripping, etching, and cleaning, etc (Wang, et al., 2014). It is further reported that tetramethylammonium hydroxide, TMAH, $(CH_3)_4NOH$) is usually one of the numerous ingredients in commercial etching/stripping mixtures or alkali washing liquid, further TMAH is a high alkaline, neuronal toxic, and chemically stable compound leading to increased complexity in treatment of wastewater.

Dye and textile industries are considered to be a significant producer of colored wastewater (Colindres, et al., 2010). It is reported in the literature that huge amount of dyes are produced annually and are being utilized in various sectors including textile, cosmetic, paper, leather, pharmaceutical and food industries (Aboulhassan, et al., 2005; Khandegar, et al., 2013). Amongst various sectors of industries utilizing dyes, the textile industry is reported to consume almost two-thirds of annually produced dyes (Aboulhassan, et al., 2005). It is reported that above 700000 tons of approximately 10000 types of dyes and pigments are produced per annum worldwide, out of which 20% of produced dyes are discharged into effluent during processing (Azbar, et al., 2004).

Textile industry discharges considerable quantity of effluents which are highly colored, toxic and recalcitrant in nature (Ledakowicz, et al., 2001). However, main characteristics of textile wastewater are the high concentration of organic compounds, heavy metals, high COD, high pH and sturdy color (Wijannarong, et al., 2013). According to literature almost 10 - 12% of synthetic dye is lost during the manufacturing process (Arslan, et al., 2000; Pearce, et al., 2003). It is estimated that global annual market of dye is more than 7 x 10^5 tons per year (Pearce, et al., 2003) (Xu, et al., 2012) (Khandegar, et al., 2013).

However, textile industry can further be classified into three major categories: cellulose fibers which consists cotton, rayon, linen, ramie, hemp and lyocell, protein fibers which includes wool, angora, mohair, cashmere and silk and synthetic fibers comprising of polyester, nylon, spandex, acetate, acrylic, ingeo and polypropylene (Ghaly, et al., 2014). Most common categories of dyes are Reactive dyes, direct dyes, naphthol dyes, indigo dyes, acid dyes, lanaset dyes, dispersed dyes, and basic dyes (Bouraie, et al., 2016; Dojcinovic, et al., 2012).

Reactive dyes are the most commonly used in textile industries (Bilinska, et al., 2015). The world use of reactive dyes increased from 60,000 tonnes in 1988 to 178,000 tonnes in 2004 (Ghaly, et al., 2014). Reactive dyes are the most frequently used in the textile industry in comparison to other, due to their exceptionally good properties – good cloth application, bright color, excellent colorfastness and ease of application. Reactive dyes are typically azo-based chromophores combined with different reactive groups (Bouraie, et al., 2016; Bilinska, et al., 2015). Bilinska, et al., 2015, further mentioned that RB5 is the most commonly used in dyeing processes among them. Reactive dyes are extremely soluble in water and have reactive groups which can form covalent bonds between chromophoric groups of dyes and fiber. RB5 is the most commonly used to dye cotton and other cellulosic fibers, wool, and nylon (Bouraie, et al., 2016). It is further mentioned that RB5 forms a covalent bond with the fiber and contains chromophoric groups such as azo, anthraquinone, triarylmethane, phthalocyanine, formazan, oxazine, etc. Various techniques used to treat RB5 are discussed in Table 2.2.

Textile industry includes various toxic chemicals such as complexing, sizing, wetting, softening, anti-fetting and finishing agent and additives such as biocides carriers, halogenated benzenes, phenols, pesticides, dyes, etc (Arslan, et al., 2000). In context, there is huge generation of wastewater from textile industry (Soares, et al., 2006). It is reported in literature, characteristics of textile wastewater generally vary in the range of, chemical oxygen demand (150 to 12,000 mg/L), total suspended solids (2900 and 3100 mg/L), total Kjeldahl nitrogen (70 to 80 mg/L), and BOD (80 to 6000 mg/L) leading to a biodegradability (BOD/COD ratio) of around 0.25, showing that it contains large amounts of non-biodegradable organic matter (Tisa, et al., 2014).

Table 2.2 Comparison of various treatment methods for RB5

Sr. No.	Treatment Method	Reactor Configuration/Specification	Operating Conditions	Results and Comment	Reference
1	Ozonation	Bubble column Reactor: 1.5L capacity (78cm height, 6cm diameter)	Time:1hr; O_3 Conc^n :3.51 g/h; Dye Conc^n: 75 mg L^{-1}; pH:12	Pseudo-first-order rate constants (k) 0.121 min^{-1}; Color 4.0 min^{-1}; Color Reduction (100%); COD Removal (61.9%)	(Arslan, et al., 2000a)
2	Ozonation	Bubble column Reactor 0.5L, 4L & 6L capacity	Time: 30 min; gas flowrate of 0.75 L/min	Decolorization of the azo dye by ozone is a pseudo-first-order reaction with respect to dye. COD removal was 27-87% and biodegradability of the wastewater increases 11-66 times	(Wu, et al., 2001)
3	Hydrogen peroxide and UV radiation (H_2O_2/UV)	Batch reactor with stirrer 3.8 L	UV intensity:150 W	90% decolorization of RB5 corresponded to a 30% removal in Dissolved Organic Carbon	(El-Dein, et al., 2003)
4	Ozonation	Bubble column Reactor (volume 1.2 L)	Time: 6 h; Dye concentration:2 g L^{-1} ; ozone conc^n: 20.5 mgL^{-1}	Ozonation as a partial step of a combined treatment concept is a potential technique for decolorization and biodegradability. COD removal was 55% and TOC removal was 75%	(Wang, et al., 2003)
5	Fenton's oxidation process	N.A	2 min rapid mixing followed by 20 min slow mixing; Dye Concentration:100 and 200 mg l^{-1} of	Optimum pH, temperature were observed as 3.0, 40 ^{0}C for 100 mgl^{-1} of RB5 using 100 mgL^{-1} of $FeSO_4$ and 400 mgL^{-1} of H_2O_2;	(Meric, et al., 2004)

				Decolorization was 99% and COD removal was 71%	
6	UV/TiO$_2$, wet-air oxidation (WAO), electro-Fenton (EF), UV/electro-Fenton (UV/EF)	300 mL glass reactor.	Titanium dioxide used was anatase; light source used was the mercury vapour UV lamp; initial conc^n (20–100 mg L^{-1}) felt (3 cm×5 cm) was used as working electrode; 200 and 300 ^oC; Time: 90 min	Among all applied AOPs processes wet-air oxidation process was found to be most effective method for decolorization and mineralization of RB5. %TOC reduction was observed 71, 77, 20, 29 for UV/TiO$_2$, WAO, EF and UV/EF process respectively	(Kusvuran, et al., 2005)
7	Ozonation with Water Recirculation	Semi batch reactor (500 mL)	Initial dye concentration: 50-150 mg/L; ozone concentration : 24-31 mg/L; O$_3$ Flow: 0.5 L min^{-1}	During this study it was observed that, complete color elimination was achieved after 2 minutes of ozonation for all dyes	(Poznyak, et al., 2007)
8	Laccase and Ultrasound Treatment	Stirred batch reactor	Power uptake 84 and 124W; Temperature: 40°C; pH: 4.5; acetate buffer: 50 mM, Laccase activity: 5×10^{-9} kat/ml	Laccase enzyme treatment and ultrasonication are two oxidizing processes which are capable of degrading azo dyes. But laccase treatment not able to degrade the azo dyes to the same extent	(Tauber, et al., 2005)
9	Photo assisted fenton degradation with iron oxide catalyst	fluidized-bed reactor	Irradiation source: 15 W UVA lamp; Total solution volume: 1200 mL; Initial dye conc^n: 0.055 mM; pH:7; H$_2$O$_2$	About 70% decolorization was measured and 45% of the total organic carbon was eliminated	(Hsueh, et al., 2006)

			Conc^n: 14.7-117.6 mM H_2O_2		
10	Ozonation	Counter current Bubble Column; Hight:3.0 m; inner diameter of 14.2 cm; effective volume V_L of 45 L	Ozone capacity:60 g/h; gas flow rate: 0.9-3.4 L/min; liquid flow rate was 2.0- 6.0 L/min	Decolorization was almost 100% and TOC removal was about 85%	(Hsing, et al., 2006)
11	Fenton and photo-Fenton oxidation	Cylindrical glass reactor of 800 mL capacity	Low-pressure mercury vapor lamp; Initial volume: 500 mL	Up to 98% decolorisation and 46% TOC removal was observed	(Lucas, et al., 2006)
12	Photocatalytic Degradation using ($SrTiO_3/CeO_2$)	Cylindrical Pyrex glass reactor(diameter 12 cm; height 15 cm; total capacity 1000 mL)	Initial dye concentration: 100 mg L^{-1}; Catalyst Conc^n: 0.01-1.5 gL^{-1}; gases at a flow rate of 0.2 m^3h^{-1}	Decolorisation was observed to be 99% and TOC removal was 50%	(Song, et al., 2007b)
13	Ozone assisted electrocoagulation	Electrode dimension: 40mm×50mm×1mm	Ozone flow: 50mg min^{-1}, initial pH 5.5, initial dye conc^n 100 mg/L, current density 10 mA/cm^2, salt concentration 5000 mg/L, temperature 20 ◦C, ozone flow rate 20 mL/min and distance between the electrodes 1 cm.	Color removal efficiency of RB5 was over 90%; COD was reduced by more than 60%; Energy consumption was 33 kWh/kg of COD removed	(Song , et al., 2007a)
14	Biodecolorization by Rhodopseudomonas palustris W1	117-ml glass serum vials	Initial dye conc^n: 200-3200 mgL^{-1}; 50 mgL^{-1} of R. palustris W1 cells; 20 h of cultivation at 30°C; 1 g	Decolorisation was observed as 79%	(Wang, et al., 2008)

			L^{-1} of $NaHCO_3$; Reaction time: 25 h		
15	Novel bacterial isolates (Paenibacilluslautus SK21 and Bacillus subtilis SK48 Hydrogen Peroxide and Horse Radish Peroxide	N.A	500 gm horse radish; decolourized supernatant, hydrogen peroxide and horse radish peroxidase in the ratio of 8:1:1; kept in sunlight for 24 hours	Under standardized conditions of pH 7, 37^{o}C / static condition with the dye concentration of 100 mg l-1. Reactive Black 5 was decolourized to 24 % in 72 hours and Decolorisation was 91%.	(Kumar, et al., 2014)
16	Non-catalytic and catalytic ozonation processes	1 L semi-batch reactor	Initial dye conc^{n}: 100 mg/L; Catalyst dosage: 0.1 g/L; ozone dosage: 115 mg/min L of liquid; pH:3-10	TOC removal above 90% was observed in the catalytic ozonation with CuS for each of the dyes separately at pH 10.	(Pirgalıoglu, et al., 2009)
17	Fenton and photo-Fenton	N.A	Initial dye conc^{n}:100 mgL^{-1}; 0.008 mol L^{-1} $FeSO_4 \cdot 7H_2O$ and 1.47 mol L^{-1} H_2O_2; UVA Light:20 W	TOC removal was from 16% to 36% for Fenton and photo Fenton process) dye removal was about 100%	(Silva, et al., 2009)
18	Ozonation	Semi-batch bubble column reactor	Ozone concentration 2 mg/L; Ozone flow of 0.3 L min^{-1}; initial conc^{n} of dye was 50 mg/L; Time:120 min	Decolorization was 99%	(Colindres, et al., 2010)
19	Combined electro coagulation–granular activated carbon adsorption–microwave regeneration process	Coconut-based granular activated carbon; 4.76 mm diameter, 10mm length	Initial dye conc^{n}: 100 mgL^{-1}; Electrode dimension: 4cm×7 cm, Gap between electrode: 1 cm; irradiation time of 30 s at 800 W	GAC only removed 36% COD; overall 61% of COD was removed; energy consumptions 0.034kWhg^{-1}	(Chang, et al., 2010)

20	Multi-stage Ozonation and Biological Treatment	Volume of 2 L equipped with a glass diffuser	Two litres of dye solution with the conc^n of 100 mgL^{-1}. Ozone dose: 0.3 to 7.2 mg O_3 mg dye^{-1}.	COD was removed approximately 79.5%.	(Fahmi, et al., 2010)
21	Sequential Anaerobic-Aerobic System	UASB reactor (2.5 L of effective volume with i.d. of 6 cm and a height of 100 cm CSAR reactor (Aeration tank: working volume: 9 L) and (Settling compartment working volume: 1.4 L).	Initial dye concentration: 150 mg/L; OLR= 2.4-22.5 kg; COD/m^3.day HRT= 3.2-30.1 h	Color removal was 99.8 and COD removal was 86.3%; Methane production efficiency was about 75%	(Kartas , et al., 2010)
22	Ozonation	1000 cm^3 bubble column reactor	Initial Volume of Dye wastewater: 500 cm^3.	Dye degradation was 69% decolorization was up to 99%; first order rate constants were 0.0013–0.0062 s^{-1} for the initial dye concentrations of 1.8211–0.3035.10^{-3} mol dm^{-3}	(Kusvuran, et al., 2010)
23	Fenton Process	250 ml beaker	Reaction Time: 120 min; Iron powder = 150 µm; Iron Dosage = 0.3 gr/150 mL; UV lamp with 40 W intensity; 150 ml of dye solution having initial concentration of 50 mg/L	53% dye removal was observed Color (90)	(Rahmani, et al., 2010)
24	Electrochemical treatment combined with UV light	Cathodes were constituted by titanium and anodes were made of titanium covered by platinum oxides; volume of	Dye Conc^n: 0.1 g L^{-1}; UV lamp: 6 W; surface area of each electrode was 486 cm^2	Decolourization kinetic constants values (k_d) were much greater than expected and a 95% of colour removal	(Riera-Torres, et al., 2010)

		the vessel was 1 L. The cell was able to treat up to 25 L h^{-1}.		can be reached in short exposition times and along with that UV irradiation showed a chloroform destruction up to a 75%	
25	Anaerobic/aerobic membrane bioreactor (MBR) and photochemical membrane reactor	An anaerobic sequential batch reactor (AnSBR) (V – 36 L) sequenced into, fill – 0.5 h, react – 21.5 h, settle – 0.5 h and decant – 0.5 h, respectively. For aerobic membrane bioreactor (AoMBR, V – 18 L).	In AnSBR, HRT, MLSS, and pH of the AnSBR were 48 h, 2,700mgl^{-1}, and 6.8–7.2, and in AoMBR were 24 h, 2100 mgL^{-1}, and 6.8–7.2, respectively.	It was observed that %COD removal was 78.2, 97.5, 85.2, 84.5, 85–90 for AnSBR, AoMBR, AnMBR suspended, AnMBR immobilized and MPR respectively.	(You, et al., 2010)
26	Photocatalytic degradation TiO_2 impregnated ZSM-5	Annular cylindrical glass tube of 500 ml; 25 × 8 cm (height × inside diameter)	UV-125 W low pressure mercury lamp was used as radiation source; 250 ml of dye solution	The optimum formulation of supported catalyst was found to be (TiO_2: ZSM-5 = 0·15:1) which gave the highest efficiency with 98% degradation of 50 mg/L RB-5 solution in 90 min. It was observed that reduction in COD was 78 – 89% along with the color removal.	(Mahadwad, et al., 2011)
27	Newly isolated Brevibacterium sp. strain VN-15	N.A.	Initial Conc^{n}: 100 mgL^{-1}; 1g L^{-1} pyruvate; 3 gL^{-1} glucose; yeast extract 1g L^{-1};	TOC reduction was observed about 83%.	(Franciscon, et al., 2012)
28	Photocatalytic process using ZnO and UV radiation	250 mL thermostated cylindrical Pyrex reactor	Initial dye conc^{n}: 0.082 g L^{-1}; Irradiation using 250 w mercury vapor	TOC removals in the range of 70–80% were achieved after 240 min.; order of efficiency in the mineralization process	(Almeida Guerra, et al., 2012)

			lamp; Reaction time: 240 min;	was as follows: Fe/ZnO> ZnO>Co/ZnO.	
29	Combined biological-photocatalytic process	Batch system (pyrex vessel) with a total capacity of 1 L	Total volume of dye sample: 800 mL; mercury lamp 150 w; 0.2 g/L of TiO_2 was; Initial dye conc^n: 50 mg/L	Complete decolorization of the dye with 200 mg/L in less than 24h. At higher concentration it was observed that decolorization and COD removal was 75% and 60% respectively.	(Jafari, et al., 2012)
30	Ionic Liquid Grafted-Magnetic Nanoparticles	N.A.	50 mL of 100 mg/L of solution; Nanosorbent: 25-150 mg; Reaction time: 60 min; pH: 2-12	Under optimal conditions 98.5% of RB5 after a single extraction was removed.	(Poursaberi, et al., 2013)
31	Electrochemical-oxidation Ti/RuO_2-SnO_2-Sb_2O_5	Titanium electrode Ti/RuO_2-SnO_2-Sb_2O_5) was used as anode and stain less steel (304) was used as cathode	Initial dye conc^n: 100 mg/L solution; Volume of wastewater: 500 mL constant current density (50 mA/cm^2); pH: 2-12; Reaction time: 60 min	It was observed that % decolorization, % COD and % TOC removal was 99.40% 55% and 37% respectively.	(Ruparelia, et al., 2012)
32	Fenton oxidation	Glass beaker of 2 L	Initial dye conc^n: 50 to 500 mg/L Fenton dosage in the range of 50 to 400 mg/L H_2O_2, 10 to 100 mg/L $FeSO_4$	Optimum conditions of 300 mg/L of H_2O_2, 50 mg/L of $FeSO_4$ and temperature and pH of 40°C and 3 for 250 mg/L of RB-5 at 10 min respectively was resulted in decolourisation of 97% and COD removal of 58.9%	(Bahmani, et al., 2013)
33	Chitosan Ion Exchangers	100mL glass flask	0.1 g of dry resin; 50mL of dye solution having a conc^n of 2×10$^-$	The resins showed high affinity for the adsorption of	(Elwakeel, et al., 2013)

			^{3} M; pH=3; Reaction volume: 100mL; Reaction time: 3 h	RB5 where uptake value was around 0.63mmol/gat 25^{0}C	
34	Funalia trogii 200800 on a fly ash-chitosan medium in a fluidized bed	Fluidized bed bio reactor (9 cm in diameter and 90 cm in the bed length) volume of reactor is 5.73 L, HRT:17.20 h.	500 mL of dye solution of 50 mg/L initial conc^{n}; Reaction time: 120 min; fly ash-chitosan beads: 0.5-10 g	The removal efficiency of RB5 was about 95 %.	(Lin, et al., 2013)
35	Double-Dielectric Barrier Discharge	Reaction tank was equipped with of two aluminium electrodes in centre.	Initial concentration: 100 mg/L, 10 mL solution; pH is 5.30	Decolorization efficiency followed the first order kinetics with a constant rate of 0.4008 min^{-1} and could reached 98.76%, while the removal rate of TOC was only 15.36%.	(Mei, et al., 2013)
36	Advanced Fenton process in conjunction with ultrasound	Glass beaker	Reaction volume: 1 L; pH: 2-5; ZVI dose: 0.1-1.0 g/L; H_2O_2 dosage from 5.15×10^{-3} M to 1.03×10^{-2}M; Applied power density: 80-120 w/L	The optimum conditions for the decolorization of RB5 were ZVI 1 g/L, initial pH 3.0, and H_2O_2 :1.03×10^{-2} mol/L with acoustic power of 120 W/L at 60 kHz. These conditions resulted in 99% decolorization.	(Weng, et al., 2013)
36	Electrochemical oxidation	Dimensionally stable anode Titanium plate 75mm X 65mm X 3mm	500 mL of the RB-5 having an initial conc^{n} : 100 mg/L; constant current density: 50 mA/cm^{2}; gap between electrode: 8 mm; Reaction time: 60 min	70% COD removal and 55% of TOC removal was observed.	(Soni, et al., 2013)

37	Fenton oxidation	batch lab scale Erlenmeyer flask 500 mL	150ml of Reactive Black 5 dye solution; Reaction time: 90 min;	At optimum condition more than 95% of COD removal percentage was observed	(Asghar, et al., 2014)
38	Adsorption using laccase-modified silica fume	100-mL Erlenmeyer flask	10mL sample solution; 5mL 0.00 lM dithizone; pH: 3-9; Contact time: 120 min; Temperature: 20-80 ^{0}C	The optimum results were obtained at pH 9, contact time of 60 min, temperature of 30°C, and an adsorbent dosage of 1 mg/mL; The adsorption capacity was found to be 322.58 mg/g	(Kalkan, et al., 2014)
39	Microbial Degradation using *Aeromonas Spp*.	N.A	Reaction volume: 100mL; Initial conc^n of dye: 200 mg L^{-1}; Reaction time: 24 h	Colour and Total Organic Carbon (TOC) was removed more than 95% and up to 50% respectively	(Shah, 2014)
40	Photocatalysis using PANI/TiO_2	Reactor height 455 mm; Diameter: 20 mm and thickness: 2 mm	Initial conc^n of dye: 50-200 mg L^{-1}; Catalyst loading : 0.25-1 gL^{-1}; Reactor volume: 1 l; Recirculation rate: 10 mL/min; Lamp power: 25 w	Polyaniline coated titanium dioxide (PANI-TiO_2) had better performance of 99.89% as compared to the 74.51% for the uncoated TiO_2 at an optimum pH 3.	(Mavuso, et al., 2014)
41	Sorption by chitosan beads	N.A.	0.5 g of sorbent in 20mL of 20 mg/L dye; Reaction time: 6 h; pH:2-10;Initial dye conc^n: 20-100 mg/L	Under optimal values of operating parameters, highest percentage uptake of dye was achieved (96.22%).	(Ong, et al., 2014)
42	Biological decolorization using *Micrococcus luteusand Candida albicans*	Conical flasks 250 ml	10-80 mgL^{-1} of RB5 and 1 gL^{-1} of yeast extract; 50 ml of MSM; pH: 5-10	The bacterium had the capacity to decolorize the dye in industrial wastewaters at a conc^n of 10 to 80 mg/L within	(Ramdan, et al., 2014)

				7 days of incubation; 70% of decolorization was observed.	
43	Biotransformation using *S. cerevisiaeor baker's yeast* Microorganisms	N.A.	Yeast concentration : 1%; 200 ml reaction mixtures of Reactive Black (25 mg/l) and 2 grams Harvested cells of S. cerevisiae	Result showed that harvested cells of *Saccharomyces cerevisiae* are able to bioconvert Ractive Black 5. Reactive Black 5 was degraded by biotransformation 85% within 24 hours in water at the room temperature	(Sadeghi, et al., 2014)
44	Ozonation	Ozone was introduced using nozzle	ozone dose:10 – 30 g/hr; pH: 4-11; Reaction time: 60 min; Temperature: 30-70 ^{0}C	Results showed that almost 100% colour removal and 90% COD reduction were achieved	(Shaikh, et al., 2014)
45	UV/TiO_2 and photo-fenton process	batch water jacketed photoreactor having capacity of 800mL	Mercury lamp of Irradiation source: mercury lamp 125W(UV-C, 254nm); H_2O_2 Conc^n: 1 – 4 mmol/L; TiO_2 dose: 1 – 4 mmol/L	Azo dye (Reactive Black 5) was found to undergo substantial and rapid decoloration by both the method. However, the decoloraztion of the azo dye by the photo-Fenton processes was much more efficient around 99%.	(Qiu, et al., 2014)
46	Submerged photocatalytic membrane distillation reactor with microwave electrodeless lamps	Cylindrical glass reactor (outer diameter 150mm and height 250 mm) was housed in microwave oven (1300W, 2.45 GHz).	Initial dye Concn:400 mg/L; 1500 mL of reaction solution, and 300 min of reaction time ; TiO_2 dose: 0.5–6 g L^{-1}; Temperature: 55 – 70 ^{0}C	Photodegradation of 400 mg/L RB5 synthetic wastewater by the SPMDR resulted in high color (100%) and TOC (80.1%) removal after 300 min. .	(Qu, et al., 2014)

47	Photocatalysis	Batch photocatalytic shallow pond reactor	RB5 concentration: 25–150 mg l^{-1}; TiO_2 dose: 1.0–2.25 g L^{-1}; UV light intensity: 9.4–12.4 Wm^{-2}; Reaction time: 180 min	ANN models have the correlation coefficients of 0.9864 and 0.983 for decolorization and degradation efficiency, respectively and pseudo-first-order kinetics was observed.	(Garg, et al., 2015)
48	Biotreatment using biochar	Biochar packed bioreactor (6.4 cm diameter and 40 cm height)	Initial $Conc^n$ of dye: 100 mgL^{-1}; 5 g biochar; reaction time: 24h; dye solution flowrate: 250 ml h^{-1}. CrVI $Conc^n$: 2-10 mgL^{-1}	Biochar produced from corncobs and other low cost agricultural waste can all be used as packing materials; Pseudomonas putida strain KI for accelerated decolorization of azo dyes and CrVI in packed bed bioreactors; complete biodegradation of Reactive Black 5 (100 mg L^{-1}) within 5 h.	(Mahmood, et al., 2015)
49	Multi –walled carbon nanotubes	Batch reactor	Contact times (30-120 min). initial dye concentration= 50-200 mgL^{-1}; Adsorbent dosage= 0.5 g/L	Maximum adsorption capacity was reached at 36.2 mg/g after 90 min.	(Shanesaz, et al., 2015)
50	Photocatalytic degradation (Reduced graphene oxide)	Photoreactor	20-60 mg of reduced Graphene Oxide (rGO); 100 mL RB5 solution having initial $conc^n$ 10 mgL^{-1}; pH =4	rGO after 48 h showed higher photocatalytic activity; it was found that an optimum experimental condition for the effective removal of RB5 (49%) was 30 mg rGO loading, 10 mgL^{-1} of RB5 and at a solution pH of 3.	(Wong, et al., 2015)

51	Cigarette filters modified with Fe^{3+}	refrigerated discontinuous reactor	100 mL of 50 mg L^{-1} aqueous solution; pH 3.0; Reaction time: 60 min; 125-W mercury vapor lamp; 1 g modified cigarette filter	Dye degradation was approximately 99.09 % after 60 min	(Glugoski, et al., 2016)

Typical characteristics of textile effluents depends upon type of textile manufactured and chemicals used (Ghaly, et al., 2014). Table 2.3 depicts characteristics of wastewater generated from different stages of textile and dyeing industries. However, main characteristics of textile wastewater are high concentration of organic compounds, heavy metals, high COD, high pH and sturdy color (Wijannarong, et al., 2013).

Table 2.3 Characteristics of waste generated from various processes of Textile and Dyeing industries (Babu, et al., 2007)

Process	Characteristics of Wastewater
Slashing/ sizing	BOD, COD, waste metals, cleaning waste
Desizing	BOD, lubricants, biocides, anti-static 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
Mercerizing	High pH; NaOH.
Dyeing	Metals; salt; surfactants; toxics; organic processing assistance; cationic materials; color; BOD; sulfide; acidity/ alkalinity; spent solvents.
Printing	Suspended solids; urea; solvents; color; metals; heat; BOD; foam.
Finishing	BOD; COD; suspended solids; toxics; spent solvents.

Owing to characteristics mentioned in Table 2.3 of textile wastewater, it poses a significant threat to environment as well as to human health. Major issues associated with human health due to the presence of dyes in wastewater are haemorrhage, ulceration of skin, nausea, severe irritation of skin and dermatitis (Ghaly, et al., 2014). Further, it is also reported that presence of dye could obstruct penetration of sunlight leading to reduced photosynthesis, which affects water ecology.

2.3. Conventional Treatment for Textile wastewater

Textile and dyeing sectors are considered to be major consumer of fresh water as well as producer of colored wastewater (Holkar, et al., 2016). Water is not only used for transmitting dyes onto fibres, but it is also utilized as a heating agent for the dye bath in the form of water vapors (Hessel, et al., 2007). The water utilized in a standard size of textile industry consumes 200 L freshwater per kg of fabric processed and generates almost 120 L wastewater per kg of fabric (Anjaneyulu, et al., 2005; Holkar, et al., 2016). A wet processing unit in textile industry utilizes huge quantities of fresh water along with a high amount of chemicals which in turn generate large quantities of effluents with a considerable concentration of organic and inorganic compounds (Tehrani-Bagha, et al., 2010).

However, dyes are deliberately designed to show resistance towards degradation, and due to this fact only its conventional biological wastewater treatment is ineffective (Wu, et al., 2008). Wastewater treatment by conventional methods are classified into primary, secondary and tertiary methods (Pophali, et al., 2011; Singh, et al., 2014). Primary treatment consists of screen and grit removal, oil and grease removal, equalization basin and primary settling and/or chemical precipitation. Biological treatment comes under secondary treatment and it may include either or combination of aerobic and anaerobic treatment (Ghaly, et al., 2014). Tertiary treatment generally comprises of filtration along with carbon adsorption and may also include physico-chemical treatment. However, it has been reported in the literature that conventional techniques have following major drawbacks:

1. Biological treatments are ineffective in complete removal of bio-resistant pollutants (Louhichi, et al., 2014).
2. Conventional techniques such as Coagulation/flocculation, adsorption generates huge amount of sludge and solid waste (Louhichi, et al., 2014).
3. Conventional treatments are ineffective in complete removal of organic pollutants (Khadhraoui, et al., 2009).
4. Conventional techniques such as coagulation, flocculation, and adsorption can remove color but are ineffective in treating COD and meet outlet norms of COD. Even color removal through these process is a costly affair (Khadhraoui, et al., 2009).
5. Adsorption is efficient in removing dyes such as cationic dyes, mordant dyes, acid dyes and to a lesser extent to disperse, direct and vat, pigment and reactive dyes. Adsorption method is not destructive process and requires regular regeneration and replacement of adsorbents after a specified period, which makes this process method uneconomical (Srinivasan, et al., 2009).
6. Effluents from textile and dyeing industries are highly colored, and therefore conventional technologies such as filtration, precipitation, and photochemical degradation are inefficient in completely removing color from effluents as well as they are not commercially accepted due to their high cost (Srinivasan, et al., 2009).
7. Owing to stable nature of dye molecules biological treatment is ineffective and results in the generation of sludge, membrane fouling and incomplete mineralization (Asghar, et al., 2015).

An advanced oxidation process is gaining a lot of attention as it serves to be a better alternative for treatment of effluents of dye and textile industry (Srinivasan, et al., 2009). Advanced oxidation processes are utilized for treatment of recalcitrant pollutants (Pophali, et al., 2011).

2.4. Advanced Oxidation Processes

Advanced oxidation processes (AOPs) are emerging as one of most appropriate technology for treating textile effluents or colored wastewater (Srinivasan, et al., 2009; Tehrani-Bagha, et al., 2010). AOPs emerge as an alternative to existing technologies for decolorization of colored effluents, which are widely used such as adsorption, precipitation, membrane filtration, chemical degradation and photochemical degradation (Louhichi, et al., 2014). AOPs are effective in oxidizing wide range of organic compounds into environmentally acceptable end products (Orge, et al., 2015). Taseidifar, et al., 2015, reported that hydroxyl radical($\bullet OH$) play vital role in AOPs, owing to its unselective nature hydroxyl radicals ($\bullet OH$) reacts with wide a range of pollutants and convert them into CO_2, H_2O, and harmless inorganic mineral salts. Puspita, et al., 2015, reported that AOPs can be compared on the basis of generation of hydroxyl radicals.

Another aspect concerning the opportunity of AOP application is that referring to the polluting load of wastes generally expressed as COD. Only wastes with relatively small COD contents (5.0 g/L) can be suitably treated by means of these techniques since higher COD contents would require the consumption of too large amounts of expensive reactants. Wastes with more massive pollutants contents can be more conveniently treated by means of wet oxidation or incineration (Figure 2.1) (Andreozzi, et al., 1999).

The existing technologies for decolorization of colored effluents, which are widely used such as Adsorption, Precipitation, membrane filtration, chemical degradation and photochemical degradation, are expensive and commercially unattractive. Commonly, physico-chemical treatment is used for removal of dye or color from textile wastewater. This method is effective for all the dyes except for highly soluble dyes and it generates an enormous quantity of voluminous sludge, which requires dewatering and further treatment/disposal as it is considered as hazardous waste. Advanced oxidation processes (treatment with ozone, H_2O_2, Fenton's reagent and UV radiation) are the potential alternatives for the decolorization of the dye colored wastewater (Srinivasan, et al., 2009).

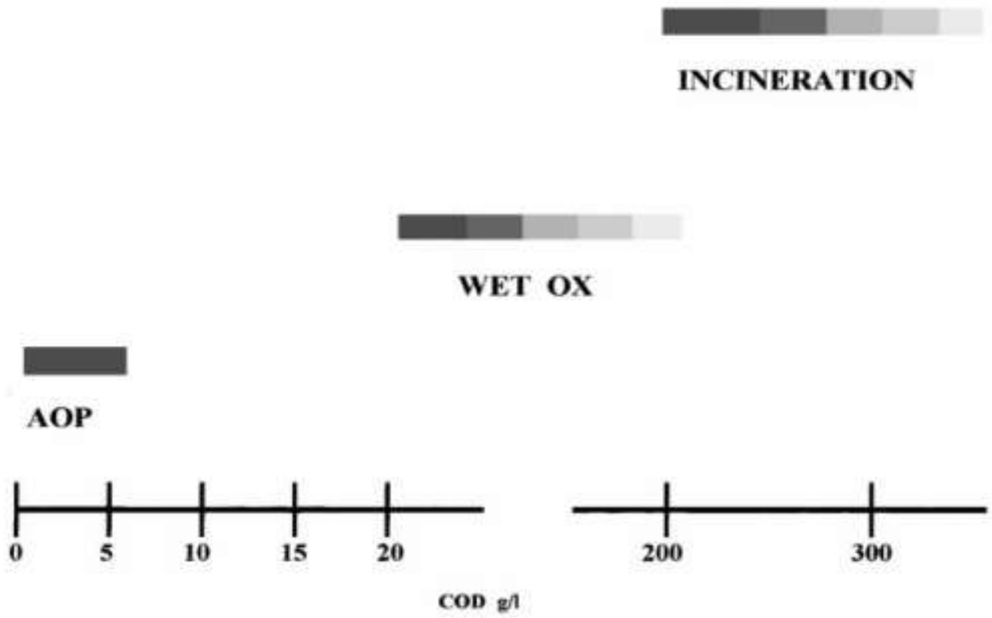


Figure 2.1 Suitability of water treatment technologies according to COD contents.

Advanced oxidation is one of the most powerful methods for decolorization of textile wastewater. Advanced oxidation processes such as UV nano-photocatalysis, Fenton's reagents, and ozonation are emerging technologies aimed at the degradation of wastewater pollutants (Soares, et al., 2006).

However, it is well reported in the literature that AOPs have significant advantages as they do not generate any by-product or sludge in most of the cases. In most of the processes, AOPs end product is CO_2 and water (Elahmadi, et al., 2009). Table 2.4 illustrates advantages and disadvantages of various AOPs.

It is well known that ozone is a strong oxidant which can form a more powerful, non-selective hydroxyl radical at high pH values (Soares, et al., 2006). Due to this high oxidation potential, ozone can proficiently break down the conjugated double bonds of dye chromophores as well as other functional groups such as the complex aromatic rings of dyes (Zhu, et al., 2014; Punzi, et al., 2015). Tokumura, et al., 2009, reported that chromophore groups are responsible for imparting color in dye molecules. However, ozone breaks the conjugated double (–N=N–) bond of chromophore resulting in color removal from effluents. Srinivasan, et al., 2009, reported a similar finding that unsaturated bonds of humic substances such as chromophore of dye molecule and other pigments are broken down by utilizing ozone resulting in color removal from effluents. The author further reported that subsequent formation of smaller non-chromophoric molecules decreases the color of the effluents.

Table 2.4 Pros and Cons of various techniques for treating dye wastewater

Sr. No	Treatment Technology	Advantages	Disadvantages	References
1	Electrochemical Oxidation	Process is fast or quick; It can handle different volume of pollution load; COD Reduction is possible; Presence of salt in water does not affect the treatment efficiency.	By product generation; Production of sludge; Cost of energy is included; Cost intensive process.	(Pearce, et al., 2003) (Allegre, et al., 2006) (Hai, et al., 2007)
2	Adsorption	Removes wide range of dyes, suspended substances and organic compounds.	Adsorbent regeneration and its disposal is an issue; Blocking of filter.	(Pearce, et al., 2003) (Allegre, et al., 2006)
3	Membrane Technologies	Used for all types of dye removal.	Production of sludge is an issue; Membrane replacement is costly;	(Pearce, et al., 2003) (Hai, et al., 2007)
4	Coagulation/ Flocculation	Economic process, cost effective, can be used for disperse, sulfur and VAT dyes.	High amount of sludge production. Azo, reactive, acid and basic dye cannot be removed.	(Pearce, et al., 2003) (Hai, et al., 2007)
5	Bio- degradation	Rate of elimination by oxidizable substances is about 90%; It is economic process and can be used for direct, disperse and basic dyes.	Most of dyes are recalcitrant in nature; Acid and reactive dyes cannot be removed.	(Allegre, et al., 2006) (Hai, et al., 2007)
6	Ozonation	Not suitable for dispersed dyes; Release aromatic amines; high efficiency for decolorization.	Ineffective for COD removal; It is costly affair	(Allegre, et al., 2006) (Anjaneyulu, et al., 2005)
7	Nano-filtration	Low molecular weight compounds can be separated from monovalent salts.	Pressure requirement is very high.	(Allegre, et al., 2006)
8	Ultra-filtration & Micro-filtration	Requires low pressure.	Quantity of wastewater which can be treated is inefficient.	(Allegre, et al., 2006)
9	Fenton Reagent	Effective decolorization of wide variety of wastes; Simple and easy to install and operate; COD reduction can be achieved.	Additional sludge production is an issue; Effective for particular pH range <3.5; Longer reaction time required.	(Anjaneyulu, et al., 2005)
10	Aerobic process	COD and Color removal can be achieved.	Detention time is very long; Removal of specific substrate; Less resistant to recalcitrant.	(Anjaneyulu, et al., 2005)
11	Ion-Exchange	Dye recovery is possible; Regeneration of adsorbent is done without any loss.	Resins used in ion-exchange are dye specific. Regeneration is specific.	(Hai, et al., 2007)
12	Sonolysis	No sludge is produced due to absence of any chemical additives.	Gas requirement is very high; Not economic process at present due to reactor specifications and limitations.	(Hai, et al., 2007)
13	Photocatalysis	Utilizes solar energy; No sludge generation; Efficient in removal of COD.	Highly depends on dispersion of light; Separation of catalyst from treated effluent is problematic and challenging.	(Hai, et al., 2007)

14	Ionizing Radiation	Effective technique with no sludge generation.	Requirement of dissolved oxygen is too high; Complete decolorization and mineralization is not possible; Scale up is costly.	(Hai, et al., 2007)
15	Wet air oxidation (WOA)	Can be used for effluents which are concentrated for biological treatment.	cannot accomplish complete mineralization of pollutants; Require high temperature and pressure conditions; Installation and operating cost is high.	(Hai, et al., 2007)

2.5. Industrial Applications of Ozone

In recent era there is tremendous growth in utilization of ozone for carrying out various applications in industry. Ozone is employed not only for purification of drinking water but at the same time it is utilized for treating wastewater generated from chemical industries, pulp & paper industries, dye & intermediates, textile, etc (Da Silva, et al., 2006). Ozonation is widely employed and preferred to be used as an alternative to treat wastewater containing recalcitrant organic compounds (Al-Abduly, et al., 2014). Improvement in ozonation technique has additionally drawn researcher’s attention due to competitive treatment cost with UV disinfection process (Singh, et al., 2015). It is attractive to adopt ozonation technique as it completely mineralizes recalcitrant and hazardous organic compounds such as dyes, phenolic compounds, pesticides, organochlorides, and ammonium compounds into environmentally acceptable end products (Sreethawong, et al., 2008). However, it is worthy to note that integrated ozonation process gives better efficiency as compared to ozonation process (Pirgalıoglu, et al., 2009). The main reason for better results is due to increase in number of ozone molecules , hydroxyl radicals and other active species like sulfate radicals which are in turn responsible for mineralization of recalcitrant organic compounds (Sreethawong, et al., 2008). It has been reported by various researchers that mass transfer of ozone from the gas-phase to the liquid-phase will serve as the rate limiting step in ozonation process. Nevertheless, it is praiseworthy to note that driving force for mass transfer of ozone vary considerably with respect to operating conditions and parameters of wastewater (Sreethawong, et al., 2008; Wu, et al., 2008).

2.6. Ozonation

Advanced oxidation process is based on generation of hydroxyl radicals ($\bullet OH$). Ozonation is advanced oxidation process which utilizes ozone as oxidizing agent. The main advantage of using ozone as oxidizer is that it does not generate any by products or solids (sludge), rather it directly converts them into carbon-di-oxide and water (De Souza, et al., 2010). Ozone as oxidizer has several advantages such as high oxidation potential of ozone (2.07eV), high efficiency for decomposition of organic matter, low sensitivity to change in temperature (Oguz, et al., 2005). Ozonation may not be economically practicable for oxidizing all organic compounds into carbon dioxide and water rather partial oxidation was suggested by several researchers (Oguz, et al., 2005; Gokcen, et al., 2006).

Using Ozonation for decolorizing wastewater has the following advantages:

1. It does not increase the volume of wastewater and sludge at the end of process (Oguz, et al., 2005; Tehrani-Bagha, et al., 2010);
2. It removes color and reduces the organic matter in one step (Oguz, et al., 2005; Tehrani-Bagha, et al., 2010);
3. It needs little space, and it is easily installed on a site (Oguz, et al., 2005; Soares, et al., 2006);
4. It is less harmful than other oxidative processes since no stock hydrogen peroxide or other chemicals are required on a site (Oguz, et al., 2005; Soares, et al., 2006; Tehrani-Bagha, et al., 2010);
5. Residual ozone can be easily decomposed to oxygen. (Oguz, et al., 2005; Soares, et al., 2006; Tehrani-Bagha, et al., 2010);
6. Danger is nominal (Wu, et al., 2008);
7. Easily operated (Oguz, et al., 2005; Soares, et al., 2006);

Disadvantages of Ozonation process:

1. It may not degrade all organic pollutants directly into end-products (CO_2 and water) rather convert them into secondary pollutants which need further treatment (Tehrani-Bagha, et al., 2010)
2. A major drawback of Ozonation processes is the high operation cost caused by the installation of an expensive ozone generation unit and the cost of electricity (Singh, et al., 2008). To reduce the costs accompanying the use of ozone, the efficiency of the Ozonation process has to be maximized by combining it with other technologies (Sreethawong, et al., 2008).
3. Continuous onsite ozone is to be produced due to its half-life is typically 20 min (Kestioglu, et al., 2005).

The ozone method is known to be effective for decomposing organic chemicals containing carbon–carbon double bonds, olefinic double bonds, acetylenic triple bonds, aromatic compounds, phenols, polycyclic aromatics, heterocyclics, carbon–nitrogen double bonds, carbon–hydrogen bonds, silicon-hydrogen and carbon–metal bonds (Turhan, et al., 2009).

Ozone is particularly effective in the removal of color and water disinfection. Ozone processes can be made more effective for example at high pH (O_3/OH^-) and by the addition of hydrogen peroxide (O_3/H_2O_2) (Tizaoui, et al., 2007). These systems favor the production of hydroxyl radicals (•OH), which are highly reactive species. OH^- and H_2O_2 initiate a series of radical reactions that enhance ozone decomposition to yield •OH. In the system O_3/OH^-, the hydroxide ion reacts with ozone to yield superoxide anion radicals ($O_2^{\bullet-}$), which in their turn are involved in a series of reactions that yield •OH. Overall 1.5 mol of O_3 yields 1 mol of •OH. In the system O_3/H_2O_2, when H_2O_2 is dissolved in water, it partially dissociates into hydroperoxide ion (HO_2^-, the conjugate base of hydrogen peroxide), which reacts rapidly with ozone to initiate a radical chain mechanism that leads to hydroxyl radicals. Overall 1 mol of O_3 yields 1 mol of •OH. Hydroxyl radicals are very reactive, non-selective oxidants, and are the most important species in an advanced oxidation process. Thus, ozone-based advanced oxidation processes are attractive processes to oxidize the complex leachate mixtures and is also used to treat wastewater from textile, leather tanning, and petrochemical industries (Tizaoui, et al., 2007).

Ozone based processes can broadly be classified into two categories: photochemical processes and non-photochemical processes (Munter, 2001). The classification is purely based on the basis of technique used for generation of hydroxyl radical. Those processes which do not require any light energy as source for generating hydroxyl radicals are known as non-photochemical processes. O_3, O_3/UV, O_3/H_2O_2, O_3/Catalyst, O_3/US are few techniques which comes under category of non-photochemical processes. However, those processes which require light energy as a source for generating hydroxyl radicals are known as photochemical processes. However, sometimes it is necessary to use UV to assist oxidative annihilation of refractory organic pollutants which are otherwise left untreated and are more toxic in nature. There are various processes which are listed under photochemical ozonation processes such as, O_3/UV, $O_3/UV/H_2O_2$, O_3/UV/PS, O_3/UV/Catalyst (Munter, 2001). Comparison of O_3, O_3/UV and O_3/PS process on dye removal is reported in Table 2.5.

Table 2.5 Comparison of O_3, O_3/UV and O_3/PS process for dye removal

Sr. No.	Treatment Method	Pollutant/Compound removed	Reactor Configuration/Specification	Operating Conditions	Results and Comment	Reference
1	Ozonation	Bomaplex Red CR-L	1000 mL cylindrical semi-batch reactor; 7-cm diameter & 40-cm height; diffuser	Dye solution: 250 mL; Dye Conc^n: 1000 mg/L; O_3 flow: 5-15 L/min; Ozonation time: 30 min	Efficiency of COD and dye removal was approximately 54% and 99%.	(Oguz, et al., 2005)
2	Ozonation	Reactive dye bath of light yellow and blue shades	Borosil glass reactor of 10 cm diameter and 200 cm height with porous diffuser	Dye Sample: 10 lits; ozone dose of 0.16 g/min; Contact time: 40 min	COD removal was 51% for blue and 48% for yellow shades and TOC removal was 51% and 42% for blue and yellow shades respectively.	(Sundrarajan, et al., 2007)
3	Ozonation	Red RB (RRB), Remazol Red (RR), Remazol Blue (RB), Remazol Black (Rbla), Remazol Violet (RV), Remazol Orange (RO), Golden Yellow (GY) and Remazol Yellow (RY).	1 l borosilicate glass reactor with glass diffuser	Ozone conc^n: 20 g h^{-1}; Dye Conc^n: 50-100 mg/L; pH 5-10	Maximum color and COD removal could be achieved at an ozone dose of 4.33 mg l^{-1} at 30 min. decolorized to 95 - 99%, The decomposition of reactive azo dyes followed a pseudo first order kinetics with rate of reaction being highest during ozonation with RR.	(Sarayu, et al., 2007)
4	Ozonation	Basic Blue 9 (Methylene Blue)	Glass column of 5 cm diameter and 110 cm height with sintered glass	2000 mL of dye solution; Ozone flow: 120 L/h; Initial dye conc^n: 50-600 mg/L; pH: 2-12; O_3 Conc^n: 4-24 g/m^3	COD of basic dyestuff wastewater was reduced to 64.96% under basic conditions in 12 min	(Turhan, et al., 2012)

5	Ozonation	C.I. Reactive Red 120	Cylindrical glass reactor (1.2 l) with sintered glass filter	Initial dye conc^{n}: 200 mg/L;ozone concentration: 8.9 -20 mg/l; Contact time: 150 min	It was observed that COD reduction was about 52-55%.	(Zhang, et al., 2004)
6	Ozonation	H-acid, a dye intermediate	1 L boro silicate glass reactor with glass reactor	Initial conc^{n}: 250- 1000 mg/L;ozone concentration: 0.25-4.33 mg/l; Contact time: 120 min; pH: 2-11.5	Maximum color (98.7) and COD (87.8%) removal was achieved at an ozone dose of 4.33 mg/l at 30 min ozonation.	(Swaminathan, et al., 2005)
7	Ozonation	Reactive Red 120	Semi-batch bubble column reactor (450 mm×85 mm ID) of the 2000 m working volume	Initial conc^{n}: 0.5 g/L; ozone concentration 10.2 mg/min; Contact time: 40 min; pH: 3-11	The colour, COD and TOC removal efficiency were obtained 100%, 60% & 37% respectively after contact time of 40 min.	(Abidin, et al., 2015)
8	Ozonation	Acid Red 131	20-L reaction vessel (height 70 cm, diameter 20 cm) equipped with venturi injector and static mixer.	The oxygen flow rate: 5 LPM; Ozone dose: 3.3 – 12 g/m^{3}: pH: 3-11; Initial conc^{n}: 20-70 mg/L; Reaction time: 25 min.	100% Color removal efficiency was obtained after 23 min of ozone treatment at pH 11.	(Adiraju, et al., 2016)
9	Ozonation	Reactive Black 5	Bubble column Reactor: 1.5L capacity (78cm height, 6cm diameter)	Time:1hr;O_3 Conc^{n} :3.51 g/h; Dye Conc^{n}: 75 mg L^{-1}; pH:12	Pseudo-first-order rate constants (k) 0.121 min^{-1}; Color 4.0 min^{-1}; Color Reduction (100%); COD Removal (61.9%)	(Arslan, et al., 2000a)
10	Ozonation	Reactive Yellow 84	Cylindrical glass reactor (1.2 l) with sintered glass filter	Initial dye conc^{n}: 200 mg/L; ozone concentration: 9.1 -18.5 mg/l; Contact time: 90 min	COD removal rate was 50% and TOC removal was 30%.	(Koch, et al., 2002)

11	Ozonation	Reactive Blue 19	Batch reactor made of Pyrex glass	Initial dye conc^n: 100-800 mg/L;1 L solution; oxygen flow rate: 0.08 L/min; ozone dose: 25 to 55 g/m^3; pH: 3, 6.5&10;	100% dye removal was observed. The COD and TOC reduction was about 55% and 17%, respectively, for 90 min ozonation of 800 mg/L dye solution.	(Tehrani-Bagha, et al., 2010)
12	Ozonation	Reactive Dyes from Textile Dyeing Industrial Effluent	Bubble column reactor	500 mL of solution; Time: 360 min; pH:8.6-9.3; Temperature: 30-45^{O}C; COD: 160-332 mg/L	ozonation can reduce color in the wastewater more than 90% at reaction times 6 hours	(Wijannarong, et al., 2013)
13	Ozonation	Orange II	Bubble column (0.095 m diameter and 1.00 m height) with 5 L working volume	Initial dye conc^n: 50-200 mg/L; Ozone Conc^n: 10 - 60 mg L^{-1}; flow rate of ozone gas: 0.2 to 2.0 L min^{-1}	Color and COD removal efficiencies were observed to be 99.7% and 72.2% at optimized conditions.	(Tokumura, et al., 2009)
14	Ozonation	Malachite green	A cylindrical glass reactor with a 1.000 L volume (diameter and height of 6 and 35 cm)	Dye Solution: 500 mL; Ozone flow: 720 mLmin^{-1}; O$_3$ Conc^n : 0.3505 mmol min^{-1}	86% of MG in the reaction mixture was removed by ozonation after 10 min, TOC removal was 47.4%.	(Kusvuran, et al., 2011)
15	Ozonation	Leather dye effluent	Acrylic cylindrical packed column (2.5cm i.d. and 30cm height) packed with glass beads of 5mm diameter equipped with porous diffuser plate	Initial Effluent Conc^n: 300-500 mg/L; Ozonation time: 60-120 min; pH: 4, 7, & 11;	Present investigation showed that a maximum of COD removal efficiency of 92% has been achieved under optimum operating conditions.	(Preethi, et al., 2009)
16	Ozonation	Leather dye	Cylindrical glass reactor of 5 L capacity (8.5 cm	Dye concentration: 30-360 mg/L; ozone at a	It has been observed that max. decolorization	(Srinivasan, et al., 2009)

			diameter and height 125 cm)	concentration of 1.6 mg/L; pH:4-11;	efficiency up to 97% could be achieved.	
17	O_3/UV	Reactive Yellow 145	Pyrex glass with a volume of 1000 mL (inside diameter 12 cm, height 15 cm).	Mercury lamp of 175 W; Initial dye concentrations: 50-500 mg/L; O_3 Conc^n: 0.45-4.8 g/h; Temperature: 20-35 ^{O}C; Reaction time: 150 min	At optimum parameters, the TOC removal efficiency of RY145 reached near to 80%.	(Song, et al., 2008)
18	O_3/UV	Rhodamine B	Batch reactor, made up of Pyrex glass (8.0 cm diameter and 13.5 cm tall)	100 ml dye solution; O_3 Conc^n: 5 g/h; UV lamp power: 8 – 32 W; Initial dye concentrations: 50-200 mg/L; Ozone dose: 10-240 ml/min; pH: 2-10;	The UV/ozone process was the best oxidization process, decolorization efficiency of 99.78% and COD removal rate of 47.43% after 15 min treatment.	(Cuiping, et al., 2011)
19	O_3/UV	Reactive Red 2	3-l hollow cylindrical glass reactor. The inner diameter and height of the photoreactor were 143 and 230 mm,	Initial dye Conc^n: 40mg/L; pH: 4-10; Ozone Flow: 500 mL/min; UV lamp: 8W; reaction time: 60 min	90% Decolorization At pH 7, EE/O results revealed that the UV/O_3/H_2O_2/Fe^{3+} system consumed half the energy of the UV/O_3	(Wu, et al., 2008)
20	O_3/UV	Acid Orange 6	Airtight reactor with an effective volume of 5.5 L	4.0 L dye solution; Ozone feed rate: 120 L/h; UV light intensity: 30 W/m^2; Ozone conc^n: 0-80 mg/L; Reaction time: 60 min;	TOC removal efficiency, in that both O_3/UV and O_3/UV/TiO_2 processes can achieve 65% of removal efficiency at pH 7	(Hsing, et al., 2007)
21	O_3/UV	Acid Red 131	20 litre reaction vessel (height 70 cm, diameter 20 cm) Venturi injector	Initial dye concentration 30-70 mg/L, sample volume 10L, ozone dose 12.7-29.5 g/m^3; pH:3-11;	A 100 % colour removal was obtained after 12 min of ozone treatment.	(Bharadwaj, et al., 2013)

22	O_3/UV	Dye- Finishing Wastewater	3.5L reactor; 10 W UV lamp	UV intensities: 0-40 W; ozone dose: 0-2.66 g/h; pH:3-10;	Effluent color could be reduced from 4,000 to 200 American Dye Manufacturers Institute (ADMI) in an hour using the UV/ozone technique.	(Liu, et al., 2004)
23	O_3/UV	Red Cl-5B	Bubble column glass reactor (internal dia: 3.3 cm) with diffuser	Initial dye concentration 100-500 mg/L; Ozone dose: 50-450 mg; pH: 3-10; Reaction time: 60 min	Resulted in more than 90% color removal and 80% COD removal for all the selected concentrations.	(Khan, et al., 2010)
24	O_3/UV	Synthetic dye wastewater	6-L working volume reactor, with a UV (TUV-15) lamp	One litre of synthetic dye wastewater; recirculation flow rates: 1.2-2.4 l/min; zone concentration: 40 g/m^3; ozone gas flow rate: 2.4 L/min; Reaction time: 150 min	Removal of COD 81.2% and TOC 71.4% was observed.	(Chung, et al., 2011)
25	Ozone/Persulfate	Stabilized leachate	Ozone reactor(height of 65 cm and an inner diameter of 16.5 cm)	Ozone gas flow rate of 200 mL/min; ozone conc^n: 80 g/m^3; Reaction time: 240 min; 2 L of leachate sample; Persulfate dosages: 5-50 g	The results revealed that the best removal values of COD, color, and NH_3–N were 72%, 93%, and 55%, respectively.	(Abu Amr, et al., 2013)
26	Ozone/Persulfate	leachate sample	Ozone reactor (height of 65 cm and an inner diameter of 16.5 cm)	2 L sample; gas flow rate of 200–1000 ml/min; ozone gas concentration: 30 – 80 g/m3; pH: 3-11	This treatment achieved 99% of colour removal and 79% of COD removal and up to 50% reduction in treatment time	(Abu Amr, et al., 2015)

2.6.1 Mechanism of Ozonation Process

Ozonation process utilizes ozone to react with recalcitrant organic compounds as well as with inorganic compounds present in aqueous solution. Ozone follows either of the following two mechanisms to treat and mineralize organic compounds: direct reaction of molecular ozone with organic pollutants or reaction of radical species which are in turn generated through reaction of ozone with aqueous solution to prepare hydroxyl radicals (Agustina, et al., 2005; Preethi, et al., 2009; Kusvuran, et al., 2011; Tootchi, et al., 2013; Uslu, et al., 2015). However, ozone is very selective in nature which preferably reacts with unsaturated bonds of chromophores (Soares, et al., 2006). Ozone is highly unstable in nature (Hassaan, et al., 2017) and it decomposes rapidly in water following series of reaction. Ozone mainly undergoes following steps- ignition, propagation, and termination to generate hydroxyl radicals (Shin, et al., 1999; Liu, et al., 2015).

$$H_2O \rightarrow 2H^+ + O^{2-} \tag{2.1}$$

$$O^{2-} + O_3 \rightarrow O_2 + O_3^- \tag{2.2}$$

$$O_3^- + H^+ \rightarrow HO_3 \tag{2.3}$$

$$O_3 + H_2O \rightarrow O_2 + 2OH^\bullet \tag{2.4}$$

$$O_2 + 2OH^\bullet \rightarrow H_2O + O_3 \tag{2.5}$$

$$O_3 + OH \rightarrow HO_4 \tag{2.6}$$

$$HO_4 + HO_3 \rightarrow H_2O_2 + O_3 + O_2 \tag{2.7}$$

However, Derco, et al., 2015, has stated that, selection of any of the mechanism depends mainly on characteristics of wastewater, pH, alkalinity or acidity, and type of organic pollutants. Additionally, generation of hydroxyl radicals significantly depends on operating parameters. The reaction mechanism mentioned above escort to mineralization or transformation of recalcitrant organic compounds into products with higher oxygen contents (Derco, et al., 2015).

2.6.2 Reactor Configuration

Effectiveness of ozonation process is governed by type of reactor used and contactor selected (Rice, et al., 1980). Table 2.6 enlist various reactor configurations which can be adopted for carrying out ozonation process. Reactor efficiency depends on hydrodynamic characteristics as well as mass transfer proficiency of reactor (Gottschalk, et al., 2009).

Table 2.6 Type of reactors used in Ozonation (Gottschalk, et al., 2009)

Sr. No.	Type of reactor	Type of hydrodynamic behavior	Power consumption KW/m^3
1	Bubble columns	Non-plug flow for liquid Plug flow for gas	0.001-0.1
2	Stirred tank reactors	Completely mixed for liquid, Non-plug flow for gas	0.5-10
3	Packed column,	Plug flow for liquid, Non-plug flow for gas	0.01-0.2
4	Plate column	Disperse flow for liquid, Non-plug flow for gas	0.01-0.2
5	Tube reactors	Plug flow for liquid, Plug flow for gas	10-500

The most commonly used reactors are - Bubble columns (BCs) and stirred tank reactors (STRs), Packed column, Plate column and Tube reactors. Bubble column and stirred tank reactors are most commonly used reactors for carrying out ozonation experiments in lab scale. It was further reported that keeping the ratio of height to diameter of Bubble column reactor small i.e. $h/d \leq 10$, the reactor can be said to act like a perfectly mixed reactor. Stirred tank reactors are assumed to behave like perfectly mixed reactors in small-scale or laboratory scale, whereas in case of Bubble column and packed towers plug flow behaviour was observed (Lin, et al., 1997; Huang, et al., 1998; Gottschalk, et al., 2009). Table 2.7 discuss advantages and disadvantages of various types of contactors (Rice, et al., 1980).

Table 2.7 Advantages and Disadvantages associated to different types of ozone contactors (Rice, et al., 1980)

Sr. No.	Type of reactor	Advantage	Disadvantage
1	Spray tower	Proficient mass transfer rate, ozone is uniformly distributed in gas phase	High energy consumption, solids can block the nozzles of spray leading to decreased in effectiveness of process, contact time is reduced
2	Packed column	Small size and ease to operate due to simplicity, Operated in the wide range of gas/liquid ratio	Plugging and channelling is major issue.
3	Plate column	plugging and channelling can be avoided, can be more operated in large gas/liquid operating range	Appropriate for large installations
4	Spargers/Bubblers	Require gravity feed, no energy required, wide gas/liquid operating range allows intermittent operations.	Longer contact time, plugging of porous media due to intermittent flow, Tendency to vertical channelling of gas bubbles leading to reduced efficiency.
5	Agitators, surface aerators, injectors, turbines, static mixture	High degree of flexibility, small space, intimate contact, good dissolution.	Requires additional energy, narrow gas/liquid operating ranges, cannot accommodate significant flow changes therefore requires multiple contactor stages

2.6.3 Factors affecting Ozonation Process

Competence to treat bio resistant organic compounds has extensive dependence on operating parameters and characteristics of wastewater. To enhance the efficiency of ozonation process optimized conditions of operating parameters must be chosen. Following are various operating parameters which affects ozonation process.

2.6.3.1 Effect of Ozone flow rate

Ozone flowrate has a prospective impact on mineralization efficiency of bio-resistant organic compounds. Literature provides appropriate evidence supporting the effect of ozone flow rate on the effectiveness of ozonation process. Increasing ozone flow rate will have a constructive effect on degradation of recalcitrant organic compounds leading to high efficiency of the process. It is evident from literature that as ozone flowrate increases, it will augment the mineralization efficacy. This is supported due to the fact that as ozone flowrate increases amount of available molecular ozone and hydroxyl radicals will increase leading to enhanced process efficiency (Muthukumar, et al., 2004; Soares, et al., 2006; Lu, et al., 2009). As ozone concentration increases it will have positive increment on TOC as well as on color removal (Muthukumar, et al., 2004).

T.E. Agustina, et al., 2005, compiled work of various researchers and compared the effect of ozone flowrate on various organic pollutants. It is reported by Li, et al., 2005, that effect of ozone dosage was determined for removing organic pollutants from secondary effluents by utilizing ozonation and biological activated carbon and it was found that DOC removal was increased from 51 to 59% on increasing ozone dosage from 3 to 9 mgL^{-1}. It is reported by Kerc, et al., 2003, that ozone dosage affects degradation of humic acid in ozonation process. Investigation study of Kerc, et al., 2003, showed that on changing ozone dosage from 1.47 to 7.35 mgL^{-1} and it was noticed that at 80% of organic matter reduction and 90% of color removal was achieved at 7.35 mgL^{-1}. F.J. Beltran, et al., 1997, has studied the effect of ozone dosage on treatment of municipal wastewater from a primary sedimentation tank and it was reported that on increasing ozone dosage from 94 to 200 mg h^{-1}L^{-1} COD removal was enhanced drastically in particular time.

Mehmet F Sevimli, et al., 2002, has reported the effect of varying ozone dosage on wastewater from the treatment plant, and reported the effect of ozone on color, COD and DOC removal and observed that increased ozone dose would have a positive impact on overall rate constant of color, COD and DOC. The increase in rate constant with increased ozone dosage was supported by two-film theory. It was praiseworthy to note that increased ozone dose will augment mass transfer which will ultimately improve ozone concentration in the aqueous phase and hence rate constant of pseudo first order increases.

2.6.3.2 Effect of Initial pH

Another parameter which highly affects the performance of ozonation process is, effect of an initial pH of the solution (Beltran, et al., 1997). Ozonation process is extremely influenced by initial pH of the solution. Literature revealed that pH is one of the major key factor in determining the rate of reaction. It has been observed and studied in results reported by various researchers that, ozonation process gives better efficiency in basic media and at pH higher than 10. This is allied to the fact that at higher pH ozone decomposes into hydroxyl radical (3.06V) and it ultimately improves mineralization rate as oxidation potential of hydroxyl radical is higher than that of molecular ozone (Adiraju, et al., 2016) and hence the efficiency of the process is altered (Agustina, et al., 2005). However, findings of some researchers are in contradiction with above statement and it may also be observed from their results that acidic media is utilized in ozonation process for mineralization of dye wastewater but it is in association with generation of more free radicals scavengers which are in turn generated from mineralization of organic matters (Cuiping, et al., 2011).

To determine the effect of pH on efficiency of ozonation process for color removal of Acid Red 131 dye study was conducted (Adiraju, et al., 2016) by varying the pH of synthetic wastewater solution. The results were quoted in terms of color removal efficiency with increase in solution pH, and it was reported that no considerable improvement shown from pH 3 to 8. However, significant results were reported on further increasing the pH up to 11. It is reported that 100% color removal was achieved after 23 min. T.E. Agustina, et al., 2005, has also reported that increasing pH will enhance the generation of hydroxyl radicals which will ultimately increase degradation of organic compounds. Marc-Olivier Buffle, et al., 2006, has investigated the effect of pH on Opfikon wastewater and it was found that alkaline pH gives better efficiency as compared to acidic media.

Investigation of M.A. Hassaan, et al., 2017, on the removal of DB-86 dye by varying pH has also been identified, and the result shows that highest removal was achieved at pH 11 and it is in association to the fact that at elevated pH ozone becomes unstable and decomposes into hydroxyl radical. X.J. Lu, et al., 2009, have studied the effect of pH on the color removal of Brilliant Red and it was observed that 100% color was removed at pH 11. However, it was noticed that only molecular ozone was available in acidic media and it is very selective in nature and hence react with only unsaturated aromatic compounds. Furthermore, on increasing pH molecular ozone decomposes into hydroxyl radicals leading to improved removal efficiency due to strong oxidation ability. S. Pirgalioglu, et al., 2009, has reported that dye removal of RB5 was most proficient in alkaline pH.

2.6.3.3 *Effect of water recirculation Flowrate*

The flowrate of the water recirculation is another significant parameter which has shown its considerable effect on treatment efficacy of ozonation process. The results compiled by researchers have shown complete agreement with it. This is due to the fact that as flowrate of liquid decreases it will eventually lead to increase in residence time of liquid inside the reactor. However, amount of hydroxyl radicals per unit volume of solution increases and thereby increasing treatment efficiency of said process (Soares, et al., 2006; Tisa, et al., 2014).

2.6.3.4 *Effect of Initial dye concentration*

To analyze the effect of a most significant parameter which has a predominant influence on the efficiency of any process is its initial dye concentration. Initial dye concentration directly influences efficacy of process. Increase in initial dye concentration will have decreased mineralization efficiency of the said process (Konsowa, et al., 2010).

However, it is perceptible from the literature that as initial dye concentration increases the ratio of active radical ($\bullet OH$) to organic pollutant reduces and ultimately efficiency of process reduces. F. Erol, et al., 2008, has investigated effect of varying initial dye concentration of RBBR on COD removal, and reported that at an initial dye concentration of 200 mgL^{-1} and reaction time of 30 min, COD reduction achieved was almost same with the value accomplished for 100 mgL^{-1}. However, it is reported that on increasing initial concentration from 200 mgL^{-1} to 400 mgL^{-1}, COD reduction was considerably decreased and it was nearly halved to the value achieved by 100 mgL^{-1} and 200 mgL^{-1}. F. Gokcen, et al., 2006, has carried out work to determine the effect of varying initial dye concentration of Acid Red-151 and it was pointed out that extent of biodegradability of Acid Red-151 solution was decreased considerably with increasing initial dye solution with a substantial decrease in BOD_5/COD ratio. A.H. Konsowa, et al., 2010, reported effect of ozonation on industrial wastewater decolorization. Further, the effect of initial dye concentration by changing initial dye from 150 to 600 mgL^{-1} on decolorization time and it was reported that increasing initial dye concentration will lead to increased time requirement for decolorization. It was also reported that at 150 mgL^{-1} concentration of dye 8 min was required for complete decolorization whereas in case of 600 mgL^{-1} initial dye concentration time required for complete decolorization was raised up to 20 min. N.M. Mahmoodi, et al., 2011, has worked to study effect of photocatalytic ozonation of RR198 and RR120 , further effect of changing initial dye concentration was also analyzed by varying initial dye concentration from 50 mgL^{-1} to 200 mgL^{-1} were reported by keeping all other parameters constant. Similar findings were reported in the literature that increasing initial dye concentration will decrease the rate of dye degradation. In context to initial dye concentration, it is worthy to note that intermediates formed by degradation of dye molecule will possibly be responsible for decreased degradation rate for dyes.

2.7. Ozone/UV

Ozonation process has a constraint as it does not entirely mineralize all refractory and bio-resistant organic pollutants into environmentally acceptable end products rather they convert them to secondary pollutants which necessitate auxiliary treatment. Thus, integrated ozonation process can be utilized as an effective tool to completely mineralize bio-refractory organic pollutants into environmentally acceptable end products (H_2O, CO_2). Furthermore, it is worth mentioning that UV act as catalyst to enhance degradation efficacy of ozone molecule and thereby generating higher amount of hydroxyl ($\bullet OH$) radicals which results in complete mineralization of refractory organic pollutants (Mokrini, et al., 1997; Andreozzi, et al., 1999; Song, et al., 2008; Pillai, et al., 2009; Vijayalakshmi, et al., 2011).

2.7.1 Mechanism

Ozonation of refractory organic pollutants in wastewater is a multifaceted technology which demands mass transfer process and series of reaction which may be associated with a direct reaction of refractory organic pollutants with molecular ozone or indirect reaction with oxidizing agent i.e. hydroxyl generated by decomposition of ozone molecule. In case of O_3/UV process, there are three possible ways to carry out chemical reactions: direct photolysis, direct ozonolysis and radical oxidation (Mishchuk, et al., 2008).

$$O_3 + hv \rightarrow O_2 + O(^1D) \tag{2.8}$$

$$O(^1D) + H_2O \rightarrow \bullet OH + \bullet OH \tag{2.9}$$

$$O(^1D) + H_2O \rightarrow H_2O_2 \tag{2.10}$$

$$H_2O_2 + hv \rightarrow 2 \bullet OH \tag{2.11}$$

2.8. O_3/UV/PS

Additionally, to O_3/UV processes, O_3/UV/PS is another promising technology drawing tremendous attention nowadays. Although the literature does not give much information about this process rather, it provides broad glance about O_3/PS and UV/PS processes. However, integrating Ozonation process with UV and Persulfate will extremely augment mineralization of refractory organic pollutants. Further, it is exemplary to note that sulfate radicals are the more powerful oxidizing agent as compared to hydroxyl radicals (Wu, et al., 2012). In aqueous solution, Persulfate decomposes into sulfate radicals$(SO_4^{\bullet -}$, $E^0=2.6V)$ which are potent oxidizing radicals with having a potential of 2.6V (Huang, et al., 2009). Nevertheless, it is commendable to note that sulfate radical further react with water to produce hydroxyl radicals $(\bullet OH)$ (Liang, et al., 2007). Sulfate radical undergoes series of reactions to mineralize refractory organic pollutants into H_2O and CO_2 (Huang, et al., 2002). To mineralize refractory organic compounds, $SO_4^{\bullet -}$ and $^{\bullet}OH$ mainly undergoes three main mechanisms: hydrogen abstraction, hydrogen addition, and electron transfer (Huang, et al., 2002; Liang, et al., 2007; Huang, et al., 2009; Gao, et al., 2012; Xu, et al., 2012; He, et al., 2013).

$$SO_4^{-\bullet} + H_2O \rightarrow H^+ + SO_4^{2-} + \bullet OH \qquad (2.12)$$

$$S_2O_8^{2-} \xrightarrow{heat/UV} 2SO_4^{-\bullet} \qquad (2.13)$$

$$SO_4^{-\bullet} + H_2O \rightarrow HO^{\bullet} + HSO_4^{-} \qquad (2.14)$$

$$SO_4^{-\bullet} + M \rightarrow M^{\bullet} + products \qquad (2.15)$$

$$HO^{\bullet} + M \rightarrow M^{\bullet} + products \qquad (2.16)$$

$$M^{\bullet} + S_2O_8^{2-} \rightarrow SO_4^{-\bullet} + products \qquad (2.17)$$

$$SO_4^{-\bullet} + HO^{\bullet} \rightarrow \text{chain termination (i.e., terminating free radicals)} \qquad (2.18)$$

$$SO_4^{-\bullet} + M^{\bullet} \rightarrow \text{chain termination (i.e., terminating free radicals)} \qquad (2.19)$$

$$2SO_4^{-\bullet} \rightarrow \text{chain termination} \qquad (2.20)$$

$$HO^{\bullet} + M^{\bullet} \rightarrow \text{chain termination} \qquad (2.21)$$

$$2HO^{\bullet} \rightarrow \text{chain termination} \qquad (2.22)$$

$$2M^{\bullet} \rightarrow \text{chain termination} \qquad (2.23)$$

2.8.1 Mechanism

Ozonation process can be carried out either by direct reaction (between ozone and organic compound) mechanism or indirect reaction (through OH^-) mechanism (Sarayu, et al., 2007). In ozonation process, ozone molecules selectively attack unsaturated bonds present in chromophores, which ultimately results in removal of the color from dye wastewater (Pirgalıoglu, et al., 2009). Ozone molecules as well as hydroxyl radicals ($\bullet OH$) helps to break an aromatic ring of dye (Sundrarajan, et al., 2007). Hydroxyl radicals($\bullet OH$) are higly non selective in nature and it reacts with huge range of organic and inorganic compounds (Yue, et al., 2012). It is reported that initial pH decreases with increase in ozonation time this is mainly because by-products of acidic nature are generated during the reaction. Increase in ozonation time will increase the COD removal but in many cases there is decrease in COD removal with increasing ozonation time this is attributed to the fact that dye molecules upon oxidation results in small organic molecules (such as acetic acid, aldehydes, ketones, etc), which may not be completely mineralized under oxidative conditions (Sarayu, et al., 2007; Sundrarajan, et al., 2007). As ozone can be directly used in its gaseous state, therefore it does not tend to increase the volume of wastewater and sludge (Sundrarajan, et al., 2007).

Ozonation is a promising treatment technology for colored wastewater containing bio-resistant organic compounds. Nevertheless, it has been reported by investigators that ozonation does not entirely degrade recalcitrant organic compounds into environmentally acceptable end products rather it escorts them to secondary pollutants like aldehydes, ketones, organic acids, etc (Sarayu, et al., 2007; Sundrarajan, et al., 2007). Thus, integrated ozonation process can be applied as a crucial technology which will give complete mineralization of bio-resistant organic compounds into environmentally acceptable end products. The energy of UV irradiation is utilized in generating hydroxyl radical from ozone molecule and sulfate radical from Persulfate. The radical so generated reacts with an organic compound to reduce them into environmentally acceptable end products. Activation of persulfate radicals can be achieved by various methods and are enlisted in table 2.8. However, sulfate radical ($SO_4^{\bullet-}$, E^0=2.6V) is a prevailing oxidizing agent which additionally reacts with water to produce hydroxyl radical ($\bullet OH$). Following are the reactions which occur during decomposition of ozone and persulfate by UV radiation:

$$S_2O_8^{2-} \xrightarrow{heat/UV} 2SO_4^{-\bullet} \tag{2.24}$$

$$SO_4^{-\bullet} + H_2O \rightarrow H^+ + SO_4^{2-} + \bullet OH \tag{2.25}$$

$$O_3 + H_2O \xrightarrow{hv} 2OH^\bullet + O_2 \tag{2.26}$$

$$SO_4^{-\bullet} + H_2O \rightarrow HO^\bullet + HSO_4^- \tag{2.27}$$

Hydroxyl radicals so produced undergoes series of reaction to degrade organic molecules into acceptable end products. Following reactions occur during degradation of recalcitrant organic compounds (Kestioglu, et al., 2005):

$$OH^\bullet + RH \rightarrow H_2O + R^\bullet \tag{2.28}$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \tag{2.29}$$

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet \tag{2.30}$$

Recently, owing to the drastic decline in production cost of ozone, there is a tremendous increase in its industrial application. Ozone has to be produced on site as it cannot be stored due to its unstable nature. In-situ production of ozone can be done using any of above-said method. (Santana, et al., 2009).

Ozone (O_3) is a powerful oxidant has been extensively used in process industries at various levels to remove pollutant present in the effluent. Ozonation is a promising treatment process due to its unique features such as no sludge generation; has a high potential for both color removal and organic reduction through a single step and easy decomposition of residual ozone. (Preethi, et al., 2009).

The advantages of ozonation for dye removal when compared with other treatment methods such as physicochemical, adsorption, biodegradation and photochemical degradation are (i) no generation of sludge/solid wastes for further disposal (ii) less operational cost and (iii) efficient degradation. (Srinivasan, et al., 2009).

However, a few disadvantages limiting industrial applications of ozonation, i.e., the high production cost of ozone and the low ozone utilization due to the poor mass transfer rate of ozone (Wang, et al., 2012).

Table 2.8 Various methods to activate persulfate radicals

Sr. No.	Activation Method	Pollutant treated	Reactor configuration	Process parameters	Result summary	References
1	Heat-assisted persulfate oxidation	Trichloroacetic acid	250 mL volume reactor	Temperature: 60-80^{0}C;	Activated peroxydisulfate in the presence of formate as an additive is a convenient method for the mineralization of refractive substrates.	(Mora, et al., 2009)
2.	Heat-assisted persulfate oxidation	Methyl tert-butyl ether	100-ml gas-tight glass syringe reactor	Sodium persulfate conc^n: 0.65 l of MTBE; 5 ml of $Na_2S_2O_8$: 7-52 mM; Reaction time: Temp: 20-50 ^{0}C.	Degradation of MTBE	(Huang, et al., 2002)
3.	Heat-assisted persulfate oxidation	Leadoctoate drier effluent	NA	500mL of the samples; 80W UV lamp; COD: 1260 mg/L; pH:7-14;	Removal of COD, lead, and turbidity was observed at the rates of 94.9, 99.9, and 96.6%, respectively.	(Rabii, et al., 2001)
4.	Thermally activated persulfate	Carbamazepine	40-mL brown borosilicate glass bottles	Temperature: 40-70 ^{0}C; persulfate dosage: 0.2–4mM; Initical CBZ conc$_n$: 10 to 80 lM; pH: 3-11	Around 87.02% of CBZ was degraded.	(Deng, et al., 2013)
5.	Thermally activated persulfate	Ibuprofen	10 mL Pyrex vials	Temperature: 50-70 ^{0}C; pH: 4-9; SPS Conc^n: 1-2.8 mM; $[IBU]_0$ 7.33–20.36 mM	Around 85% degradation was observed.	(Ghauch, et al., 2012)
6.	Thermally activated persulfate	Methylene blue	capped 1 L volumetric flask	Temperature: 30–70 ^{0}C; $[MB]_0$: 15.6–311.8 mM;	Results showed complete MB discoloration under tested conditions.	(Ghauch, et al., 2012)

				[I]PB: 0.24–48.2 mM; SPS: 1–100 mM; pH:4-9		
7.	Thermally activated persulfate	Chloramphenicol	150-mL glass water jacketed beakers	100 mL of CAP solution; Temperature: 50-90^{0}C; [SPS]$_0$/[CAP]$_0$ = 1:1 to 80:1; pH:3-11	Degradation around 90% was observed.	(Nie, et al., 2014)
8.	Thermally activated persulfate	Antipyrine	45-mL culture bottles	pH :4.5–11.0; Reaction time: 120 min; 40 mL Antipyrine solution	study achieved a 80% removal of Antipyrine within 2 h	(Tan, et al., 2013)
9.	Thermally activated persulfate	Bisphenol A	2 L-capacity glass beakers	Temperature (40–50–60–70◦C),; (pH = 3.0, 6.5, 9.0 and 11.0); persulfate concentration (0–20 mM); Reaction time: 120 min	TOC removal observed to be 35-43%.	(Olmez-Hanci, et al., 2013)
10.	Thermally activated persulfate	Methylene blue	250 mL Erlenmeyer flask as completely mixed batch reactor	Temperature (55–80 ^{0}C); Initial pH (2.3–9.3); Persulfate concentration (500–2000 (mg/L))	Color removal efficiency was 98%.	(Kordkandi, et al., 2014)
11.	Thermally activated persulfate	Perfluorooctanoic acid	1000-mL plastic bottles made of polyethylene	Temperatures (20–40 ^{0}C); pH = 2.5, 3.6, 7.1 and 11.0; persulfate doses: 20–200 mM	Decomposition efficiency was noted to be 80.5%.	(Lee, et al., 2012)
12.	Persulfate (Iron activated)	Reactive Red 45	Glass water-jacketed batch reactor equipped with low pressure mercury lamp	pH:3-7; t = 60 min; [$S_2O_8^{2-}$]$_0$ = 50-138.4 mM [Fe^{2+}] = 1-1.64 mM; [Fe^{0}] = 1-4.27 mM	The developed MM also shows a high accuracy in predicting RR45 dye model pollutant degradation according to the simplified mechanism, which was confirmed by calculated	(Kusic, et al., 2011)

					RMSD (≤2.7%) for each experimental value.	
13.	UV/peroxydisulfate oxidation	C. I. Basic Blue 3	Batch photoreactor of 500 ml in volume	$[BB3]_0$: 10-25 mg/L; Radiation intensity from 9.5 to 33.1 W/m^2; $[S_2O_0^{2-}]_0$:0.1 – 2.0 mM;	It could be stated that the complete removal of color was achieved within 20 min.	(Khataee, et al., 2010)
14.	UV/peroxydisulfate oxidation	C.I. Basic Yellow 2	Photooxidative reactor	BY2: 10-50 ppm; 0.1 - 5mM $K_2S_2O_8$; UV-light intensities: 5.5 to 40 W/m.	The conversion ratios of BY2 at the volumetric flowrates of 330, 500 and 650 ml/min were 84%, 78% and 69% at 1 h, respectively.	(Salari , et al., 2009)
15.	UV/peroxydisulfate oxidation	2,2,3,3-tetrafluoro-1-propanol	Square shallow dish-like chamber made by SS 304 (20 cm × 20 cm × 5 cm) having capacity of 1 L equipped with 13 W UV lamps	pH: 1.5-10; $[persulphate]_0/[TFP]_0$: 0-8; UV lamp: 1-3;	Above 99.5% TOC was reduced in 60 min was observed at specific operating conditions.	(Shih, et al., 2013)
16.	Ultraviolet activated persulfate	Phenol	3 L reaction flask equipped with 15W mercury lamp	Reaction time: 1 h; pH: 3-10; SPS/phenol molar ratios (i.e., 8.4 or 84 mM of SPS to 0.5 or 5 mM of phenol	High initial persulfate concentration (i.e., 84 mM) and a lower initial phenol concentration (i.e., 0.5 mM) resulted in rapid and complete phenol degradation within 20 min	(Lin, et al., 2011)
17.	Ultraviolet activated persulfate	Phenol	1900 mL capacity cylindrical batch photoreactor	Initial concentrations (5–30 mM for PS and PMS; 5–40 mM for H_2O_2); pH:3	Apparent phenol degradation rate constants varying between 0.069±0.002 – 0.382±0.003 min^{-1} with	(Olmez-Hanci, et al., 2013)

					complete TOC removals (P97%) under optimized condition	
18.	Persulfate ions photolysis	Acetic acid	5L cylindrical batch reactor	pH: 2-11; $[S_2O_8^{2-}]_i$ = 1755 μM	Acetic acid is oxidized by $SO_4^{-\cdot}$ radicals without significant formation of intermediate by-products. Maximum acetic acid degradation occurred at pH 5.	(Criquet, et al., 2009)
19.	Ultraviolet activated persulfate	Tylosin	NA	Volume of sample: 100 ml; Peroxydisulfate conc^n: 0.5 to 20 mM; Tylosin conc^n: 20 to 80; pH: 2.4 to 9.8.	More than 90% removal was observed when peroxydisulfate was added to the solution in optimum levels of tylosin and peroxydisulfate concentration.	(Rasoulifard, et al., 2012)
20.	Ultraviolet activated persulfate	Sulfamethazine	Stainless steel cylindrical reactor (id. dia. of 70 mm and height of 300 mm)	Mercury lamp 15 W; 1000 mL solution of SMT having initial conc^n: 0.02 mM); $K_2S_2O_8$ (0.05–0.5 mM)	Highest mineralization extent was accomplished at pH 11 and Degradation was found to be 96.5%.	(Gao, et al., 2012)
21.	PS/Fe(II)/UV-Vis	Carbamazepine	Stirred cylindrical closed cells (40 mm id; 25 mm high, made of Pyrex glass	Initial CBZ concentration : 50 mM; 1500W Xenon lamp source	It was observed that efficiency of CBZ abatement compared to direct photolysis and 60% of the initial concentration of CBZ was removed in 1 h with a k_{app} of 5.41×10^{-3} min^{-1}.	(Ahmed, et al., 2014)

22.	Bimetallic and Trimetallic iron-based systems for persulfate activation	Sulfamethoxazole	20 mL Pyrex vials; trimetallic systems (AgCoFe and CoAgFe)	[SMX]0 = 39.5 µM, [PS]0 = 1.0 mM. Reaction time: 1 – 4 hr	TOC removal was close to 58%.	(Ayoub, et al., 2014)
23.	Fe(II)-EDTA activated persulfate	Orange G	Effective volume of 250 mL; Graphite rods (50.0 mm in length and 8.0 mm diameter)	$K_2S_2O_8$ from 0.0 to 8.0 mmol L^{-1}; pH: 3-9; EDTA concentrations were 0.0 – 2.0 mmol L^{-1}.	Under an optimal condition, OG removal rate was found to be 97.4%	(Niu, et al., 2012)
24.	Fe(II)-EDDS activated persulfate	Orange G	Batch mode experiments performed in a 150 mL Erlenmeyer flask	50 mL of OG; initial OG concentration: 0.25 to 2.5 mM. Temperature: 25 ^{0}C Reaction time: 180 min; pH: 3- 10	Decolorization up to 71.8% due to the insufficient PS dosage was noted.	(Han, et al., 2014)
25.	Fe^{2+}/heat/$S_2O_8^{2-}$	Antimicrobial micropollutants	Polytetrafluoroethylene (PTFE) tubes (50 mL capacity)	$S_2O_8^{2-}$ = 22.7 mM and $Fe^{2+}/S_2O_8^{2-}$ = 0.5 ; Temperature: 75^{0}C Reaction time: 120 min.	Degradation rates of OTC, CIP, and TCS were found to be 95%, 84%, and >99%, respectively. And overall rate of solubilization of the metal and the rate of precipitation of phosphate were 53% and 74%, respectively.	(Oncu, et al., 2015)
26.	Heat and metal ions co-activated persulfate	p-Nitrophenol	50 ml sealed vial with an initial PNP concentration of 0.72 mmol L^{-1} and $Na_2S_2O_8$ concentration of 30 mmol L^{-1}	Reaction temperature: 25-90 ^{0}C; metal ions (Cu^{2+}, Fe^{2+}):PS viz. 1:100, 1:10, 1:1	TOC removal efficiency reported to 85.81% at 70^{0}C	(Zhang, et al., 2015)

27.	Persulfate activated by ferrous ion	Diesel	Volatile organic analysis vials (40 mL)	2 g of the contaminated Soil; 10mLof the oxidant solution	Oil was removed by approximately 60% in 150 days of reactio	(Yen , et al., 2011)
28.	Irradiation / Persulfate	Micropollutants	Continuous flow reactor (depth: 1 cm, width: 1.5 cm, volume under the beam: 3.75cm^3).	Initial persulfate Conc^n (500–2000µM) were irradiated at 30-75 Gy	500µM persulfate improved the degradation of BT, IB and Pg by 17%, 36% and 24% respectively	(Roshani, et al., 2011)
29.	Microwave-induced persulfate	Perfluorocarboxylic acids	Microwave digestion system	The reaction was carried out at 60 ^{0}C (45W microwave power), 90 ^{0}C (70Wmicrowave power) and 130 ^{0}C (140W microwave power); dosages of persulfate (5–50 mM); pH: 2-11..5	Decomposition rate in acidic conditions is 1.1–7.4 times faster than in alkaline condition. Degradation was around 78%.	(Lee, et al., 2009)
30.	Microwave-enhanced persulfate	Landfill leachate	Microwave reactor	Microwave power (128–775W); was added in to a 50mL sample to have persulfate ion ($S_2O_8^{2-}$) concentrations of 952, 2381, and 4762 mg/L, respectively; pH:3-9	The results showed that total organic carbon (TOC) removal of 79.4%, color removal of 88.4%,	(Chou, et al., 2015)
31.	Microwave-activated persulfate	Acid Orange 7	Modified domestic MW furnace equipped with 500-mL Pyrex three-necked flask reactor	AO7 solution (250 mL); Initial Conc^n: 100-1000 mg/L; Reaction time: 11 min; SPS/AO7 was 10:1; 20:1; 50:1; or 100:1.	It was observed that almost complete color was eliminated and COD was removed between 83%–95%.	(Shiying, et al., 2009)
32.	Microwave-activated persulfate	Sulfanilic acid	NA	100 mL of SA solution having conc^n of 50 mg L^{-1};	In the presence of GAC, PS decreased rapidly by	(Wei, et al., 2012)

				pH: 3-8; GAC doses: 20-40 g/L	MW and 80% of PS decayed within 30 s.	
33.	Microwave-activated persulfate	Sulfamethoxazole	Closed-vessel microwave digestion system can operated up to power: 1200 W, Temp: 300 ^{0}C and Pressure: 35 bars	SMX Conc^n (0.5 mM); pH: 4.6, 7.0 and 8.7; 20 mL of SMX solution with 0.5 mL appropriate concentrations of persulfate was held in 100 mL TFM vessel; Temperature:60, 90, 130 ^{0}C	The results indicated that SMX was completely degraded by MW/PS and pseudo-first - order kinetics was observed. SMX degradation occurred with higher reaction rate and shorter process time	(Qi, et al., 2014)
34.	Electro-activated persulfate	Dinitrotoluenes	Double jacket cylinder equipped with a magnetic stirrer; cathode and anode plates were made of platinum with dimensions of 20 mm×20 mm×1 mm	Reaction volume: 450 mL of wastewater; Electrodr potential: 3-6 v; Temperature: 303-318 K; Persulphate conc^n: 07 - 1.7wt%; pH: 0.5-3.0	Complete removal of DNTs under the optimal conditions of E.P. = 6 V, T = 318 K, N2 = 150 mL min^{-1}, pH = 0.5 and persulfate anion concentration = 1.7 wt%. TOC removal was observed to be 95%.	(Chen, et al., 2014)
35.	Sonoelectro - activated persulfate	Aniline	Double jacket cylinder equipped with a magnetic stirrer; cathode and anode plates were made of platinum with dimensions of 20 mm×20 mm×1 mm	450 mL of wastewater with aniline concentration of 75 mg L^{-1}; power intensity (160–320 W); electrode potentials of 3 V up to 6 V; pH values of 3.0-7.0; persulfate concentrations of 1.0 wt% up to 3.0 wt%	Aniline contaminants were removed completely under the optimal conditions of E.P. = 6 V, T = 318 K, persulfate anion concentration = 2.5 wt%, pH = 3.0 and N_2 = 150 mL min^{-1}. TOC removal was observed to be 95%.	(Chen, et al., 2015)

36.	Persulphatre activation using temperature, citrate - chelated iron, alkaline conditions and persulfate-H_2O_2 binary mixtures	PAHs	40-mL borosilicate glass volatile organic analysis (VOA) vials	Temperature: 40, 50, 60^0C; Citrate-chelated iron (mole ferrous iron/mole persulfate = 1/10, 1/4, 1/2); Alkaline conditions (pH 10,11, 12), and persulfate-H_2O_2 binary mixtures (mole H_2O_2/mole $Na_2S_2O_8$= 1/100, 1/10, 1/1)	Degradation was observed to be 99%. And among different methods, thermal activation was found to be most effective way for persulfate activation compare to other activation methods studied in present study.	(Zhao, et al., 2013)
37.	Persulfate activated with zero-valent iron	p-Chloroaniline	Batch experiments were performed in rotary shaker at 25 ^{0}C and 125 rpm.	PCA of 0.5 mL; Initial concentration: 0.05 mM; pH: 4-11; ZVI Dosage: 0.35, 0.7, 2.0, 3.5 and 5.0 g L^{-1} ZVI; Temperature: 15, 22.5, 30, 40 and 50 ^{0}C.	PCA degradation was 100 % at 4.0 pH and was achieved within 12 min. Four intermediates were detected and identified as aniline, N-(4 -chlorophenyl)-p -phenylene di-imine, 1-(4-Chlorophenyl)-3-phenlurea and 5-chloro-2-((4- chlorophenyl) diazenyl) phenol respectively.	(Hussain, et al., 2012)
38.	Persulfates activated by carbon nanotubes	Phenol	100-mL Pyrex vials	Temperature: 20 ± 2 ^{0}C; pH 3–10: Reaction time:60 min; 0.1 g/L CNT	The activated persulfate system catalyzed by CNT selectively oxidized organic compounds, particularly exhibiting higher reactivity toward phenolic compounds and several pharmaceuticals.	(Lee, et al., 2015)

					100% removal of phenol was obtained.	
39.	US/Fe^0/PS	Sulfadiazine	400 mL of reaction solution in jacket-glass reactor	US input power: 20, 40, 90 and 140W; sulfadiazine: 10-20 mg L^{-1}; $[PS]_0$= 1.84 mM; [PS]:$[Fe^0]_0$= 1:0.2 to 1:1; pH: 3-10;	The degradation efficiency of SD was 99.1% at 90 W US. With Increase in temperature from 10 to 50 ^{0}C, the rate constant k_{obs} increased from 3.56 to 27.39 h^{-1}.	(Zou, et al., 2014)
40.	Ferrous-activated persulfate	Arsenic(III) and diuron	Batch reactions were performed at ambient temperature in a 250 mL glass reactor	100 mL reaction solution; $K_2S_2O_8$: 0.1, 0.2, 0.5, 1.0 and2.0 mM; molar ratio of $S_2O_8^{2-}$/Fe(II)/diuron: 20:10:1	Degradation of arsenic(III) and diuron was 75% and 96.9% respectively.	(Zhou, et al., 2013)

2.9. Parameters affecting Integrated Ozonation Processes

2.9.1 Effect of Ozone Flowrate

Ozone flowrate profoundly influences the mineralization of recalcitrant organic compounds by ozonation and integrated ozonation process. It is evident from previous research work that there is increasing trend in removal efficiency of organic matter with an increase in flow rate of ozone (Gao, et al., 2012). Ozone flowrate increases the efficacy of process because as ozone flowrate increases, number of ozone molecule available per unit volume of wastewater increases which thereby increases the mineralization efficiency of recalcitrant organic compounds present in wastewater (He, et al., 2009).

Chen, et al., 2009, reported effect of varying ozone dosage on decolorization of two dyes, Oange 13 and Blue 19 at ozone dosage of 1.3, 2.7, and 4.0 gL^{-1} respectively. It was reported that at higher pH dosage decolorization efficiency was enhanced. Further, remarkable enhancement in decolorization efficiency was resulted when ozone dosage was increased from 1.3 gL^{-1} to 2.7 gL^{-1}. Moreover, no major improvement in decolorization was reported when ozone dosage was increased from 2.7 gL^{-1} to 4.0 gL^{-1}.

Investigations of Sevimli, et al., 2002, on the treatment of wastewater collected from treatment plant revealed that on increasing ozone dosage would have increased efficiency in removal of COD, color, and DOC respectively. It was further reported that logarithmic relationship between ozone dosage and rate constants established. Increase in value of rate constant was resultant of increased ozone flowrate which follows two film theory. According to two film theory, overall mass transfer mechanism follows following steps: (i) diffusion of ozone through gas phase to interface between gas and aqueous phases (ii) transport across interface to the aqueous phase boundary (iii) transfer into bulk aqueous phase. Increased ozone dosage will ultimately lead to increased rate of reaction and hence enhanced mass transfer. Linda Zou, et al., 2008, has reported that increase of ozone dose significantly enhances the efficiency of color removal from actual-treated wastewater and it was found that color removal was rapid at the first 10 min in the oxidation process. However, the removal rate of color was increased with increasing ozonation dosage.

2.9.2 Effect of Initial pH

Initial pH of solution plays a vital role in deciding mineralization efficacy of refractory organic pollutants by ozonation and integrated ozonation processes. Literature gives an extensive overview regarding the effect of pH on mineralization of dye molecules. Mineralization of dye molecule is mainly based on two mechanisms, either by direct oxidation of molecular ozone or by radical oxidation favored by hydroxyl radicals. Alkaline pH is favorable for decomposition of molecular ozone and formation of hydroxyl radicals. However**,** it is worthy to note that some contradictions may also be available in literature and it is purely due to structure and bonds of dye molecules, for example, mineralization of RB5 is favourable at high pH values (alkaline conditions) whereas, in case of AR-151 higher rate of dye mineralization in acidic and basic conditions were reported and in neutral condition it shows lowest mineralization efficiency (Pachhade, et al., 2009; Pirgalıoglu, et al., 2009).

S.S. Abu Amr, et al., 2013, reported that at elevated pH, the reactivity of Persulfate is enhanced resulting in a generation of sulfate radicals which thereby increases the mineralization efficiency of the process. At elevated pH sulfate radical reacts with water and generate hydroxyl radicals resulting in increased amount of oxidizing agent and thereby giving complete mineralization of recalcitrant organic compounds.

2.9.3 Effect of UV Intensity

It is evident from the investigation of various researchers that UV light intensity plays a crucial role in enhancing the performance of ozonation and integrated ozonation process. UV plays a role of a catalyst in generating an excess amount of hydroxyl and sulfate radicals (Khataee, et al., 2010; Xu, et al., 2012; Torres-Luna, et al., 2013).

B. W. Liu et al. 2004 has reported work on decolorization of dye finishing wastewater by UV/Ozone process. Information given by author reveals that UV light act as an initiator for degradation of ozone into hydroxyl radicals and hence degradation of organic pollutants was enhanced leading to improved efficiency of process. To carry out investigation UV light of two different intensities were (i.e. 20W and 40W) employed to determine its effect on wastewater and it was found that at UV intensity of 20W 35 min was required to reduce color from 4,300 to 180 ADMI using 20W of 185 and 254nm UV. In addition, further increasing UV intensity to 40W reduced the time required to decrease the color from 3,820 to 150. P. Paraskeva, et al., 2006, studied the effect of UV on secondary municipal effluent by UV and results revealed that increased UV irradiation reduced number of total E.coli. It was further reported that on increasing UV irradiation from 300 mWs/cm^{2}ml to 500 mWs/cm^{2}ml, E.coli was reduced from 100-200 CFU/100 ml to 10CFU/100 ml.

2.9.4 Effect of Persulfate Dosage

Persulfate dosage is among one of the most vital parameter which decide mineralization efficacy of organic pollutants by O_3/UV/Persulfate process. Persulfate dosage has a positive effect on the effectiveness of Persulfate process. It is evident from past studies that as Persulfate dosage increases generation of sulfate radical also increases which lead to efficient degradation of organic pollutants into environmentally acceptable end products (Abu Amr, et al., 2013). However, it is praiseworthy to note that optimum dosage of Persulfate has to be identified, as increasing dosage beyond optimum limit will serve as scavenger for present process and reduces its treatment effectiveness (Chu, et al., 2011; Gao, et al., 2012; Abu Amr, et al., 2013).

Chen, et al., 2014, has worked to mineralize dinitrotoluenes in industrial wastewater. The study determined the effect of a change in persulfate dosage on TOC removal activity. It is reported that TOC removal efficiency demonstrated increasing trend with increased concentration of persulfate anions. Additionally, it is worthy to note that increasing persulfate anions above (2.1 wt%) removal rate of dinitrotoluenes was decreased and it was due to side reaction between excess persulfate anions and sulfate radicals. Wen-Shing Chen, et. al., 2015, has studied impact of persulfate anion concentration on the sonoelectrlytic behaviours and it was found that increasing persulfate dosage below 3.0 wt% enhanced the TOC removal efficiency of the process. Nevertheless, it is reported that on increasing persulfate dosage above 3.0 wt% removal rate of aniline was drastically decreased this has attributed to the fact that increase persulfate dosage may act as an inhibitor by reacting with sulfate radicals and thereby reducing efficacy of TOC removal of said process. In addition to this, J. Deng, et al., 2013, has reported the effect of CBZ degradation on three UV- based AOPs. The Author further mentioned that degradation follows pseudo-first-order reaction, with an addition of 0.5 mM oxidant degradation rate was 0.0282 min^{-1} which was increased to 0.1805 min^{-1} on increasing oxidation dosage to ten times. Furthermore, it was also reported that optimum dosage of oxidant has to be selected otherwise excess of oxidant dosage will act as a scavenger and decrease the efficiency of the process.

2.9.5 Effect of Water recirculation Flow

It is significant to know the effect of water recirculation flowrate on the degradation of organic pollutants which eventually governs efficiency of the process. It is apparent from the literature that increase in water recirculation flow will eventually decrease the performance of O_3/UV/PS process. However, in context to above statement it is worthy to note that as flow rate decreases, residence time increases and amount of hydroxyl and sulfate radical per unit volume of effluent also increases which ultimately enhances the treatment competence of specified process (Soares, et al., 2006; Tisa, et al., 2014).

2.10. Outcome of Literature Review

Reviewing literature and after studying work of various researchers, it can be concluded that textile effluents containing dyes need to be adequately treated before final disposal. Conventional methods such as primary, secondary and tertiary treatments which involve adsorption, coagulation, flocculation, etc. are ineffective treatment technologies for effluents generated from textile and dye industries. Advanced oxidation processes (AOPs) serves to be potential alternative to treatment to conventional processes, and it can effectively treat colored effluents into environmentally acceptable end products. However, the efficiency of AOPs depends on various operating parameters and as well as on characteristics of pollutant. Among various available AOPs ozonation was found to be an attractive alternative as it removes recalcitrant organic compounds completely. Integration of ozonation process with other AOPs helps in enhancing treatment efficacy of the process. Nevertheless, it was established by reviewing work of previous researchers that operating parameters play a crucial role in deciding the effectiveness of any AOPs. In ozonation and integrated ozonation process operating parameter which profoundly affects process efficiency are ozone flow rate, pH, water recirculation rate, UV intensity, persulfate dosage and initial dye concentration of the solution. Additionally, reactor setup also affects the process efficacy due to change in contacting pattern of ozone and wastewater which ultimately affects the degradation of persistent organic compounds or recalcitrant organic compounds.

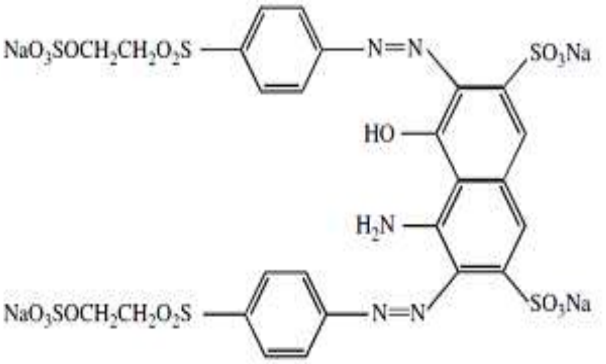
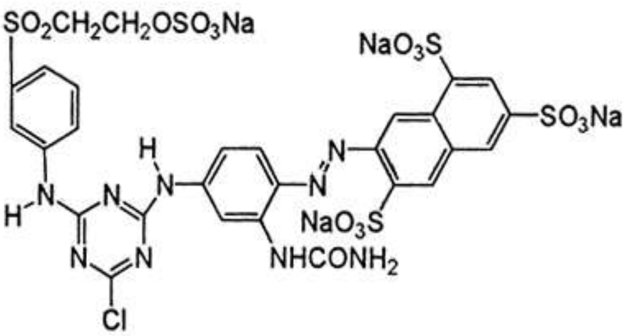
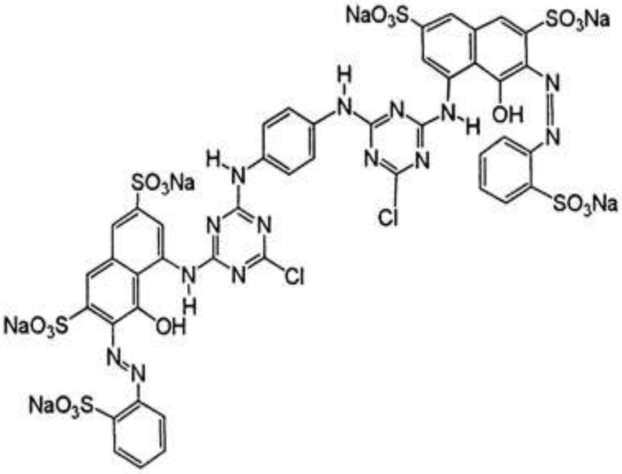
3 Materials and Methods

Literature review helped in concluding that ozonation and integrated ozonation can be selected as a treatment technique among various available AOPs. Present chapter covers various chemicals, and protocols required for the research. Moreover, it also explains three different reactor configurations chosen to conduct present study. Various analytical methods which are adopted to analyze efficiency of selected processes and performance of the chosen reactor configurations are also included in this section. Design of experiments is utilized for deciding sequence of experiments are also discussed under this section.

3.1 Materials

Present work focuses on ozonation and integrated ozonation process (O_3/UV, O_3/UV/PS) for treatment of synthetic dye wastewater. Three different dyes used in the present study are Reactive Black 5, Reactive Red 120, and Reactive Yellow 145. In the present study, three different processes namely: O_3, O_3/UV, and O_3/UV/PS were employed to determine most efficient process in terms of degradation of dye along with cost-effectiveness. Additionally, three different reactor configurations, namely, Bubble column, Bubble column with recirculation and Venturi were also utilized and compared on the basis of degradation efficiency of dye for all three selected processes and dyes.

Table 3.1 Characteristics of dyes studied in this work (Arslan, et al., 2000; Zhang, et al., 2004; Song, et al., 2008)

Dye Name	Chemical Structure	Other Details	
Reactive Black 5		Molecular Formula Molecular weight CAS number	$C_{26}H_{21}N_5Na_4O_{19}S_6$ 991.82 g mol^{-1} 17095-24-8
Reactive Yellow 145		Molecular Formula Molecular weight CAS number	$C_{28}H_{20}ClN_9Na_4O_{16}S_5$ 1026.25 g mol^{-1} 93050-80-7
Reactive Red 120		Molecular Formula Molecular weight CAS number	$C_{44}H_{24}Cl_2N_{14}Na_6O_{20}S_6$ 1469.98 g mol^{-1} 61951-82-4

Three different dyes used for conducting present study were purchased from Evergreen Industries (Vatva, Ahmedabad) and used without any further purification. Characteristic of dyes used in the present study are shown in Table 3.1. All reagents and chemicals used for conducting present experimental study were of analytical grade. Potassium Iodide (KI) (Ranbaxy Laboratory Limited), Sodium Thiosulphate ($Na_2S_2O_3$) (High Purity Laboratory

Chemical), Sodium hydroxide (NaOH), Sulphuric acid (H_2SO_4) (S.D. Fine Chem. Limited), and Sodium persulfate ($Na_2S_2O_8$)(S.D. Fine Chem. Limited) were purchased from respective vendors. Phillips (TUV G5 T5 11W) UV Light was used as UV light source.

3.2 Methods

Experiments were carried out at room temperature in a glass reactor with an effective volume of 3L volume. Ozone was produced via Corona Discharge Ozone generator supplied by Aquazone solutions, Ahmedabad. Pure oxygen was fed to the ozone generator from oxygen cylinder (Tapan Oxygen, Ahmedabad). Ozone was supplied to the reactor via silicone tubing. To measure inlet and outlet ozone concentration, ozone analyzer was used which was supplied by Eltech Engineers, Mumbai. Sintered glass disc (Dia = 3 cm) was used to introduce moderately fine bubbles of ozone in bubble column and was purchased from Associated Scientific Mfg. Industries, Kolkata. Venturi was procured from Ozone solutions., USA.

3.3 Experimental protocols

The complete experiment work was divided in to two groups as preliminary study and detailed studies. The sequence followed for carry out present research work are as follows.

Preliminary studies

As a part of preliminary studies some of the experiments were performed. The purposes of preliminary studies were to select (1) Appropriate process and process parameters (2) Compare reactor performance (3) Model pollutant.

A. For selection of appropriate process and process parameters, experiments were conducted using O_3, O_3/UV and O_3/UV/PS processes in Bubble column reactor for RB5. Parametric study was carried out in Bubble column using RB5 as a model pollutant.

B. Few experiments were performed on different reactor configuration by keeping process parameters constant.

C. As a model pollutant, reactive dyes were chosen.

Detailed studies

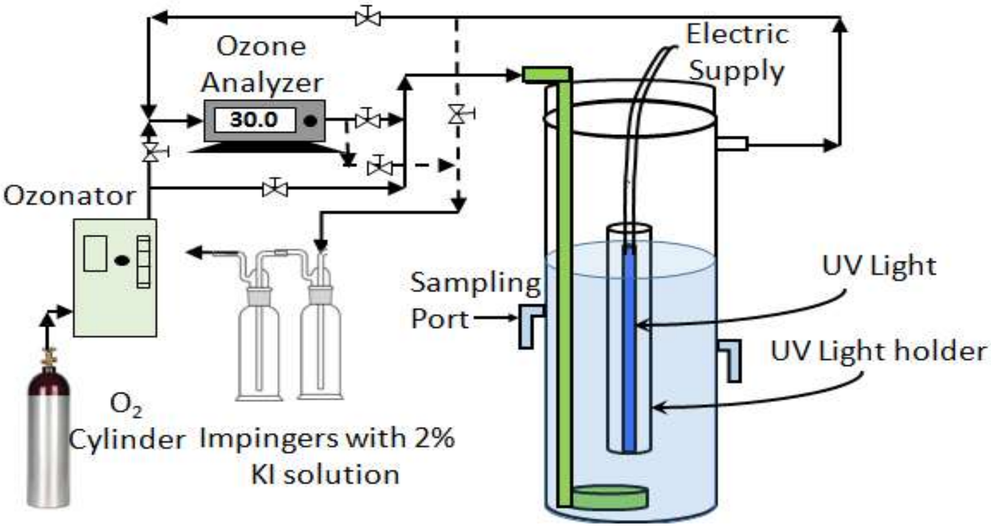
1. Design of experiments was utilized to decide random experiments to compare reactor configuration namely, Venturi and Bubble column with recirculation.

    a. 1st set of experiments were performed by considering pollutants (reactive dyes) itself as a process variable
    b. 2nd set of experiments were performed on individual dye
2. Performing experiments, considering best suitable process parameters and reactor configuration to get degradation efficiency.

3.4 Reactor Configuration

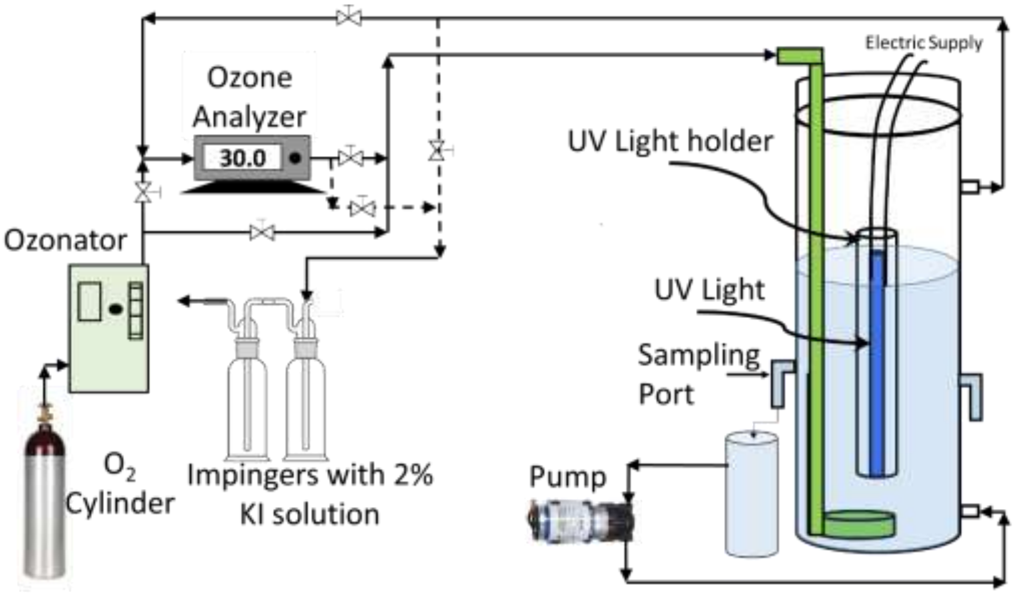
All the experiments of present study were carried out in a continuous recirculation mode except Bubble column reactor. The inner diameter and height of the reactor were 0.07 m and 0.87 m respectively. The reactor configuration is as shown in Figure 3.1. Ozone was generated by supplying oxygen to Ozonator (Aquazone Solutions, Ahmedabad. India). Oxygen flow meter available for carrying out present study has maximum capacity of 60 LPH, thereby restricting the present study to the Solutions maximum allowable ozone flowrate of 1.86 g hr^{-1}. Ozone flowrate was set in the range of 1.35 to 1.86 g hr^{-1}. Water recirculation flow was in rage of 0.5 – 2.85 LPM. For intimate contact of pollutant and ozone different reactor configuration has been analyzed, (1) Bubble column, (2) Bubble column with recirculation and (3) Venturi. Initial pH of solution was adjusted using 1 N NaOH and 1 N H_2SO_4 solution. The excess ozone was trapped in 2% KI solution, and was measured by Idometric method (Eaton, et al., 1998). For conducting all experiments 3L of synthetic wastewater was utilized. Initial concentration of dye has been varied from 500 to 1500 mgL^{-1}.

Figure 3.1 (a) represents setup of Bubble column reactor. The reactor configuration was same as described above with an additional arrangement of sampling port which was attached near bottom of reactor. Ozone was introduced in Bubble column in the form of fairly fine bubbles using sintered glass disc. Ozone cylinder was connected to ozonator to generate ozone and it was supplied into reactor. Impinger bottles filled with 2% KI solution was attached with outlet gas port of reactor to trap unreacted ozone and determine amount of unreacted ozone in outlet gas concentration. Additionally, ozone analyzer was attached to measure inlet and outlet ozone concentration.

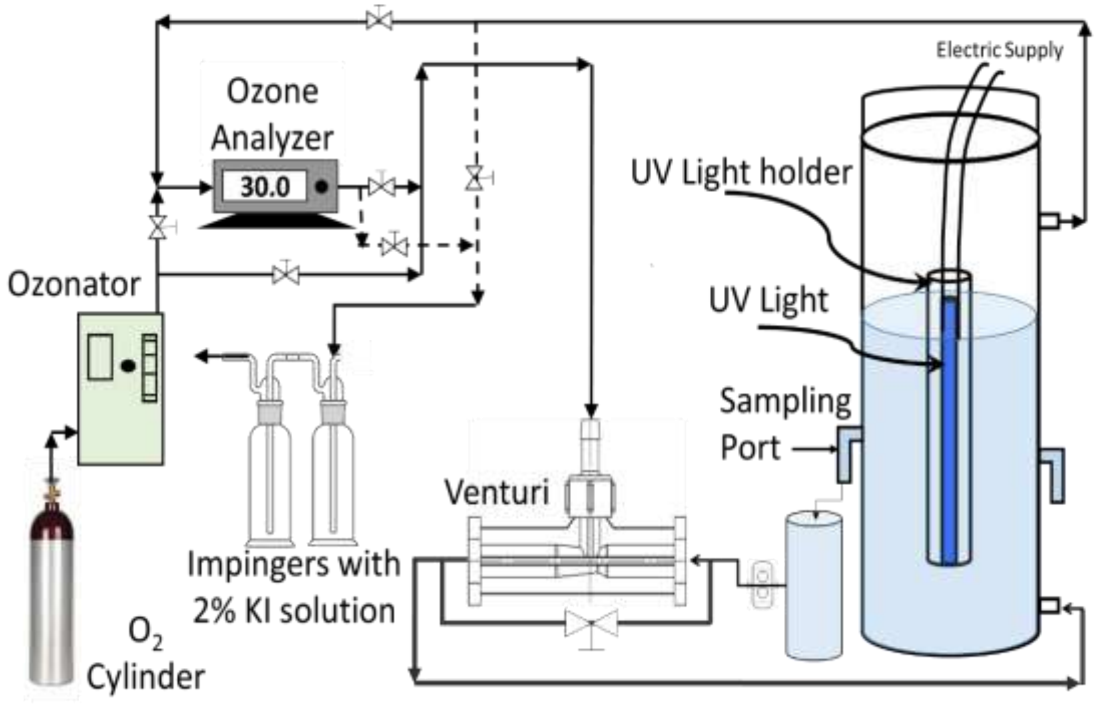


3.1 (a). Bubble column reactor

Figure 3.1 (b) represents setup of Bubble column with recirculation reactor. In case of Bubble column with recirculation reactor dimensions of reactor remains same as discussed earlier. Recirculation of synthetic wastewater into reactor was achieved using pump which was connected at sampling port near middle of reactor. Oxygen cylinder was connected to ozonator to generate ozone and it was supplied into reactor through sintered glass disc. Off gases were trapped in impinge bottles containing 2% KI solution for determining unreacted ozone. Ozone analyzer was used to measure inlet and outlet ozone concentration.



3.1 (b). Bubble column with recirculation



3.1 (c). Venturi reactor

Figure 3.1 Reactor Configuration

Figure 3.1 (c) represents setup of Venturi column reactor. Reactor configuration was same as utilized in earlier two cases. Sampling port attached near middle of reactor which is attached to a tank connected with motor followed by Venturi. Ozone was mixed with synthetic dye wastewater using recirculation loop having Venturi arrangement. Synthetic wastewater was drawn from middle of reactor and ozone was introduced in Venturi which was installed at outlet of the pump. Furthermore, ozone analyzer was employed to determine inlet and outlet ozone concentration.

3.5 Analytical measurements

To analyze efficacy of treatment technologies various analytical measurements were adopted. Following analytical measurements which were utilized during present study.

3.5.1 Measurement of pH

According to literature review, efficiency of organic matter removal depends on initial pH of the solution. Therefore, for each experiment, pH of untreated and treated dye solution at different time interval was measured with a calibrated digital pH meter (Hanna - Hi 96107, Piyush Chemicals).

3.5.2 Organic matter removal measurements

Degradation of any recalcitrant organic pollutants is measured by means of alteration of those recalcitrant organic pollutants into biodegradable compounds i.e. CO_2 and H_2O. The difference between total organic carbon present in initial solution of wastewater containing dye and treated solution is an evaluation of carbon transformed into carbon-di-oxide. During experiments samples were taken at predefined time interval and samples for TOC for all experiments were collected on same sampling time. TOC samples were analyzed for non-purgeable organic carbon (NPOC) by acidifying with 1N HCl. Samples used for the fractionation to determine organic functionalities were acidified to pH<2, followed by a nitrogen purge, digestion in the presence of a Pt catalyst (supported by Al_2O_3) at high temperature, and quantitative analysis of the produced CO_2.

The removal of organic matter was calculated from TOC measurements as follows (Shin, et al., 1999):

$$\%TOCremoval = \frac{TOC_0 - TOC_f}{TOC_0} \tag{3.1}$$

Where, TOC_0 corresponds to the initial value and TOC_f is the value at time t. TOC was measured by TOC Analyzer TOC-$V_{CPH/CPN}$ supplied by Shimadzu Corporation, Japan.

3.6 Oxygen-equivalent chemical-oxidation capacity (OCC)

OCC is a parameter used to assess the performance of various AOPs. It computes arbitrary units of oxidant added in wastewater to degrade pollutants. OCC is defined as kg O_2 that are equivalent to the amount of oxidant reagents used in each AOP to treat unit volume (m^3) of wastewater (Canizares, et al., 2006). OCC is related based on kind of oxidant used in AOPs applied in this study according to Eqs. (3.2)-(3.4) (Louhichi, et al., 2008; Guin, et al., 2014). All equations were formed from stoichiometric balance of the no. of electron exchanged in the reduction of the respective oxidants.

$$1OCC(kgO_2m^{-3}) = 1.00[O_3](kgO_3m^{-3}) \tag{3.2}$$

$$1(kgO_2m^{-3}) = \frac{\left[I_0(cm^{-2}s^{-1}) \times A(cm^2) \times t(s) \times 10^6(cm^3m^{-3})\right]}{6.023 \times 10^{26}(kmol^{-1}) \times V(cm^3)} \frac{1kmolO_2}{4kmol^-} \frac{32kgO_2}{kmolO_2} \tag{3.3}$$

$$1OCC(kgO_2m^{-3}) = 0.0701[Na_2S_2O_8](kgNa_2S_2O_8m^{-3}) \qquad - \tag{3.4}$$

3.7 Electrical Energy per Order (EE/O)

In addition, parameter for comparing and analyzing effectiveness of various AOPs was performed on the basis of electrical energy consumption of each AOP. It is measure of electric cost when different energy doses such as UV light, ozone and Persulfate dosage are used or applied for mineralization of pollutants in constant volume. James R. Bolton, et al., 1996, has explained EE/O as “Electrical Energy per Order (EE/O) is the electrical energy in kilowatt hours (kWh) required to bring about the degradation of a contaminant by one order of magnitude in 1 m^3 (1000 L) of contaminated water or air”.

$$\frac{EE}{O} = \frac{P * t * 1000}{V * 60 * \log(C / C_O)} \tag{3.5}$$

where,

EE/O = Electric Energy, KWh or KWh /order of contaminant/m^3.

P = Rate of power of AOP (KW).

t = Treatment time (min).

V = Volume of wastewater treated in time t, (L).

C_O = Initial concentration of contaminant (mol/L).

C = Final concentration of contaminant (mol/L).

3.8 Design of Experiments

Design of experiments was utilized to get random experiments for comparing reactor configuration in selected process. Taguchi method was applied for deciding minimum number of experiments. The factors and level chosen in experiments are shown in Table 3.2 and 3.3. L18 orthogonal array mixed level design was selected for chosen variables with different levels for each factor. Appendix 2 shows Taguchi design for O_3/UV/PS process. Based on Taguchi design, the experiments were carried out and %TOC removal observed as response. Experimental data were analysed using Minitab 17 statistical software.

Table 3.2 Factors and their levels in experiment for all reactive dyes in different reactor configuration

Factor	Parameter	Level 1	Level 2	Level 3
Factor A	Water recirculation flow, LPM	0.5	2.85	
Factor B	Dye	RB5	RR120	RY145
Factor C	Initial pH	4	8	12
Factor D	Ozone flow, LPH	40	50	60
Factor E	UV Intensity, W	22	44	66
Factor F	TOC:PS ratio	1:20	1:40	1:60
Factor G	Initial Concentration, mgL^{-1}	500	1000	1500

Table 3.3 Factors and their levels in experiment for individual dyes in different reactor configuration

Factor	Parameter	Level 1	Level 2	Level 3
Factor A	Water recirculation flow, LPM	0.5	2.85	
Factor B	Ozone flow, LPH	40	50	60
Factor C	Initial pH	4	8	12
Factor D	UV Intensity, W	22	44	66
Factor E	TOC:PS ratio	1:20	1:40	1:60
Factor F	Initial Concentration, mgL^{-1}	500	1000	1500

4 Results and Discussion

The present chapter includes results of experiments for degradation of dyes using ozone based AOPs in TOC removal performed according to methods described in Chapter 3. Minitab 17 was used to programme a Taguchi orthogonal array in order to design the experiments. O_3, O_3/UV and O_3/UV/PS processes were performed in different reactor configuration for TOC removal. Additionally, some of the parameters such as OCC, EE/O, kinetic rate constants were calculated using experimental data and further compared with the reported results. Results were utilized to select best operating parameters and reactor.

4.1 Preliminary Studies

For the selection of process and operating parameters few experiments were performed in beginning of the present investigation, as a part of preliminary studies. The discussion in this section is related to the experiments performed for screening of parameters using bubble column reactor for all three selected processes for degradation of RB5. O_3/UV/PS process was selected for comparing the effectiveness of chosen reactor configuration. Finally, assessing performance of selected processes, Venturi reactor was utilised to conduct present experiments on RB5.

4.1.1 Effect of Ozone Flowrate

As discussed in previous chapter, in ozonation and integrated ozonation process, ozone flowrate has potential to influence the mineralization of recalcitrant organic compounds. Results compiled by various researchers revealed that increase in ozone flowrate will have positive impact on removal of recalcitrant organic compounds (Matheswaran, et al., 2009). It is evident that as ozone flowrate increases, driving force to transfer of ozone in dye solution increases (Adiraju, et al., 2016) also, amount of molecular ozone and hydroxyl radicals also increases which thereby increases the mineralization rate (He, et al., 2009). However, it is worthy to note that same ozone flowrate will have different removal efficiencies for ozonation and integrated ozonation processes. Oxygen flow meter available for carrying out present study has maximum capacity of 60 LPH, thereby restricting the present study to the maximum allowable flowrate of 1.86 gh^{-1}. As ozone flowrate was increased from 1.35 gh^{-1} to 1.86 gh^{-1}, there was remarkable increase in mineralization efficiency of organic compounds. In present study, experiments were conducted in Bubble column reactor with 500 mgL^{-1} initial dye (RB5), 6 pH, UV light of 11W and having 1:10 TOC: PS ratio.

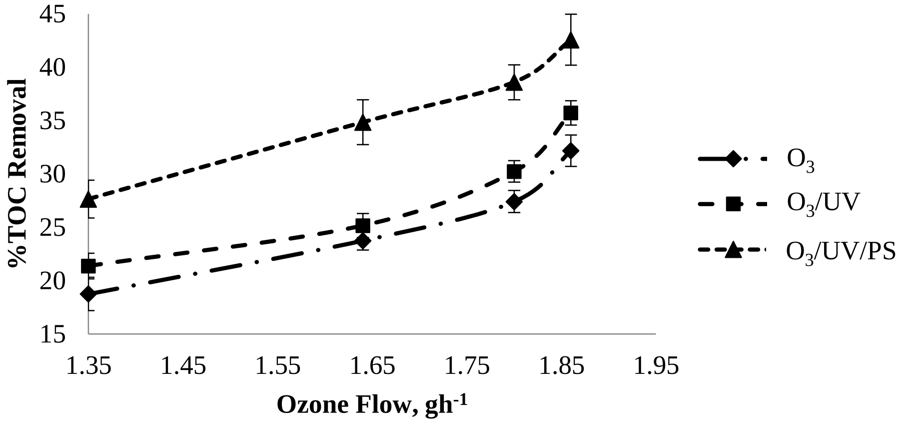


Figure 4.1 Effect of ozone flowrate on TOC Removal

(Process conditions: Dye: RB5; Reactor configuration: Bubble column; Initial dye conc^n: 500 mgL^{-1}; pH:6; UV intensity:11W; TOC:PS ratio: 1:10; Reaction time: 90 min)

Its self-evident from given Figure 4.1 that as flowrate of ozone was increased from 1.35 gh^{-1} to 1.86 g/h^{-1}, %TOC removal was considerably increased in all three processes. Maximum removal efficiency of TOC was observed in case of O_3/UV/PS with 43% removal at 1.86 g/h^{-1}. Similar findings are reported by Li, et al., 2005 in which effect of ozone dosage was determined for removing organic pollutants from secondary effluents by utilizing ozonation and biological activated carbon and it was found that DOC removal was increased from 51 to 59% on increasing ozone dosage from 3 to 9 mgL^{-1}. Matheswaran, et al., 2009 has investigated effect of ozone dosage on phenol degradation by ozonation process and it was found that %TOC removal was enhanced with increasing ozonation dosage.

4.1.2 Effect of Initial pH

Initial pH of any process plays vital role in deciding efficiency of AOPs (Beltran, et al., 1997; Agustina, et al., 2005). Effectiveness of ozonation and integrated ozonation process is highly influenced by pH of its solution. Researchers from past have reported that high pH favour ozonation process and it augment mineralization of organic pollutants, as at high pH hydroxyl radical generation take place (Adiraju, et al., 2016). In integrated ozonation process additional to hydroxyl radical generation, sulfate radicals are also available to increase the effectiveness of process. In present study, experiments were conducted in bubble column reactor with 500 mgL^{-1} initial dye (RB5), 1.86 gh^{-1} ozone flowrate, UV light of 11W and having 1:10 TOC: PS ratio.

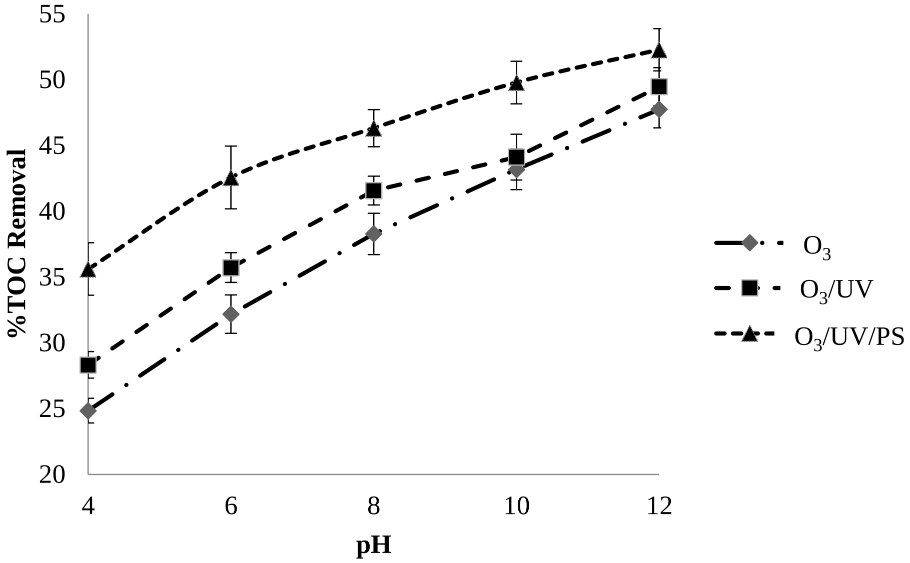


Figure 4.2 Effect of pH on %TOC Removal

(Process conditions: Dye: RB5; Reactor configuration: Bubble column; Initial dye conc^{n}: 500 mgL^{-1}; O_3 flow:1.86 gh^{-1}; UV intensity:11 W; TOC:PS ratio: 1:10; Reaction time: 90 min)

It is noteworthy to mention from the Figure 4.2, that for all three processes pH 12 gives maximum removal efficiency. At pH 12, O_3 process gives 48% TOC removal whereas O_3/UV and O_3/UV/PS gives removal efficiency of 50% and 52% respectively. This is in accordance with results quoted and discussed in available literature that, alkaline pH accelerates the efficiency of ozonation and integrated ozonation processes. S.S. Abu Amr et al., 2015 has reported that at elevated pH, reactivity of Persulfate is enhanced resulting in generation of sulfate radicals which thereby increases the mineralization efficiency of process. At elevated pH sulfate radical reacts with water and generate hydroxyl radicals resulting in increased amount of oxidizing agent and thereby giving complete mineralization of recalcitrant organic compounds. Srinivasan, et al., 2009, has reported degradation of Sandopel Brown BRR dye using ozonation process.

4.1.3 Effect of UV Intensity

UV acts as catalyst to generate hydroxyl and sulfate radicals which are in turn responsible for mineralization of pollutants into environment friendly end products (Cuiping, et al., 2011). It is well reported by investigators from past that increase in UV intensity will augment the efficiency of process (Khan, et al., 2010). In present study, TOC removal as well as concentration reduction was studied for all three processes, i.e. O_3, O_3/UV, O_3/UV/PS.

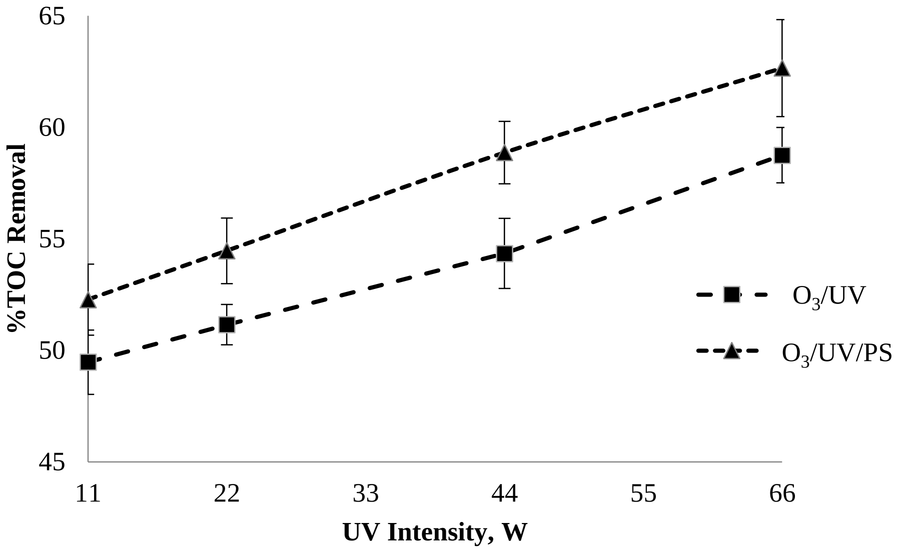


Figure 4.3 Effect of UV intensity on %TOC Removal

(Process conditions: Dye: RB5; Reactor configuration: Bubble column; Initial dye conc^n*: 500 mgL*$^{-1}$*;* O_3 *flow: 1.86 gh*$^{-1}$*; pH:12; TOC:PS ratio: 1:10; Reaction time: 90 min)*

In present study, experiments were conducted in bubble column reactor with 500 mgL^{-1} initial dye (RB5), 1.86 gh^{-1} ozone flowrate, 12 pH and having 1:10 TOC: PS ratio. The intensity of UV light was varied from 11W to 66 W.

Figure 4.3 illustrates the effect of UV light intensity in TOC removal for O_3/UV and O_3/UV/PS process. The Intensity of UV light was increased from 11W to 66 W and it was clearly noticeable from Figure 4.3 that increase in UV intensity enhances the process efficiency. It is worthy to note that for both the processes increasing UV intensity has enhanced removal efficiency of TOC with maximum TOC removal of 59% and 63% at 66W for O_3/UV and O_3/UV/PS process respectively. B. Cuiping et al., 2011 has reported similar findings for removal of Rhodamine B. It was reported that UV act as an initiator to convert ozone into hydroxyl radicals and thereby increasing degradation efficiency for pollutants. Liu, et al., 2004 carried out study on decolorizatoin of dye finishing wastewater using O_3/UV process and it was investigated that increasing UV intensity from 20W to 40W reduces decolorization time by 10 min and it further enhances efficiency of said process.

4.1.4 Effect of Persulfate Dosage

Persulfate dosage is among one of most crucial parameter which decides mineralization efficacy of organic pollutants by O_3/UV/Persulfate process. Persulfate dosage has positive effect on effectiveness of Persulfate process. It is in evident from past studies that as Persulfate dosage increases generation of sulfate radical also increases which lead to effective degradation of organic pollutants into environmentally acceptable end products. However, it is worthy to note that optimum dosage of Persulfate has to be identified as increasing dosage beyond optimum limit which serve as scavenger for present process and reduces its treatment effectives. In present study, experiments were conducted in bubble column reactor with 500 mgL^{-1} initial dye (RB5), 1.86 gh^{-1} ozone flowrate, 12 pH and 66W UV intensity.

Figure 4.4 depicts the effect of TOC:PS ratio in mineralization of RB5 in terms of %TOC removal. Optimum value of TOC:PS ratio obtained in present study is 1:40 and changing this ratio will reduce the efficiency of process drastically. TOC removal of 74% was obtained at TOC:PS ratio of 1:40. Literature supports the above findings also, W. S. Chen et al., 2014 has worked to mineralize dinitrotoluenes in industrial wastewater and determined the effect of change in persulfate dosage on TOC removal activity, and reported that TOC removal efficiency demonstrated increasing trend with increased concentration of persulfate anions.

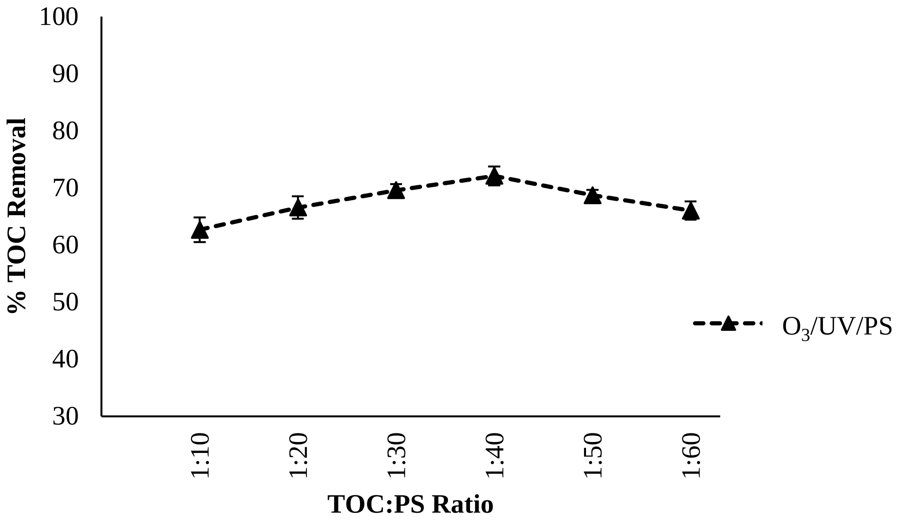


Figure 4.4 Effect of TOC:PS ratio on %TOC removal

(Process conditions: Dye: RB5; Reactor configuration: Bubble column; Initial dye conc^n: 500 mgL^{-1}; O_3 flow: 1.86 gh^{-1}; pH:12;UV intensity: 66 w; Reaction time: 90 min)

Additionally, it is worthy to note that increasing persulfate anions above (2.1 wt%) removal rate of dinitrotoluenes was decreased and it was due to side reaction between excess persulfate anions and sulfate radicals. Wen-Shing Chen, et al., 2015 has studied impact of persulfate anion concentration on the sonoelectrlytic behaviours and it was reported that increasing persulfate dosage below 3.0 wt% enhanced the TOC removal efficiency of process. Further reported that on increasing persulfate dosage above 3.0 wt% removal rate of aniline was drastically decreased this is attributed to the fact that increase persulfate dosage may act as inhibitor by reacting with sulfate radicals and thereby decreasing efficacy of TOC removal of said process. J. Deng, et al., 2013 has determined the effect of CBZ degradation on three UV- based AOPs, and further reported that degradation follow pseudo first order reaction, with addition of 0.5 mM oxidant degradation rate was 0.0282 min^{-1} which was increased to 0.1805 min^{-1} on increasing oxidation dosage to ten times. Furthermore, it was also reported that optimum dosage of oxidant has to be selected otherwise excess of oxidant dosage will act as scavenger and decrease the efficiency of process.

4.1.5 Effect of Reactor Configuration

Performance of chosen reactor configuration is necessary and for achieving same three different reactor configuration namely: Bubble column, Bubble column with recirculation and Venturi were studied for carrying out O_3/UV/PS process under optimized conditions.

O_3/UV/PS process gives different removal efficiency under different reactor configuration for same selected parameters of 500 mgL^{-1} initial dye, 60 LPH ozone flowrate, 12 pH, 66W UV light intensity and 1:40 TOC:PS ratio. The present study was carried out at above said conditions and it was found that Venturi gives improved removal efficiency for TOC than that of Bubble column and Bubble column with recirculation reactor.

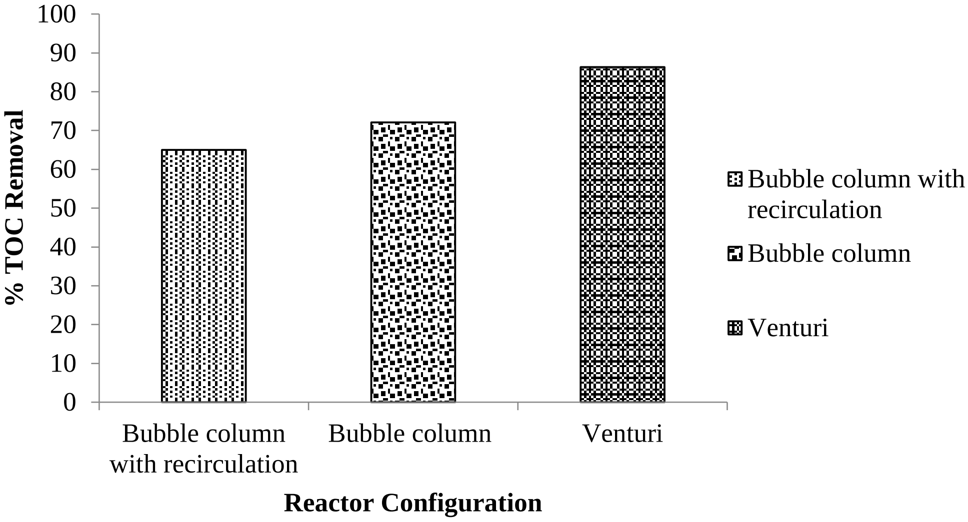


Figure 4.5 Effect of reactor configuration on %TOC removal

(Process conditions: Dye: RB5; Initial dye conc^n: 500 mgL^{-1}; O_3 flow: 1.86 gh^{-1}; pH: 12; UV intensity: 66 w; Water recirculation flow: 2.86 LPM; Reaction time: 90 min)

It is evident from obtained results shown in Figure 4.5 that, Venturi gives highest removal efficiency of 86.34% followed by Bubble column and Bubble with recirculation, 72.12% and 65% respectively. The difference in efficiencies shown by three reactors is due to contacting pattern and mass transfer coefficient between ozone and liquid.

4.1.6 Comparison of Processes

Assessment of process is essential to determine its proficiency towards treatment of recalcitrant organic compounds under same reactor configuration and operating parameters. O_3, O_3/UV and O_3/UV/PS process were analyzed based on above optimized parameters and reactor configuration. To conduct present analysis experiments were conducted in Venturi reactor with selected operating parameters like 500 mgL^{-1} initial dye concentration of RB5, 12 pH, 66 W UV intensity, 1:40 TOC:PS ratio and were compared on the basis of %TOC removal. Experimental study was carried out for 90 min and TOC removal with respect to time were analyzed for above mentioned processes.

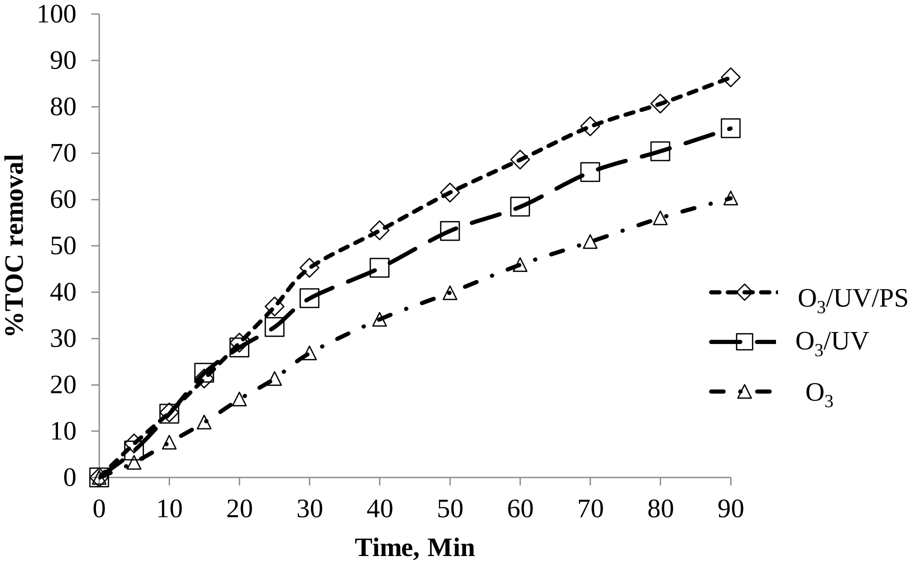


Figure 4.6 Effect of applied process on %TOC Removal

(Process conditions: Reactor configuration: Venturi; Dye: RB5; Initial dye conc^n: 500 mgL^{-1}; O_3 flow: 1.86 gh^{-1}; pH: 12; UV intensity: 66 w; Water recirculation flow: 2.86 LPM; Reaction time: 90 min)

Figure 4.6 predicts that %TOC removal increases with increase in reaction time. Additionally, it is commendable to note that efficiency of O_3/UV/PS process is highest among the three compared process. However, removal efficiency in case of O_3/UV/PS process was 86.34% followed by 75.34%, 60.29% for O_3/UV and O_3 process respectively. Consequently, it can be concluded that O_3/UV/PS process serves to be proficient process among the three examined processes.

4.2 Design of experiments (DOE) and Taguchi method

As a result of preliminary studies, the process and operating parameters were finalized. Further experiments were designed using DOE in this phase and studies undertaken to evaluate reactor configuration and contributing parameters considering dye as one of the variable and also, separately for individual dye. Main effect plot, signal to noise ratio, interaction of variables and percentage contribution are also covered in this section.

Design of Experiments is widely used to optimize processes parameters and to increase the quality of products using engineering concepts and statistics. DOE is used to optimize operational parameters by considering interactions amongst them. DOE has been utilized as an important mathematical tool in the area of AOPs (Loures, et al., 2014).

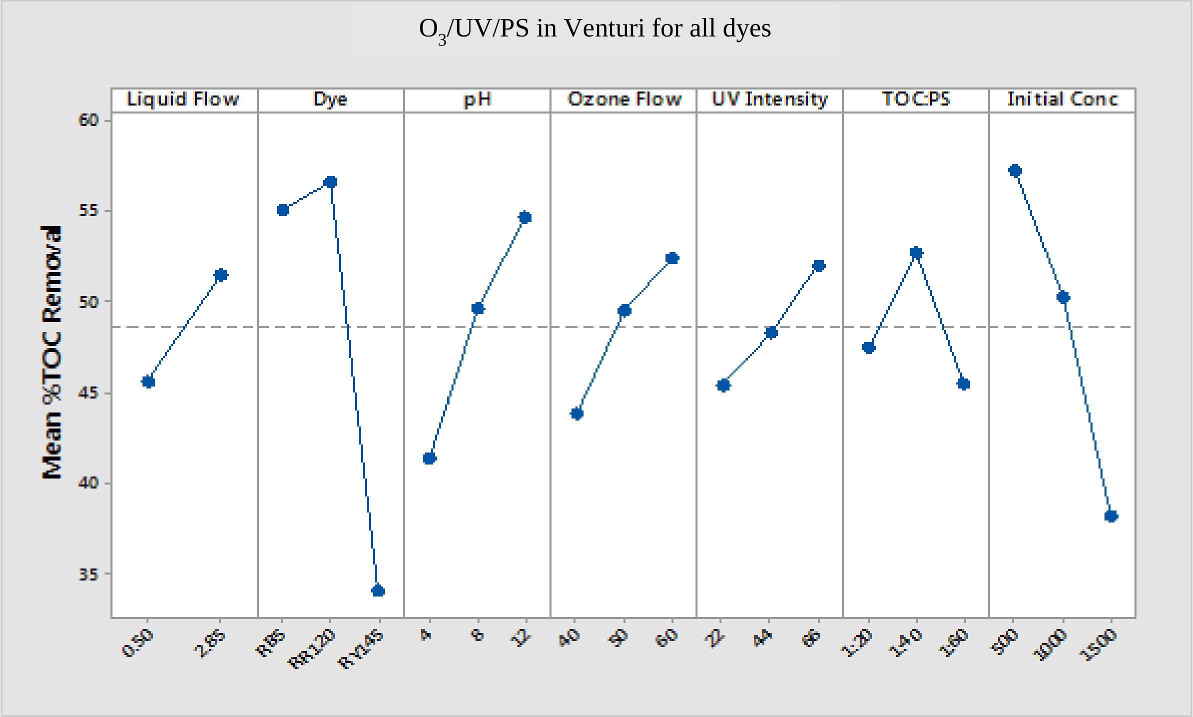
The Taguchi technique is a robust statistical method, which is widely used in engineering analysis and is a powerful design. This method uses orthogonal arrays for an evaluation of factors by drastically reducing the number of experiments, thereby reducing time and cost. Furthermore, it provides a simple, effective and organized approach to specifying the optimum parameters in the process (Kıvak, 2014; Ahmad, et al., 2015).

4.2.1 Mean effect plot for TOC removal

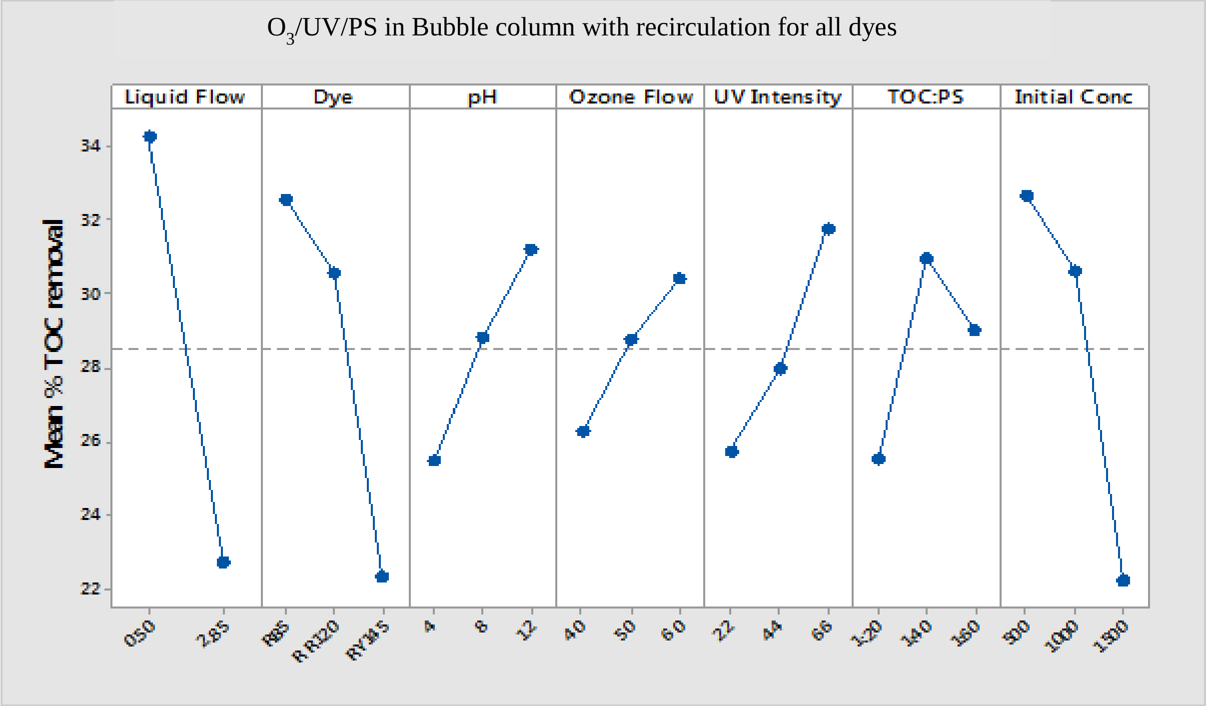
Main effect plot for % TOC removal using O_3/UV/PS process is shown in Figure 4.7. The plot is utilized to explain the relationship between variables and output response. In case of Venturi reactor, effect of water recirculation flow on %TOC removal illustrates that, increase in liquid flowrate will have positive impact on %TOC removal from synthetic dye wastewater in Venturi configuration. Similar findings were reported in literature and this is attributed to the fact that on increasing liquid flowrate, Venturi reactor provides good intimate contact between ozone molecules and pollutants. It was observed that, TOC removal for was increase from 45.66% to 51.48% by increasing flow from 0.5 LPM to 2.86 LPM for all dyes taken in to study.

Opposite behaviour was noticed that in Bubble column with recirculation type of reactor by increase in flow of wastewater, %TOC removal was decreased as shown in Figure 4.7. This is attributed to the fact that, by increasing the flow of wastewater, contact time of liquid and gas was reduced. As point of introduction of water and ozone gas is same from bottom of the column, ozone bubbles size was increased due to wastewater flow. TOC removal was decreased from 34.27% to 22.72%.

Treatment efficiency of any process depends on kind of pollutant present in wastewater. As shown in the Figure 4.7, %TOC removal was higher in RB5 and RR120 compare to RY145. It was observed %TOC removal was 55.08, 56.58 and 33.05 for RB5, RR120 and RY145 respectively. Similar findings observed in case of Bubble column reactor with recirculation also. %TOC removal in RB5, RR120 and RY145 was 32.58, 30.57 and 22.35 respectively.



O_3/UV/PS in Venturi for all dyes



O_3/UV/PS in Bubble column with recirculation for all dyes

Figure 4.7 Main effect plot for O_3/UV/PS process for Venturi and Bubble column with recirculation reactor

As shown in Figure 4.7, effect of varying pH from acidic to basic media on %TOC removal shows increasing trend (Pachhade, et al., 2009). In context to this it should be noted that degradation of dye molecules in synthetic wastewater is either due to molecular ozone or due to hydroxyl radicals generated by decomposition of ozone molecules (Lu, et al., 2009).

However, it is worthy to note that ozone molecule is main oxidizing agent under acidic condition whereas hydroxyl radical serves to be predominant oxidizing agent under basic condition (Pachhade, et al., 2009). From Figure 4.7, it is evident that pH 12 shows highest TOC removal of 54.67% followed by pH 8 and pH 4 with 49.64% & 41.41% respectively for all selected dyes in Venturi reactor. Same increasing trend was observed in Bubble column with recirculation reactor. %TOC removal was 25.46, 28.81 & 31.23 at pH 4, 8 and 12 respectively. Thus, pH 12 was taken as optimum pH for subsequent studies.

Effect of ozone flowrate on %TOC removal is as shown in above Figure 4.7. It is observed that increase in ozone flowrate will consequently lead to enhanced %TOC removal for all reactive dyes considered for study. This is attributed to the fact that as ozone flowrate increases driving force for ozone to synthetic dye wastewater also increases resulting in enhanced mineralization (Ruan, et al., 2010). It is apparent from Figure 4.7 that %TOC removal at 40 LPH was 43.88% whereas on increasing ozone flowrate to 50 LPH and 60 LPH efficiency of process to %TOC removal was also improved and was 49.47% and 52.36% respectively. Similar pattern observed for Bubble column with recirculation reactor. TOC removal increased from 26.28% to 30.44% as ozone flow increased from 40 LPH to 60 LPH.

In addition, increase in UV intensity will have positive impact on removal of TOC from synthetic wastewater. As intensity of UV light increases production of hydroxyl radicals also increases which consequently enhance efficiency of process in terms of TOC removal (Zou, et al., 2008). Furthermore, UV irradiations in the range of 185 and 254 nm wavelengths can dissociate the chemical bonds present in dye molecules such as, C–C, C=C, C–H, C–N, C=N, and C–O (Liu, et al., 2004). TOC removal was utmost in case of UV intensity of 66 W which was 52.00% followed by TOC removal of 48.28% & 45.44% at 44 W and 22 W respectively in Venturi reactor. In Bubble column with recirculation reactor also same trend was observed. By increase in UV intensity from 22W to 66W, TOC removal was increased from 25.72% to 31.79%.

Further, effect of TOC: PS dosage on %TOC removal is as shown in Figure 4.7. It is evident from obtained results that optimum TOC: PS dosage has to be selected. This is attributed to the fact that high dosage of persulfate act as scavenger and decreases efficiency of said process (Liang, et al., 2014). In present study, 1:40 was found to be optimum value of TOC: PS for all selected dyes and reactor configuration. Mean TOC removal was 52.69% and

30.96% at TOC:PS ratio of 1:40 for all dyes in Venturi reactor and Bubble column with recirculation reactor respectively.

Effect of initial concentration on %TOC removal was also examined and it was noticed that increased initial concentration will have decreased mineralization efficiency of synthetic wastewater in terms of %TOC removal (Wu, et al., 2006). As initial dye concentration in synthetic wastewater increases, the ratio of ozone molecules to dye molecules decreases and additionally requirement of ozone also increases with increased initial dye concentration (Tehrani-Bagha, et al., 2010). The result obtained from this study also reflects similar trend where %TOC removal decreases from 57.26% to 38.217% on increasing initial dye concentration from 500 to 1500 mgL^{-1} for all reactive dyes taken for study in Venturi reactor. %TOC removal was decreased from 32.65% to 22.22% in case of Bubble column with recirculation reactor on increase in initial dye concentration.

Similar observations were noticed for experiments performed by O_3/UV/PS process in Venturi and Bubble column with recirculation for individual dyes. Refer Annexure 3 for respective main effect plots.

4.2.2 Interaction Plot

The efficiency of O_3/UV/PS process highly governed by operating parameters and interaction amongst them (Ahmad, et al., 2015). To determine the interaction between operating parameters it is necessary to draw a matrix of interaction plot (Panda, et al., 2013).

Major significance of interaction plot is to determine interactions during DOE. Figure 4.8 illustrate the effect of interaction of operating parameters and their effect on TOC removal. It should be noted that, parallel lines in an interaction plot signifies that there is no interaction between operating parameters (Panda, et al., 2013). From Figure 4.8, it is noticeable that parameters such as TOC:PS ratio vs. Initial dye concentration, UV intensity vs. Initial dye concentration, O_3 flowrate vs. Initial dye concentration, O_3 flowrate vs. pH, O_3 Flowrate vs. UV intensity, and O_3 flowrate vs. TOC:PS ratio shows considerable interactions in between for TOC removal. Conversely, set of parameters such as Initial dye concentration vs. Water recirculation flow, Water recirculation flow vs. O_3 flowrate, Water recirculation flow vs. pH, and Water recirculation flow vs. TOC:PS ratio does not show any interactions amongst them.

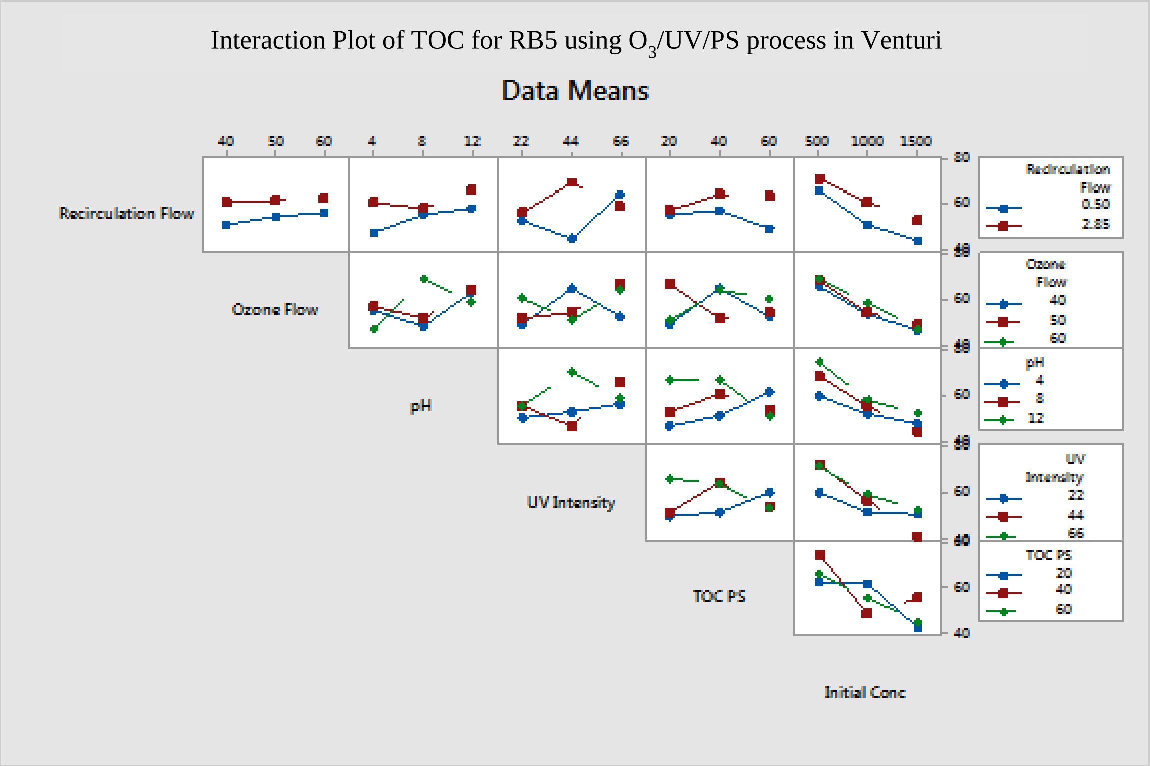


Figure 4.8 Interaction plot for TOC removal of RB5 using O_3/UV/PS process in Venturi

Additionally, set of two operation parameters, pH vs. Initial dye concentration and Water recirculation flow vs. UV intensity have shown slight interaction effect on TOC removal. Similar kind of observations were noticed for RR120 and RY145. Interaction plots are as shown in Appendix 4. However, interaction plot fails to give any idea about statistical significance of interaction (Panda, et al., 2013).

4.2.3 Analysis of the signal-to-noise (S/N) ratio

The main feature of Taguchi method is that it depends on the signal-to-noise (S/N) ratio instead of the particular experimental results. Here, ‘signal’ denotes the mean value while ‘Noise’ indicates the standard deviation term. Lower variability is ensured by maximizing this ratio. This method categorizes S/N ratios as smaller is better, normal is better, and larger is better (Ahmad, et al., 2015).

For analysis of the results, response values were converted into S/N ratio. For O_3/UV/PS process, maximum TOC removal percentages are desired so, ‘larger is better’ formula was used to determine the S/N value for each response.

In the present study, six parameters were selected for each dye to perform O_3/UV/PS process in Venturi reactor and from Table 4.1, it is clear that for all selected dyes initial dye concentration was the most contributing factor. Similar observations were resulted in RR120 and RY145 dyes also. Refer Appendix 5. This observation was also confirmed from the literature that decolourization efficiency using ozonation process decreases as dye concentration increased from 30 to 360 mgL^{-1} (Srinivasan, et al., 2009).

Table 4.1 Response value for S/N ratio for RB5 in Venturi reactor

Level	Water Recirculation flow	Ozone flow	pH	UV Intensity	TOC:PS ratio	Initial concentration of dye
1	34.41	34.80	34.47	34.61	34.78	36.62
2	35.67	35.09	34.90	34.85	35.47	34.91
3		35.23	35.74	35.66	34.86	33.58
Delta	1.26	0.43	1.27	1.05	0.69	3.04
Rank	3	6	2	4	5	1

4.2.4 Analysis of Variance

To determine statistical significance among the factors, Analysis of variance (ANOVA) was performed. ANOVA evaluates significance of the controlling factors by calculating the F-ratio (variance ratio) and the percentage contribution.

Table 4.2 ANOVA for RB5 in Venturi reactor

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Water recirculation flow	1	152.49	152.491	16.24	0.016
Type of Dye	2	1904.41	952.204	101.39	0.000
pH	2	537.61	268.807	28.62	0.004
Ozone Flow	2	222.93	111.463	11.87	0.021
UV Intensity	2	129.66	64.830	6.90	0.050
TOC:PS	2	164.07	82.037	8.74	0.035
Initial dye conc^n	2	1114.32	557.158	59.33	0.001
Error	4	37.57	9.391		
Total	17	4263.06			
Standard deviation = 3.06454		R^2 = 99.12%	R^2(adjusted) = 96.25%		

Table 4.2 shows the analysis of variance for the COD removals in Venturi reactor for selected dyes. According to this table, all the main factors of the process like type of dye, initial concentration of dye, pH and Water recirculation flow were significant ($P < 0.05$) with the F values of 101.39, 59.33, 28.62, and 16.24, respectively. The percentage contribution is defined as the portion of a total observed variance in the experiment for each significant factor (Zirehpour, et al., 2014).

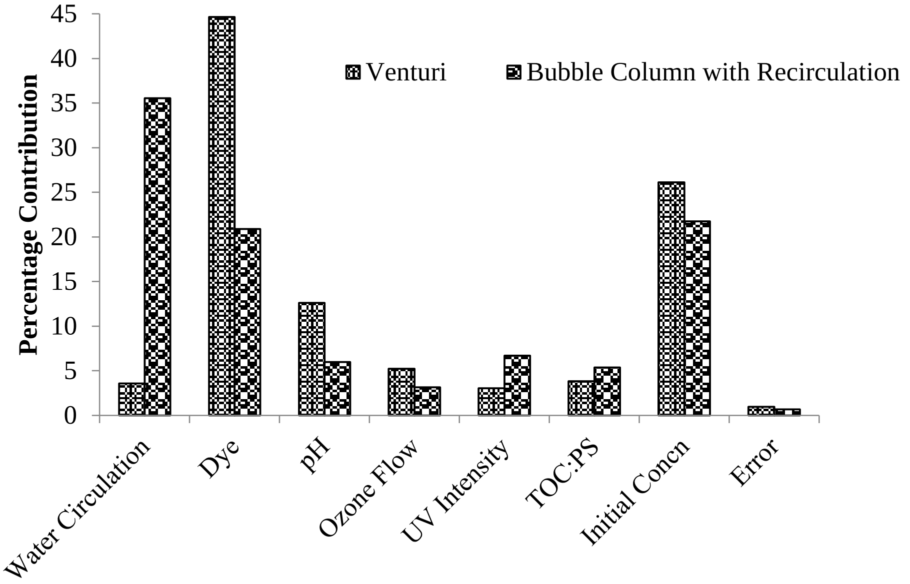


Figure 4.9 Percentage contribution for selected dyes in Venturi and Bubble column with recirculation reactor

Figure 4.9 reveals that in Venturi reactor, type of dye and its concentration had a significant effect on treatment performance, especially TOC removal efficiency. On the contrary, in Bubble column with recirculation reactor, water recirculation showed significant effect. So it is concluded that the Bubble column with water recirculation is not suitable to TOC removal.

Further percentage contribution was plotted vs. selected dyes in Venturi and Bubble column with recirculation reactor as shown in Figure 4.10. In case of Venturi reactor, initial dye concentration was the governing parameter. In Bubble column with recirculation reactor water recirculation rate was the limiting parameter i.e. selection of Bubble column with recirculation was improper and it resulted lower degradation of reactive dyes due to lower mass transfer of ozone into wastewater.

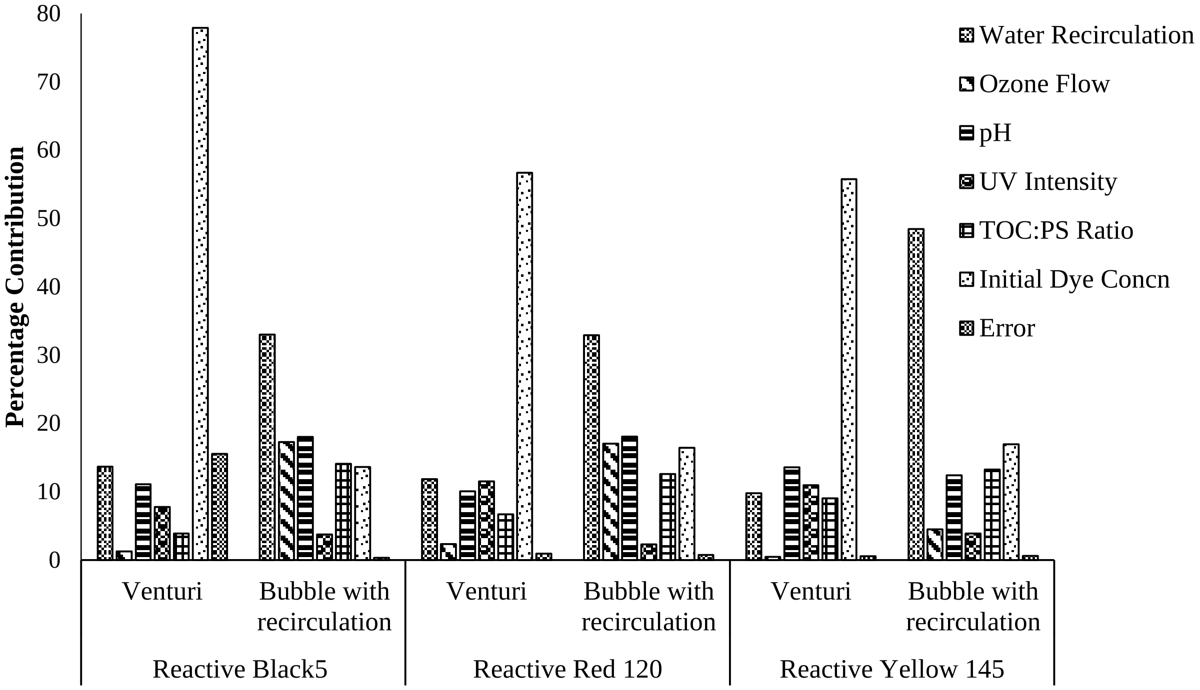


Figure 4.10 Percentage contributions of variables for individual dye in Venturi and Bubble column with recirculation reactor

Figure 4.9 and 4.10 shows the columns marked as 'error' that refer to errors caused by uncontrollable factors (noise) that are not included in the experiment and the experimental error. In general, the value should be lower than 50% to be reliable (Zirehpour, et al., 2014). The maximum calculated error was about 15% for RB5 treatment in Venturi reactor experiments. It can be seen that errors in all experiments were significantly less than limit. It proves that, all important and effective factors have been considered and errors are insignificant.

4.3 Kinetic Studies

After optimizing operating parameters and reactor configuration next step was to analyze kinetics of all three processes namely; O_3, O_3/UV and O_3/UV/PS. It is necessary to determine alterations in rate of reaction with respect to change in various operating parameters. For conducting kinetic studies all experiments were conducted in reactor having Venturi arrangement.

4.3.1 Effect of Ozone Flowrate

As discussed in previous section that ozone flowrate will have proficient effect in mineralization efficiency of process and it was evaluated in terms of %TOC removal. However, rate of reaction also varies with change in ozone flowrate. In present study O_3/UV/PS process was carried out in all three reactor configurations keeping initial concentration of RB5 dye to be 500 mgL^{-1}, pH 6, intensity of UV light 11W and TOC: PS ratio 1:10. However studies of all three reactors have revealed same results that with increase in flowrate of ozone rate of reaction considerably increases. Additionally, it is worthy to note that efficiency of Venturi reactor was highest amongst all three reactor configurations.

Its self-evident from given Figure 4.11 that as flowrate of ozone was increased from 1.35 gh^{-1} to 1.86 gh^{-1}, value of rate constant k was considerably increasing under all three reactor configurations. However, Venturi reactor has shown maximum rate of reaction of 0.0081 min^{-1} at 1.86 gh^{-1} as compared to rate of reaction of 0.0063 and 0.0058 which was shown by Bubble column reactor and bubble column with recirculation under 1.86 gh^{-1} respectively.

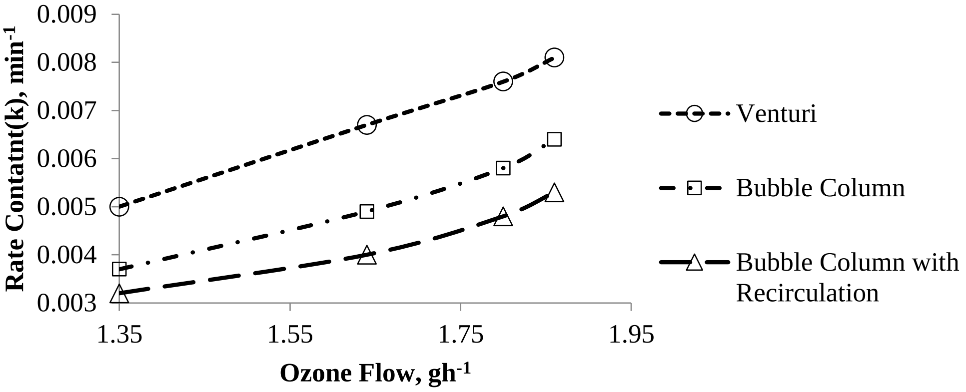


Figure 4.11 Effect of ozone flowrate on kinetics of reaction in different reactor configuration

(Process conditions: Applied process: O_3/UV/PS; Dye: RB5; Initial dye conc^n: 500 mgL^{-1}; pH:6; UV intensity:11 W; TOC:PS ratio: 1:10; Water recirculation flow: 0.5 LPM; Reaction time:90 min)

4.3.2 Effect of pH

Effect of pH was studied under all three reactor configurations. As discussed in preceding sections, as pH increases it will have proficient effect in removal efficiencies of recalcitrant organic compounds and hence it will also enhance the rate of reaction with increasing pH. In present study efficiency of O_3/UV/PS process was examined under all three reactor configurations keeping initial concentration of RB 5 dye to be 500 mgL^{-1}, ozone flow rate

1.86 gh^{-1}, intensity of UV light 11W and TOC: PS ratio 1:10. However, under all three reactor configurations increasing pH will have positive effect in rate of reaction and thereby enhancing the overall efficiency of process. Nevertheless, it is estimable to note that at 12 pH, Venturi has shown highest rate of reaction with 0.0096 min^{-1} followed by 0.0078 and 0.0071 min^{-1} for Bubble column reactor and Bubble column with recirculation, respectively as shown in Figure 4.12.

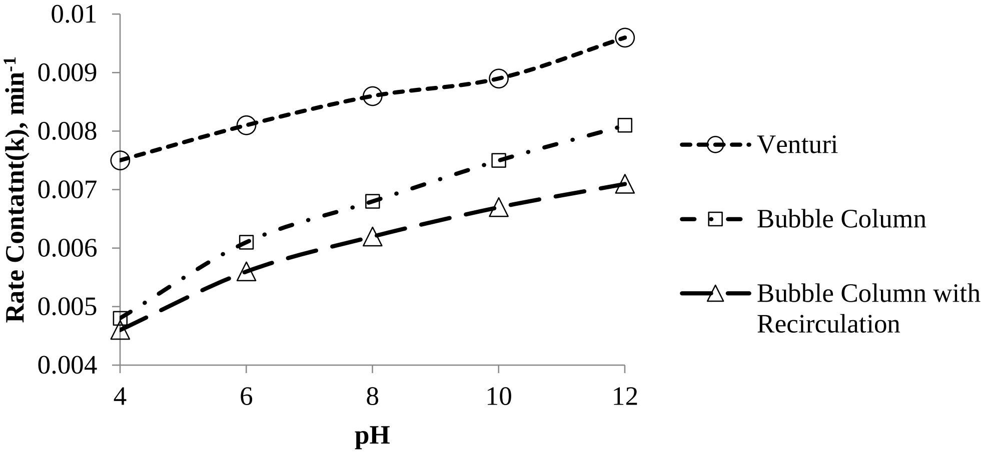


Figure 4.12 Effect of pH on kinetics of reaction in different reactor configuration

(Process conditions: Applied process: O_3/UV/PS; Dye: RB5; Initial dye conc^n: 500 mgL^{-1}; O_3 flow: 1.86 gh^{-1}; UV intensity:11 W; TOC:PS ratio: 1:10; Water recirculation flow: 0.5 LPM; Reaction time:90 min)

4.3.3 Effect of UV Intensity

To determine the effect of UV intensity on effectiveness of three different reactor configurations, present study was carried out using O_3/UV/PS process. For investigating effect of UV intensity, studies were carried out in all three reactors at same initial conditions of 500 mgL^{-1} RB5, 1.86 gh^{-1} ozone flowrate, 12 pH and 1:10 TOC: PS ratio.

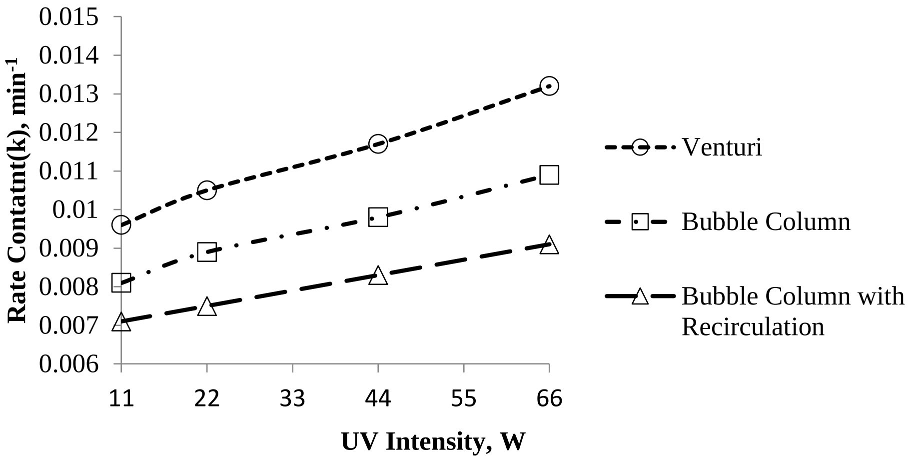


Figure 4.13 Effect of UV intensity on kinetics of reaction in different reactor configuration

(Process conditions: Applied process: O_3/UV/PS; Dye: RB5; Initial dye conc^n: 500 mgL^{-1}; O_3 flow: 1.86 gh^{-1}; pH:12; TOC:PS ratio: 1:10; Water recirculation flow: 0.5 LPM; Reaction time:90 min)

Present Figure 4.13 illustrates changes in k values as function of UV intensity. In this study, effect of UV intensity on rate constant shows increasing trend with increase in UV intensity. As the intensity of UV light was increased from 11W to 66 W, it was observed that under all three reactor configurations maximum rate of reaction was observed at 66 W. However, Venturi reactor gives maxim rate of reaction at 66W with 0.0133 min^{-1} followed by 0.0109 min^{-1} and 0.0091 min^{-1} for Bubble column and Bubble column with recirculation respectively.

4.3.4 Effect of Persulfate Dosage

To establish the effect of Persulfate dosage on effectiveness of three different reactor configurations, study was conducted using O_3/UV/PS process. For exploring the effect of persulfate, studies were carried out in all three reactors at same initial conditions of 500 mgL^{-1} RB5, 1.86 gh^{-1} ozone flowrate, 12 pH and 66W UV intensity.

This study demonstrates the changes of ‘k’ as a function of TOC: PS ratio. The Figure 4.14 represents the variation in k value with changing TOC:PS dosage. TOC: PS dosage was increased from 1:10 to 1:60, the value of rate constant k has also shown increasing pattern but after particular optimum dosage of TOC: PS further increase in its dosage will substantially decrease the value of rate constant k. However, all three reactors show enhanced rate of reaction at TOC: PS dosage of 1:40 with maximum rate of reaction shown by Venturi reactor of 0.0171 min^{-1} followed by 0.0145 min^{-1} and 0.0115 min^{-1} for Bubble column and Bubble column with recirculation respectively at said TOC:PS dosage.

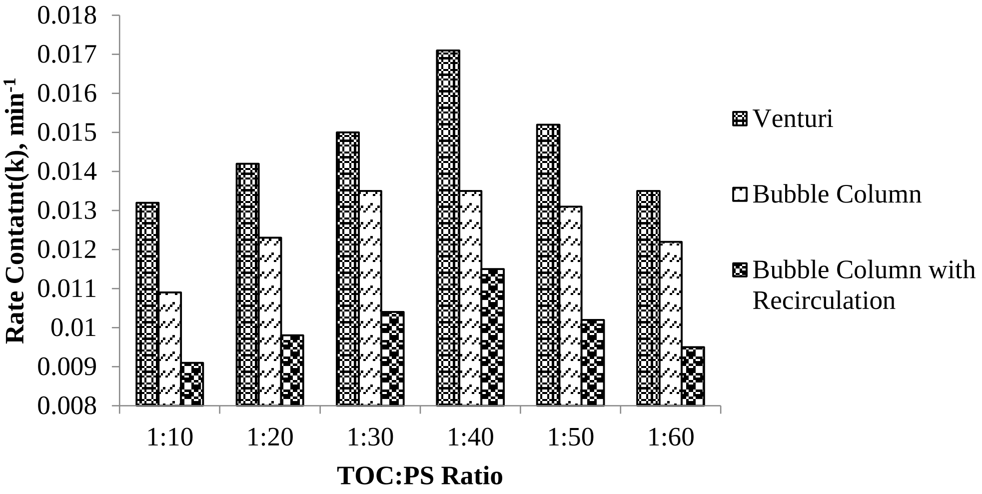


Figure 4.14 Effect of TOC:PS dosage on kinetics of reaction in different reactor configuration

(Process conditions: Applied process: O_3/UV/PS; Dye: RB5; Initial dye conc^n: 500 mgL^{-1}; O_3 flow: 1.86 gh^{-1}; pH:12; UV intensity:66 W; Water recirculation Flow: 0.5 LPM; Reaction time: 90 min)

4.3.5 Effect of Water recirculation flow

Water recirculation has significant effect on treatment efficiency of any process. Literature gives complete evidence in support with this fact. It is due to that, as recirculation of water decreases, residence time of water in reactor increases which will lead to increase in amount of hydroxyl and sulfate radicals per unit volume of solution and thereby enhancing treatment efficacy of process (Soares, et al., 2006; Tisa, et al., 2014).

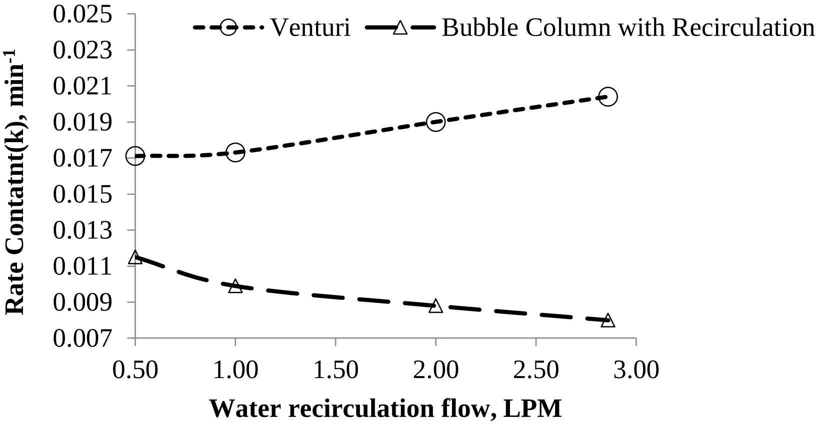


Figure 4.15 Effect of water recirculation flow on kinetics of reaction in different reactor configuration

(Process conditions: Applied process: O_3/UV/PS; Dye: RB5; Initial dye conc^n: 500 mgL^{-1}; O_3 flow: 1.86 gh^{-1}; pH:12; UV intensity:66 W; TOC:PS ratio:1:40; Reaction time: 90 min)

As shown in Figure 4.15, the effect of water recirculation was analyzed using O_3/UV/PS process under optimized conditions as mentioned in previous section to compare the effectiveness of Bubble column with recirculation and Venturi reactor. To compare effectiveness of both reactors experiments were conducted for 500 mgL^{-1} RB5 at 1.86 gh^{-1} ozone flowrate, 12 pH, 66W UV intensity, 1:40 TOC:PS dosage. In case of Venturi reactor, value of rate constant increases with increased water recirculation flowrate whereas in case of Bubble column with recirculation value of rate constant decreases with increasing flowrate.

4.3.6 Effect of Applied Process

Furthermore, it is essential to determine kinetics of different processes to compare their effectiveness and proficiency. For determining kinetics of O_3, O_3/UV and O_3/UV/PS process, study was carried out at 1.86 gh^{-1}, 12 pH, 66W UV intensity, and 1:40 TOC: PS which were same as that discussed in section 4.1 of this chapter.

Venturi reactor was utilized for conducting all experiments. Investigational study was conceded for 90 min and ln(C_0/C) with respect to time was analyzed for above mentioned processes. For determining rate constant, the slope of ln(C_0/C) vs t by fitting the data at 0 to 90 min, as shown in Figure 4.16. Here C_0 and C are the initial TOC and TOC at time t, respectively.

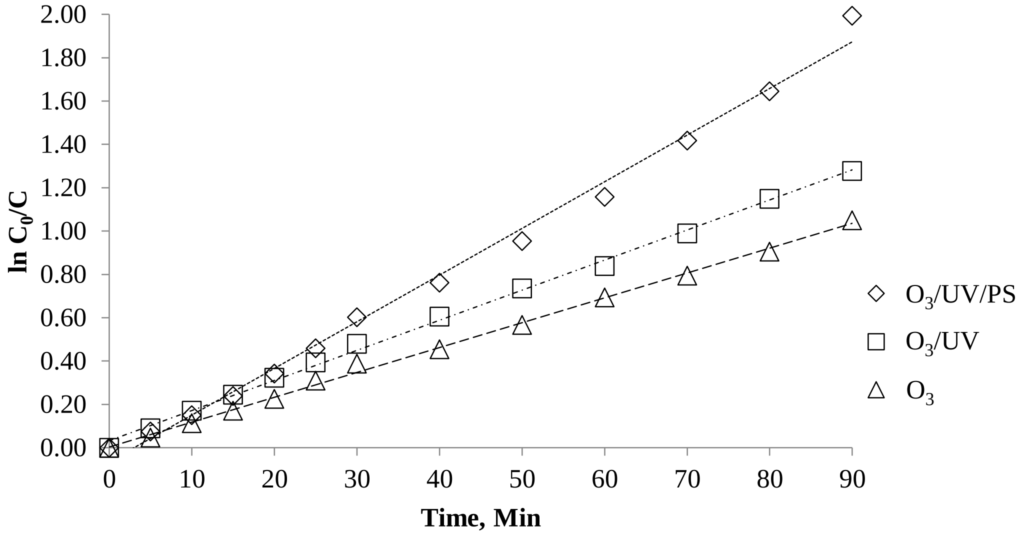


Figure 4.16 Effect of applied process on kinetics of different processes

(Process conditions: Reactor configuration: Venturi reactor; Initial dye conc^n: 500 mgL^{-1}; O_3 flow: 1.86 gh^{-1}; pH:12; UV intensity:66 W; TOC:PS ratio: 1:40; Water recirculation flow: 2.86 LPM; Reaction time: 90 min)

The slope of all three processes was compared to determine the proficiency of process. In present study degradation of RB5 follows the pseudo first order kinetics since the plot of $\ln(C_0/C)$ vs. t presents a straight line under all three processes. The value of slope was highest in O_3/UV/PS process with 0.020 min^{-1} and R^2 value of 0.989 followed by 0.015 min^{-1} and 0.010 min^{-1} slope values along with R^2 values of 0.998 for O_3/UV and O_3 processes respectively.

4.3.7 Effect of Initial Dye Concentration

After analyzing and determining the effect of operating parameters such as, effect of varying reactor configuration and effect of varying process, it is advantageous to analyze efficiency of optimized process on change in initial dye concentration of wastewater. To analyze the effect of most significant parameter which has predominant influence on efficiency of any process is its initial dye concentration. Initial dye concentration directly influences efficacy of process. Increase in initial dye concentration will have decreased mineralization efficiency of said process.

However, it is perceptible from literature that as initial dye concentration increases the ratio of active radical ($\bullet OH$ & SO_4^{2-}) to organic pollutant reduces and it also reduces permeability of UV light into the effluent to activate generation of active species (Salari, et al., 2009; Srinivasan, et al., 2009; Torres-Luna, et al., 2013).

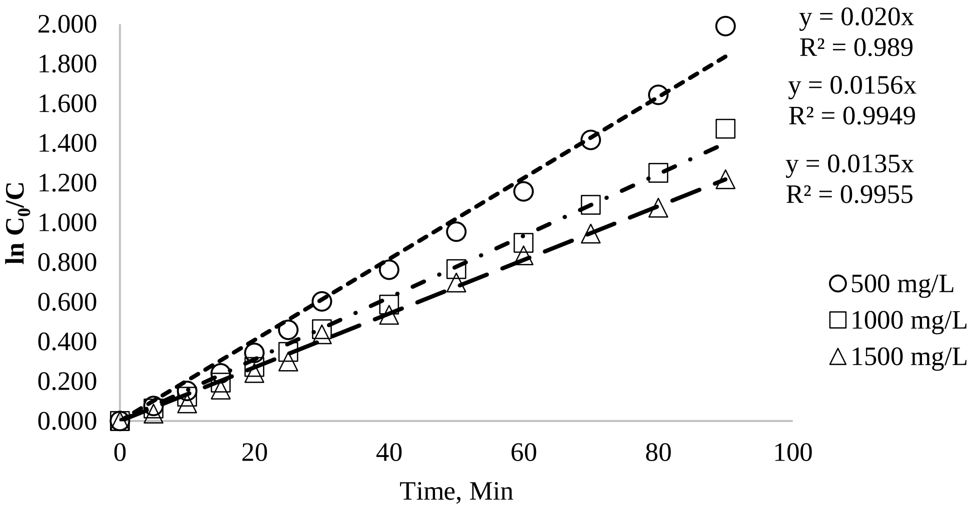


Figure 4.17 Effect of Initial dye concentration on kinetics

(Process conditions: Dye: RB5; Reactor configuration: Venturi reactor; O_3 flow: 1.86 gh^{-1}; pH:12; UV intensity:66 W; TOC:PS ratio: 1:40; Water recirculation flow: 2.86 LPM; Reaction time: 90 min)

In present study after optimizing all parameters and determining proficient reactor configuration and process it is worthy to determine efficacy of obtained results towards variation in initial dye concentration of wastewater. To determine efficacy of O_3/UV/PS process experiments were conducted at 1.86 gh^{-1} ozone flowrate, 12 pH, 66W UV intensity, 1:40 TOC:PS ratio. Initial dye concentration of 500 mgL^{-1}, 1000 mgL^{-1} and 1500 mgL^{-1} was selected for conducting present investigation.

The slope of all three initial concentrations was compared to determine the proficiency of process towards initial concentration. In present study degradation of RB5 follows the pseudo first order kinetics since the plot of $\ln(C_0/C)$ vs. t presents a straight line under all three processes. The value of slope was highest in 500 mgL^{-1} with 0.130 $min^{-1}$and R^2 value of 0.835 followed by 0.129 min^{-1} and 0.093 min^{-1} slope values along with R^2 values of 0.931 and 0.960 for 1000 mgL^{-1} and 1500 mgL^{-1} respectively.

Similar findings were reported by various researchers. Wang, et al., 2012 has reported that apparent rate constants decreased from 0.92 to 0.59 min^{-1} when tetracycline concentration increased from 200 to 800 mg L^{-1}. Moussavi, et al., 2009, has carried out work to determine effect of varying initial dye concentration of Reactive Red 198 and it was pointed out that The COD removal efficiency for the initial concentrations of 100, 200, 300, 400 and 500 mgL^{-1} were 69%, 62%, 54%, 48% and 40%, respectively. Behin, et al., 2015, has investigated that Higher decolorization was achieved at low concentrations of AB214. In UV assisted O_3 treatment, the percentage of decolorization efficiency for initial dye concentration values of 100, 200, 300, 400 and 500 mgL^{-1} in first 20 min was to be 99.9, 93.4, 88.6, 89.6 and 86.6%, respectively, for Mordent violet 40 (Hassaan, et al., 2016).

In context to obtained results, it is worthy to note that intermediates formed by degradation of dye molecule will possibly be responsible for decreased degradation rate for both dyes (Moussavi, et al., 2009).

4.4 Oxygen-equivalent chemical-oxidation capacity (OCC)

In present study under optimized conditions with 500 mgL^{-1} of initial dye concentration, 12 pH, 66W UV intensity, 1:40 TOC:PS ratio all three processes were analyzed to compare amount of reagent required per unit volume of synthetic wastewater. Investigations revealed that in case of O_3/UV/PS process 0.0532 g oxidant was required for treating 1g of TOC whereas the amount of oxidant to treat 1g of TOC was increased up to 0.0603 g and 0.0858 g in case of O_3/UV and O_3 process respectively for RB5.

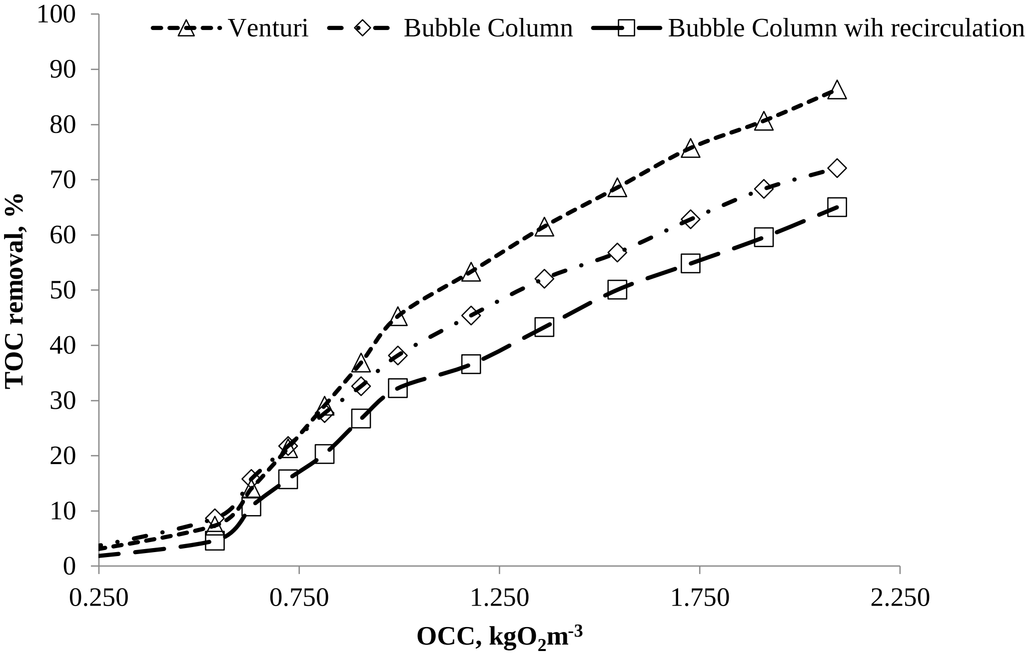


Figure 4.18 TOC removal with respect to OCC

(Process conditions: Dye: RB5; Reactor configuration: Venturi reactor; O_3 flow: 1.86 gh^{-1}; pH:12; UV intensity:66 W; TOC:PS ratio: 1:40; Water recirculation flow: 2.86 LPM; Reaction time:90 min)

Additionally, it is commendable to note that though O_3/UV/PS utilizes least amount of reagent to treat unit volume of wastewater but still it gives maximum efficiency. As shown in Figure 4.18, O_3/UV/PS process utilizes 0.0532 g oxidant for treating 1g of TOC and it gives 86.34% of TOC removal whereas even after utilizing 0.0603 g and 0.0858 g oxidant in case of O_3/UV and O_3 process the TOC removal efficiency was 75.34% and 60.29%, respectively. H. Barndok, et al., 2014a. has reported similar findings by utilizing OCC parameter for comparing performance of three different AOPs namely electro oxidation, O_3 and O_3/H_2O_2 utilizing different oxidants. It was reported that amount of OCC required was 0.298Q(kAh/m^3), 1.00[O_3](kg O_3/ m^3) and 0.471 [H_2O_2](kg H_2O_2/ m^3) were utilized by electrooxidation,O_3 and O_3/H_2O_2 process respectively. H. Barndok, et al., 2014b, has also compared OCC for 1,4 dioxane from industrial wastewater utilizing O_3 and O_3/H_2O_2 process and it was further noticed that OCC required for O_3 process is1.00[O_3](kg O_3/ m^3) and that for O_3/H_2O_2 process is 0.471 [H_2O_2](kg H_2O_2/ m^3) which supports the findings reported in present study.

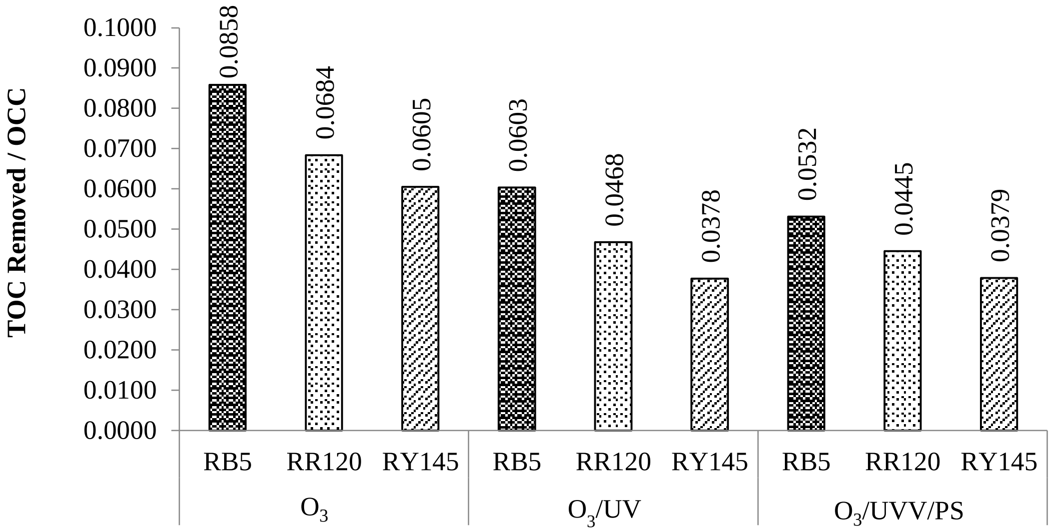


Figure 4.19 Effectiveness of the treatment process for degradation of the selected dyes

(Process conditions: Reactor configuration: Venturi reactor; O_3 flow: 1.86 gh^{-1}; pH:12; UV intensity:66 W; TOC:PS ratio: 1:40; Water recirculation flow: 2.86 LPM; Reaction time: 90 min)

In this research an attempt has been made to quantify the effect of OCC by calculating ratio of TOC removed to OCC. This is depicted in Figure 4.19 which represents ratio of TOC removed to OCC for all the three AOPs and all the three dyes selected for the study.

For all the dyes selected for this study, breaking of azo bond is comparatively easy by selected AOPs which resulted in high values of percentage colour removal efficiency. However, mineralization of intermediates is difficult which resulted in less values of percentage removal of TOC. It is reported in literature that, the oxidation of dye molecules yields ozonation by-products which cannot be oxidized by ozone molecules easily, such as organic acids, aldehydes and ketones (Sundrarajan, et al., 2007; Preethi, et al., 2009). Further, the study presents that though colour removal of RY145 is comparable with other dyes across all AOPs applied, TOC removal for RY145 is quite less. This could be attributed to presence of urea group in RY145, because it is reported that compounds like urea, ethylene diamine, hydrazine, and dimethyl nitrosomine are oxidizing very slowly by ozone (Kerwin, 2011). Along with this RR120 and RY145 contains Cl^- in their structure. Electron withdrawing group (NO_2, Cl) containing aromatic compounds shown slow reactivity with molecular ozone but are oxidized by $HO^\bullet$ (Kerwin, 2011). Thus it can be concluded that degradation of RY145 is more difficult.

4.5 Electrical Energy per Order (EE/O)

The EE/O value for degradation of RB5 was calculated using equation 3.5. The EE/O value was calculated for all three processes using initial dye concentration of 500 mg L^{-1}, ozone flowrate of 1.86 g hr^{-1}, pH 12, power of 0.1 KW and time 90 min in Bubble column reactor. The investigation of present study reveals that lowest electric energy of 150 KWh /order of contaminant/m^3 were consumed by O_3/UV/PS process followed by 216 and 296 KWh /order of contaminant/m^3 for O_3/UV and O_3 processes respectively. However, it is commendable to note that only O_3/UV/PS process consumes higher energy than that of O_3 process but in return mineralization efficiency in terms of %TOC removal was enhanced and it was 72.12% in case of O_3/UV/PS process which was only 32.18% in O_3 process. Additionally, it is very creditable to observe that O_3/UV process consumes same amount of electric energy than O_3/UV/PS process but it shows lower mineralization efficiency than O_3/UV/PS process in Bubble column reactor. Similar results were obtained by researchers in past, P. Asaithambi, et al., 2015, has compared performance of various AOPs for degradation of distillery effluent. It was reported that higher electrical energy per order values were obtained for process with lower efficiencies and electrical energy per order (kWh/ m^3 order1) values in the decreasing order are O_3/UV< O_3/UV/H_2O_2< O_3/UV/Fe^{2+}< O_3< O_3/ Fe^{2+}< UV/H_2O_2< UV/H_2O_2/ Fe^{2+}< O_3/UV/ Fe^{2+}/ H_2O_2. K. Kestioglu, et al., 2005, has also utilized EE/O to determine cost associated with UV based processes. Hajira Khan, et al., 2010, has also reported EE/O for comparing performance of different AOPs namely UV, O_3, H_2O_2/UV, O_3/UV, H_2O_2/ O_3, and H_2O_2/ O_3/UV for decolorization of RedCl-5 dye. Investigation also reported that ozone based processes were more effective on the basis of removal efficiency as well as on the basis of EE/O.

Table 4.3 compares all three chosen reactors for the O_3/UV/PS process on the basis of %TOC removal, reaction kinetics and EE/O. From the results obtained in table it is quite clear that best efficiency was obtained under Venturi configuration. It can be observed that EE/O value is highest for O_3 in Bubble column, whereas lowest for Venturi reactor. This again proves better performance of Venturi reactor.

Table 4.3 Summary of experimental studies

Sr. No.	Reactor Configuration	Applied AOPs	% TOC Removal	Rate constant k, Min^{-1}	R^2	EE/O
1	Bubble Column	O_3/UV/PS	72.12	0.0122	0.9973	149.61
		O_3/UV	58.75	0.0103	0.9962	215.8
		O_3	32.18	0.0045	0.9928	296.46
2	Bubble Column with Recirculation	O_3/UV/PS	65.02	0.0115	0.9975	184.48
3	Venturi	O_3/UV/PS	86.34	0.0205	0.9890	101.20

Finally based on DOE and various experimental studies, optimized reactor and process parameters were chosen and tabulated in Table 4.4.

Table 4.4 Optimized parameters for selected process

Reactor Configuration	Process	Process variables	Selected value
Venturi	O3/UV/PS	Ozone Flow	60 LPH
		pH	12
		UV Intensity	66 W
		TOC:PS ratio	1:40
		Water recirculation flow	2.85 LPM

Table 4.5 gives comprehensive glance of degradation efficiency on selected dyes using O_3/UV/PS process and process parameter as finalised in Table 4.4.

Table 4.5 Comparison of degradation efficiency of three selected reactive dyes

	RB5	RR120	RY145
% TOC Reduction	86.34	82.14	59.47
k	0.020	0.019	0.01
EE/O	101.20	116.97	223.12
TOC/OCC	0.053	0.043	0.039

It can further be concluded from the result quoted in Table 4.5, that efficiency of process depends on characteristics of the pollutants. In present study best efficiency was obtained for RB5, followed by RR120 and RY145.

5 Summary and Conclusion

The study was initiated with different ozone based AOPs for treating reactive dye wastewater in different reactor configuration. Initially, the studies were carried out in bubble column reactor with RB5 dye and efforts have been made to determine effects of various operating parameters such as ozone flowrate, pH, UV intensity and TOC: PS ratio on selected processes i.e. O_3, O_3/UV, and O_3/UV/PS at constant parameters such as, initial concentration of RB5 at 500 mg/L, 12 pH, 60 LPH flow of O_3, UV intensity 66 W (if applicable) and TOC:PS ratio 1:40 (if applicable). The studies revealed that %TOC removal was 47.75, 58.75 and 72.12 for O_3, O_3/UV and O_3/UV/PS, respectively. The initial studies concluded that O_3/UV/PS is efficient for TOC removal. Further, the experiments carried out with the aim to provide an efficient contact area for pollutant-ozone-catalyst, employing a bubble column with recirculation revealed that %TOC removal was 41.67, 43.21 and 65.02 for O_3, O_3/UV, and O_3/UV/PS, respectively for the same set of parameters as mentioned earlier and with water recirculation flow at 0.5 LPM. The similar experiments carried out with Venturi reactor revealed that %TOC removal was 51.45, 65.38 and 79.62 for O_3, O_3/UV, and O_3/UV/PS, respectively for the same set of parameters. The comparison of different reactor configurations revealed that Venturi reactor provides better removal of TOC than Bubble column with recirculation for all the three AOPs selected for the research. Based on the initial studies, further experiments were carried out with O_3/UV/PS. However, the *prima facie* better performance of Venturi reactor needs to be proven scientifically.

Thus, the design of experiments planned with parameters such as a dye, water recirculation flow, pH, ozone flow, UV intensity, TOC:PS ratio and initial dye concentration, for both the reactor configuration. The study revealed that in a Bubble column with recirculation reactor, water recirculation had a significant effect on overall all treatment performance, i.e., % TOC removal, whereas, for Venturi reactor dye had a significant effect on overall all treatment performance. This important conclusion provides insight that reactor configuration can provide variation in significant effect of parameters. Ideally, the significant effect of pollutant itself on treatment performance should be observed as in the case of Venturi reactor. Further, it can be concluded that performance of Bubble column with recirculation reactor blanketed by water recirculation flow and real significant parameter are not highlighted. Thus, Bubble column reactor with recirculation is not suitable for efficient performance. In addition, the main effect plot also revealed that for Bubble column reactor with recirculation, increased water recirculation causes deterioration in the performance of the reactor, whereas in the case of Venturi increased water recirculation causes improvement in the performance of the reactor.

Further, the design of experiments planned excluding dye for remaining set of parameters, and the entire set of experiment conducted for three different dye, i.e., RB5, RR120, and RY145, for both the reactor configurations, with anticipation to get an initial concentration of dye as significant parameter. The study confirmed that irrespective of dye, in Venturi reactor initial concentration is significant parameter. In contrast, bubble column with recirculation still reflects the water recirculation had a significant effect on treatment performance with all the three dyes. This results confirmed the superior performance of Venturi reactor compared to bubble column with recirculation.

The interaction plots for the parameters illustrated the effect of the interaction of operating parameters and their effect on TOC removal. It was revealed that parameters such as TOC:PS ratio vs. initial dye concentration, UV intensity vs. initial dye concentration, O_3 flowrate vs. initial dye concentration, O_3 flowrate vs. pH, O_3 Flowrate vs. UV intensity, pH vs. initial dye concentration, Water recirculation rate vs. UV intensity and O_3 flowrate vs. TOC:PS ratio shows interactions in between for TOC removal. Conversely, the remaining set of parameters such as initial dye concentration vs. Water recirculation rate, Water recirculation rate vs. O_3 flowrate, Water recirculation rate vs. pH, and Water recirculation rate vs. TOC:PS ratio does not show any interactions amongst them for all the three dyes selected for the study. In addition, the signal-to-noise (S/N) ratio that initial dye concentration was the most contributing factor for all the selected dyes in Venturi reactor, whereas it is water recirculation for bubble column with the recirculation. This result reinforces the superior performance of Venturi reactor.

Based on the design of experiments best operating parameters were chosen to be 1.86 g hr^{-1} ozone flowrate, 12 pH, 66W UV intensity and 1:40 TOC:PS ratio. It was also investigated that TOC removal of synthetic dye solution of selected reactive dyes follows pseudo first order kinetics with respect to the dye. The apparent rate constant increased with the applied ozone dose, solution pH, and UV intensity and decreased with the initial dye concentration irrespective of the chosen reactor. The rate of degradation was maximum at an optimum dosage of TOC:PS ratio i.e. 1:40. Compared to Bubble column with recirculation, degradation rate was higher in Bubble column and Venturi reactor. In addition, kinetic studies were conducted in three different reactor configurations for O_3/UV/PS process. The kinetic rate constants obtained were, 0.0122 min^{-1}, 0.0115 $min^{-1}$and 0.0205 min^{-1} for Bubble column without recirculation, Bubble column with recirculation and Venturi. Thus, O_3/UV/PS was found to be a most efficient process with Venturi reactor amongst the O_3 and O_3/UV processes.

Further, studies were carried out with the optimized parameter for O_3/UV/PS in Venturi reactor for an individual dye to identify kinetic rate constant, EE/O and TOC/OCC. Studies revealed %TOC removal 86.34, 82.14 and 59.47 for RB5, RR120, and RY145, respectively. In addition, the results revealed that kinetic rate constants are 0.02, 0.019 and 0.01 min^{-1} for RB5, RR120, and RY145, respectively. Thus, degradation of RY145 was found to be more difficult. In addition, the result of EE/O which is used to analyze the effectiveness of selected AOPs on the basis of electrical energy consumption, was 125.35, 144.88 and 276.40 for RB5, RR120, and RY145, respectively, which reflects higher energy consumption per order reaction for RY145. Similarly, TOC/OCC results were 0.053, 0.043 and 0.039 for RB5, RR120, and RY145 respectively, which reflects recalcitrant nature of RY145.

Finally, the research concluded that O_3/UV/PS process provides efficient removal of TOC. However, its performance depends on reactor configuration. Venturi reactor is more efficient than Bubble column reactor with recirculation. Amongst the dyes selected for the studies, RY145 is most recalcitrant.

Future scope of the work:

1. To evaluate potential of process industrial wastewater can be studied with optimized parameters and reactor configuration.
2. More efficient method for persulfate activation may be identified and used.
3. Various combination of catalyst may be used for improvement in TOC removal efficiency.

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Appendices

Appendix 1

Table 4.1 Raw data for Effect of ozone flowrate on TOC Removal

	O_3						O_3/UV						O_3/UV/PS					
Ozone Flow, g hr^{-1}	Initial TOC mg/L	Final TOC (mg/L) (1)	Final TOC (mg/L) (2)	Final TOC (mg/L) (3)	Average TOC removal (%)	Standard Deviation	Initial TOC mg/L	Final TOC (mg/L) (1)	Final TOC (mg/L) (2)	Final TOC (mg/L) (3)	Average TOC removal (%)	Standard Deviation	Initial TOC mg/L	Final TOC (mg/L) (1)	Final TOC (mg/L) (2)	Final TOC (mg/L) (3)	Average TOC removal (%)	Standard Deviation
1.35	130.12	103.54	107.54	106.07	18.75	2.02	132.31	103.76	102.58	105.73	21.38	1.59	132.88	98.54	95.99	93.84	27.66	2.35
1.64	130.12	100.36	99.2	98.02	23.77	1.17	132.31	97.31	100.13	99.58	25.17	1.49	132.88	84.27	89.68	85.77	34.85	2.79
1.80	130.12	95.85	93.15	94.32	27.42	1.35	132.31	93.57	92.41	90.92	30.24	1.33	132.88	81.26	79.6	83.9	38.60	2.17
1.86	130.12	87.88	86.56	90.32	32.18	1.91	132.31	86.58	84.99	83.57	35.72	1.51	132.88	77.54	72.71	78.69	42.47	3.17

Table 4.2 Raw data for Effect of pH on %TOC Removal

	Ozonation						O_3/UV						O_3/UV/PS					
	Initial TOC mg/L	Final TOC (mg/L) (1)	Final TOC (mg/L) (2)	Final TOC (mg/L) (3)	Average TOC removal (%)	Standard Deviation	Initial TOC mg/L	Final TOC (mg/L) (1)	Final TOC (mg/L) (2)	Final TOC (mg/L) (3)	Average TOC removal (%)	Standard Deviation	Initial TOC mg/L	Final TOC (mg/L) (1)	Final TOC (mg/L) (2)	Final TOC (mg/L) (3)	Average TOC removal (%)	Standard Deviation
pH 4	129.73	98.65	96.23	97.63	24.84	1.21	130.42	94.83	92.18	93.45	28.32	1.33	132.88	88.34	83.07	85.28	35.61	2.65
pH 6	130.12	87.88	86.56	90.32	32.18	1.91	132.31	86.58	84.99	83.57	35.72	1.51	132.88	77.54	72.71	78.69	42.57	3.17
pH 8	129.73	82.34	79.45	78.42	38.28	2.03	130.42	77.65	74.77	76.19	41.57	1.44	132.88	71.18	69.52	73.28	46.32	1.88
pH 10	129.73	73.36	71.9	75.85	43.19	2.00	130.42	70.83	75.32	72.47	44.12	2.27	132.88	67.12	64.39	68.66	49.17	2.16
pH 12	129.73	69.06	68.6	65.7	47.75	1.82	130.42	66.33	67.53	63.84	49.47	1.88	132.88	61.46	65.67	63.12	52.28	2.12

Table 4.3 Raw data for Effect of UV intensity on %TOC Removal

	O_3/UV						O_3/UV/PS					
UV Intensity (W)	Initial TOC mg/L	Final TOC (mg/L) (1)	Final TOC (mg/L) (2)	Final TOC (mg/L) (3)	Average TOC removal (%)	Standard Deviation	Initial TOC mg/L	Final TOC (mg/L) (1)	Final TOC (mg/L) (2)	Final TOC (mg/L) (3)	Average TOC removal (%)	Standard Deviation
11	130.42	66.33	67.53	63.84	49.47	1.88	132.88	61.46	65.67	63.12	52.28	2.12
22	131.62	64.31	65.47	63.1	51.15	1.19	129.24	59.14	60.59	56.81	54.47	1.91
44	131.62	62.34	59.66	58.27	54.35	2.07	129.24	51.22	54.81	53.44	58.87	1.81
66	131.62	54.73	52.48	55.66	58.37	1.64	129.24	45.97	51.4	47.41	62.66	2.81

Table 4.4 Raw data for Effect of TOC:PS ratio on %TOC removal

	O_3/UV/PS					
TOC:PS Ratio	Initial TOC mg/L	Final TOC (mg/L) (1)	Final TOC (mg/L) (2)	Final TOC (mg/L) (3)	Average TOC removal (%)	Standard Deviation
1:10	129.24	45.97	51.4	47.41	62.66	2.81
1:20	131.29	41.11	46.15	44.42	66.57	2.56
1:30	131.29	40.21	41.13	38.39	69.60	1.39
1:40	131.29	36.56	38.8	34.45	72.12	2.18
1:50	131.29	41.04	42.34	39.85	68.71	1.25
1:60	131.29	42.38	46.58	44.84	66.03	2.11

Table 4.5 Raw data for Effect of reactor configuration on %TOC removal

Reactor Configuration	**Initial TOC (mg/L)**	**Final TOC (mg/L) (1)**	**Final TOC (mg/L) (2)**	**Final TOC (mg/L) (3)**	**Average TOC removal (%)**	**Standard Deviation**
Bubble Column	131.29	36.56	38.8	34.45	72.12	2.18
Bubble column with recirculation	129.82	64.47	66.04	66.88	49.32	1.22
Venturi	128.86	19.32	15.75	17.73	86.34	1.79

Table 4.6 Raw data for Effect of applied process on %TOC Removal

	O_3/UV/PS					O_3/UV					Ozonation				
Time (min)	**TOC reduction in % (1)**	**TOC reduction in % (2)**	**TOC reduction in % (3)**	**Average TOC reduction in %**	**Standard Deviation**	**TOC reduction in % (1)**	**TOC reduction in % (2)**	**TOC reduction in % (3)**	**Average TOC reduction in %**	**Standard Deviation**	**TOC reduction in % (1)**	**TOC reduction in % (2)**	**TOC reduction in % (3)**	**Average TOC reduction in %**	**Standard Deviation**
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	6.32	8.68	7.02	7.34	1.22	6.54	7.14	3.79	5.82	1.79	2.76	3.13	3.93	3.27	0.60
10	13.33	14.48	14.29	14.04	0.62	14.63	15.32	11.33	13.76	2.13	8.58	5.89	8.29	7.59	1.47
15	21.74	21.29	21.04	21.36	0.36	23.13	23.96	20.62	22.57	1.74	12.86	11.12	11.81	11.93	0.88
20	27.98	28.95	30.27	29.06	1.15	28.18	29.00	27.03	28.07	0.99	18.16	15.94	16.68	16.92	1.13
25	34.89	36.82	38.90	36.87	2.01	32.75	33.30	31.40	32.49	0.98	22.86	20.18	21.02	21.35	1.37
30	43.49	45.48	46.79	45.25	1.66	39.07	39.76	37.16	38.66	1.35	27.70	25.67	27.20	26.85	1.06
40	52.10	54.08	53.83	53.34	1.08	45.85	46.64	43.21	45.23	1.80	35.89	32.49	34.11	34.17	1.70
50	60.69	62.35	61.52	61.52	0.83	53.41	54.28	51.97	53.22	1.17	41.98	38.55	39.17	39.90	1.83
60	66.96	70.15	68.67	68.59	1.59	58.51	59.56	57.20	58.43	1.18	48.09	45.29	44.42	45.93	1.91
70	74.59	76.39	76.31	75.76	1.01	66.14	66.96	64.66	65.92	1.17	53.58	49.60	49.49	50.89	2.33
80	79.10	81.17	81.78	80.68	1.40	70.81	71.20	69.27	70.43	1.02	58.58	54.57	54.97	56.04	2.21
90	85.01	87.78	86.24	86.34	1.39	75.64	76.37	74.02	75.34	1.20	62.41	58.74	59.73	60.29	1.90

Table 4.11 Raw data for Effect of ozone flowrate on kinetics of reaction in different reactor configuration

	Venturi						Bubble column						Bubble column with recirculation					
Ln (Ozone Flow), g hr^{-1}	k (min^{-1}) (1)	k (min^{-1}) (2)	k (min^{-1}) (3)	Average k (min^{-1})	Ln(k)	Standard Deviation	k (min^{-1}) (1)	k (min^{-1}) (2)	k (min^{-1}) (3)	Average k (min^{-1})	ln(k)	Standard Deviation	k (min^{-1}) (1)	k (min^{-1}) (2)	k (min^{-1}) (3)	Average k (min^{-1})	ln(k)	Standard Deviation
0.3001	0.0055	0.0045	0.0051	0.0050	-5.2983	0.00050	0.0034	0.0037	0.004	0.0037	-5.5994	0.00030	0.0029	0.0032	0.0033	0.0031	-5.7446	0.00021
0.4947	0.0068	0.0071	0.0062	0.0067	-5.0056	0.00046	0.005	0.0043	0.0048	0.0047	-5.3602	0.00036	0.0041	0.0035	0.0039	0.0038	-5.5468	0.00031
0.5878	0.007	0.0078	0.0073	0.0074	-4.8796	0.00040	0.0055	0.0058	0.0051	0.0055	-5.2030	0.00035	0.0046	0.0049	0.0043	0.0046	-5.3817	0.00030
0.6206	0.0081	0.0081	0.008	0.0081	-4.8159	0.00006	0.0063	0.0069	0.0058	0.0063	-5.0515	0.00055	0.006	0.0058	0.0055	0.0058	-5.1499	0.00025

Table 4.12 Effect of pH on kinetics of reaction in different reactor configuration

	Venturi					**Bubble column**					**Bubble column with recirculation**				
	k (min^{-1}) (1)	**k (min^{-1}) (2)**	**k (min^{-1}) (3)**	**Average k (min^{-1})**	**Standard Deviation**	**k (min^{-1}) (1)**	**k (min^{-1}) (2)**	**k (min^{-1}) (3)**	**Average k (min^{-1})**	**Standard Deviation**	**k (min^{-1}) (1)**	**k (min^{-1}) (2)**	**k (min^{-1}) (3)**	**Average k (min^{-1})**	**Standard Deviation**
1.3863	0.0072	0.0077	0.0076	0.0075	0.00026	0.0044	0.0052	0.0049	0.0048	0.00040	0.005	0.0041	0.0048	0.0046	0.00047
1.7918	0.0081	0.0081	0.008	0.0081	0.00006	0.0063	0.0069	0.0058	0.0063	0.00055	0.006	0.0058	0.0055	0.0058	0.00025
2.0794	0.0081	0.0085	0.0091	0.0086	0.00050	0.0065	0.0069	0.0062	0.0065	0.00035	0.0064	0.0062	0.0059	0.0062	0.00025
2.3026	0.0084	0.0093	0.009	0.0089	0.00046	0.0068	0.0072	0.0066	0.0069	0.00031	0.0071	0.0067	0.0063	0.0067	0.00040
2.4849	0.009	0.0101	0.0097	0.0096	0.00056	0.0082	0.0074	0.0079	0.0078	0.00040	0.0077	0.007	0.0067	0.0071	0.00051

Table 4.13 Effect of UV intensity on kinetics of reaction in different reactor configuration

	Venturi					**Bubble column**					**Bubble column with recirculation**				
UV Intensity (W)	**k (min^{-1}) (1)**	**k (min^{-1}) (2)**	**k (min^{-1}) (3)**	**Average k (min^{-1})**	**Standard Deviation**	**k (min^{-1}) (1)**	**k (min^{-1}) (2)**	**k (min^{-1}) (3)**	**Average k (min^{-1})**	**Standard Deviation**	**k (min^{-1}) (1)**	**k (min^{-1}) (2)**	**k (min^{-1}) (3)**	**Average k (min^{-1})**	**Standard Deviation**
11	0.009	0.0101	0.0097	0.0096	0.00056	0.0082	0.0074	0.0079	0.0078	0.00040	0.0077	0.007	0.0067	0.0071	0.00051
22	0.0099	0.011	0.0105	0.0105	0.00055	0.0094	0.0083	0.0094	0.0090	0.00064	0.0077	0.0072	0.0075	0.0075	0.00025
44	0.0122	0.0121	0.0109	0.0117	0.00072	0.0102	0.0095	0.0098	0.0098	0.00035	0.0086	0.008	0.0083	0.0083	0.00030
66	0.0124	0.0138	0.0132	0.0131	0.00070	0.0116	0.01	0.0111	0.0109	0.00082	0.0092	0.0087	0.0094	0.0091	0.00036

Table 4.14 Effect of TOC:PS dosage on kinetics of reaction in different reactor configuration

	Venturi					Bubble column					Bubble column with recirculation				
TOC:PS Ratip	k (min^{-1}) (1)	k (min^{-1}) (2)	k (min^{-1}) (3)	Average k (min^{-1})	Standard Deviation	k (min^{-1}) (1)	k (min^{-1}) (2)	k (min^{-1}) (3)	Average k (min^{-1})	Standard Deviation	k (min^{-1}) (1)	k (min^{-1}) (2)	k (min^{-1}) (3)	Average k (min^{-1})	Standard Deviation
1:10	0.0124	0.0138	0.0132	0.0131	0.00070	0.0116	0.01	0.0111	0.0109	0.00082	0.0092	0.0087	0.0094	0.0091	0.00036
1:20	0.0146	0.0142	0.0137	0.0142	0.00045	0.0131	0.0116	0.0121	0.0123	0.00076	0.0096	0.0101	0.0098	0.0098	0.00025
1:30	0.0152	0.0151	0.0148	0.0150	0.0002	0.0134	0.0131	0.0139	0.0135	0.00040	0.01	0.0104	0.0108	0.0104	0.00040
1:40	0.0162	0.0171	0.018	0.0171	0.0009	0.0145	0.0137	0.0152	0.0145	0.00075	0.0111	0.0114	0.0121	0.0115	0.00051
1:50	0.0155	0.0144	0.0159	0.0153	0.0008	0.013	0.0128	0.0136	0.0131	0.00042	0.0101	0.0097	0.0107	0.0102	0.00050
1:60	0.0144	0.0132	0.0129	0.0135	0.0008	0.0128	0.0117	0.0121	0.0122	0.00056	0.0092	0.0093	0.0099	0.0095	0.00038

Table 4.15 Effect of water circulation rate on kinetics of reaction in different reactor configuration

	Venturi					Bubble column with recirculation				
Recirculation flow (LPM)	**k (min^{-1}) (1)**	**k (min^{-1}) (2)**	**k (min^{-1}) (3)**	**Average k (min^{-1})**	**Standard Deviation**	**k (min^{-1}) (1)**	**k (min^{-1}) (2)**	**k (min^{-1}) (3)**	**Average k (min^{-1})**	**Standard Deviation**
0.5	0.0162	0.0171	0.018	0.0171	0.0009	0.0111	0.0114	0.0121	0.0115	0.00051
1.0	0.0158	0.0185	0.0179	0.0174	0.0014	0.0104	0.0095	0.0098	0.0099	0.00046
2.0	0.0181	0.0198	0.0191	0.0190	0.0009	0.0092	0.0088	0.0083	0.0088	0.00045
2.86	0.0196	0.0211	0.0207	0.0205	0.0008	0.0101	0.0096	0.0095	0.0097	0.00032

Table 4.16 a. Effect of applied process on Kinetics_O_3/UV/PS Process

Time (min)	**TOC (mg/L) (1)**	**TOC (mg/L) (2)**	**TOC (mg/L) 3)**	**Average TOC (mg/L)**	**ln (TOC_0/TOC_t) (1)**	**ln (TOC_0/TOC_t) (2)**	**ln (TOC_0/TOC_t) (3)**	**Average of ln (TOC_0/TOC_t)**	**Standard Deviation**
0	128.86	128.86	128.86	128.86	0.00	0.00	0.00	0.00	0.00
5	120.72	117.67	119.82	119.40	0.07	0.09	0.07	0.08	0.01
10	111.68	110.2	110.44	110.77	0.14	0.16	0.15	0.15	0.01
15	100.84	101.43	101.75	101.34	0.25	0.24	0.24	0.24	0.00
20	92.81	91.56	89.86	91.41	0.33	0.34	0.36	0.34	0.02
25	83.9	81.42	78.73	81.35	0.43	0.46	0.49	0.46	0.03
30	72.82	70.25	68.57	70.55	0.57	0.61	0.63	0.60	0.03
40	61.73	59.17	59.49	60.13	0.74	0.78	0.77	0.76	0.02
50	50.65	48.52	49.59	49.59	0.93	0.98	0.95	0.96	0.02
60	42.57	38.47	40.37	40.47	1.11	1.21	1.16	1.16	0.05
70	32.74	30.43	30.53	31.23	1.37	1.44	1.44	1.42	0.04
80	26.93	24.26	23.48	24.89	1.57	1.67	1.70	1.65	0.07
90	19.32	15.75	17.73	17.60	1.90	2.10	1.98	1.99	0.10

Table 4.16 b. Effect of applied process on Kinetics_O_3/UV Process

Time (min)	TOC (mg/L) (1)	TOC (mg/L) (2)	TOC (mg/L) 3)	Average TOC (mg/L)	ln (TOC_0/TOC_t) (1)	ln (TOC_0/TOC_t) (2)	ln (TOC_0/TOC_t) (3)	Average of ln (TOC_0/TOC_t)	Standard Deviation
0	263.39	263.39	263.39	263.39	0.00	0.00	0.00	0.00	0.00
5	245.73	245.78	250.39	247.30	0.07	0.07	0.05	0.06	0.01
10	231.42	230.29	237.46	233.06	0.13	0.13	0.10	0.12	0.02
15	212.35	218.23	219.94	216.84	0.22	0.19	0.18	0.19	0.02
20	193.21	206.73	201.32	200.42	0.31	0.24	0.27	0.27	0.03
25	180.04	189.12	188.62	185.93	0.38	0.33	0.33	0.35	0.03
30	158.92	172.91	165.58	165.80	0.51	0.42	0.46	0.46	0.04
40	137.24	156.62	145.72	146.53	0.65	0.52	0.59	0.59	0.07
50	113.67	128.46	125.07	122.40	0.84	0.72	0.74	0.77	0.06
60	100.4	113.05	108.34	107.26	0.96	0.85	0.89	0.90	0.06
70	81.23	96.13	88.45	88.60	1.18	1.01	1.09	1.09	0.08
80	68.37	82.81	75.13	75.44	1.35	1.16	1.25	1.25	0.10
90	53.1	67.48	60.45	60.34	1.60	1.36	1.47	1.48	0.12

Table 4.16 c. Effect of applied process on Kinetics_O_3 Process

Time (min)	TOC (mg/L) (1)	TOC (mg/L) (2)	TOC (mg/L) 3)	Average TOC (mg/L)	ln (TOC_0/TOC_t) (1)	ln (TOC_0/TOC_t) (2)	ln (TOC_0/TOC_t) (3)	Average of ln (TOC_0/TOC_t)	Standard Deviation
0	372.26	372.26	372.26	372.26	0.00	0.00	0.00	0.00	0.00
5	358.53	360.56	356.07	358.39	0.04	0.03	0.04	0.04	0.01
10	334.21	345.06	342.56	340.61	0.11	0.08	0.08	0.09	0.02
15	310.62	321.73	320.64	317.66	0.18	0.15	0.15	0.16	0.02
20	283.31	301.53	292.36	292.40	0.27	0.21	0.24	0.24	0.03
25	268.93	279.71	278.04	275.56	0.33	0.29	0.29	0.30	0.02
30	232.38	247.83	241.61	240.61	0.47	0.41	0.43	0.44	0.03
40	209.47	224.62	219.41	217.83	0.58	0.51	0.53	0.54	0.04
50	172.26	202.16	181.54	185.32	0.77	0.61	0.72	0.70	0.08
60	152.09	170.91	161.25	161.42	0.90	0.78	0.84	0.84	0.06
70	134.82	156.66	142.78	144.75	1.02	0.87	0.96	0.95	0.08
80	119.71	132.58	128.63	126.97	1.13	1.03	1.06	1.08	0.05
90	101.07	118.12	110.82	110.00	1.30	1.15	1.21	1.22	0.08

Table 4.17. Effect of initial dye concentration on kinetics_Venturi reactor

	500 mg/L		**1000 mg/L**		**1500 mg/L**	
Time (Min)	**Average TOC (mg/L)**	**ln (TOC_0/TOC_t)**	**Average TOC (mg/L)**	**ln (TOC_0/TOC_t)**	**Average TOC (mg/L)**	**ln (TOC_0/TOC_t)**
0	128.86	0.000	263.39	0.000	372.26	0.000
5	119.40	0.076	247.30	0.063	358.39	0.038
10	110.77	0.151	233.06	0.122	340.61	0.089
15	101.34	0.240	216.84	0.194	317.66	0.159
20	91.41	0.343	200.42	0.273	292.40	0.241
25	81.35	0.460	185.93	0.348	275.56	0.301
30	70.55	0.602	165.80	0.463	240.61	0.436
40	60.13	0.762	146.53	0.586	217.83	0.536
50	49.59	0.955	122.40	0.766	185.32	0.698
60	40.47	1.158	107.26	0.898	161.42	0.836
70	31.23	1.417	88.60	1.089	144.75	0.945
80	24.89	1.644	75.44	1.250	126.97	1.076
90	17.60	1.991	60.34	1.474	110.00	1.219

Table 4.18 TOC removal with respect to OCC

OCC Kg O_2/m^3	Average %TOC removal		
	Venturi	Bubble column	Bubble column with recirculation
0.000	0.00	0.00	0.00
0.539	7.34	8.63	4.61
0.631	14.04	15.78	10.82
0.722	21.36	21.72	15.72
0.813	29.06	27.69	20.30
0.905	36.87	32.59	26.70
0.996	45.25	38.15	32.21
1.179	53.34	45.40	36.56
1.361	61.52	52.06	43.27
1.544	68.59	56.78	50.06
1.727	75.76	62.81	54.82
1.910	80.68	68.31	59.57
2.092	86.34	72.12	65.02

Table 4.19 Effectiveness of the treatment system for degradation of the selected dyes

Type of AOP’s	Dye	Average Initial TOC (mg/L)	Average Final TOC (mg/L)	Average TOC Removed (kg/m^3)	OCC (kg/m^3)	TOC removed/OCC
O_3	RB5	132.39	52.57	0.0798	0.930	0.0858
	RR120	108.35	44.74	0.0636	0.930	0.0684
	RY145	135.47	79.20	0.0563	0.930	0.0605
O_3/UV	RB5	131.74	32.49	0.0993	1.6449	0.0603
	RR120	109.45	32.53	0.0769	1.6449	0.0468
	RY145	133.89	71.78	0.0621	1.6449	0.0378
O_3/UV/PS	RB5	128.86	17.6	0.1113	2.0266	0.0532
	RR120	109.84	19.61	0.0902	2.1133	0.0445
	RY145	134.77	54.62	0.0802	2.0927	0.0379

Appendix 2

Taguchi design for O_3/UV/PS process

a. Experiments for Venturi and Bubble column with recirculation configuration Considering dye as variable

Experiment No.	**Water recirculation Flow**	**Type of Reactive Dye**	**pH**	**Ozone Flow**	**UV Intensity**	**TOC:PS**	**Initial Conc**
1	1	1	1	1	1	1	1
2	1	1	2	2	2	2	2
3	1	1	3	3	3	3	3
4	1	2	1	1	2	2	3
5	1	2	2	2	3	3	1
6	1	2	3	3	1	1	2
7	1	3	1	2	1	3	2
8	1	3	2	3	2	1	3
9	1	3	3	1	3	2	1
10	2	1	1	3	3	2	2
11	2	1	2	1	1	3	3
12	2	1	3	2	2	1	1
13	2	2	1	2	3	1	3
14	2	2	2	3	1	2	1
15	2	2	3	1	2	3	2
16	2	3	1	3	2	3	1
17	2	3	2	1	3	1	2
18	2	3	3	2	1	2	3

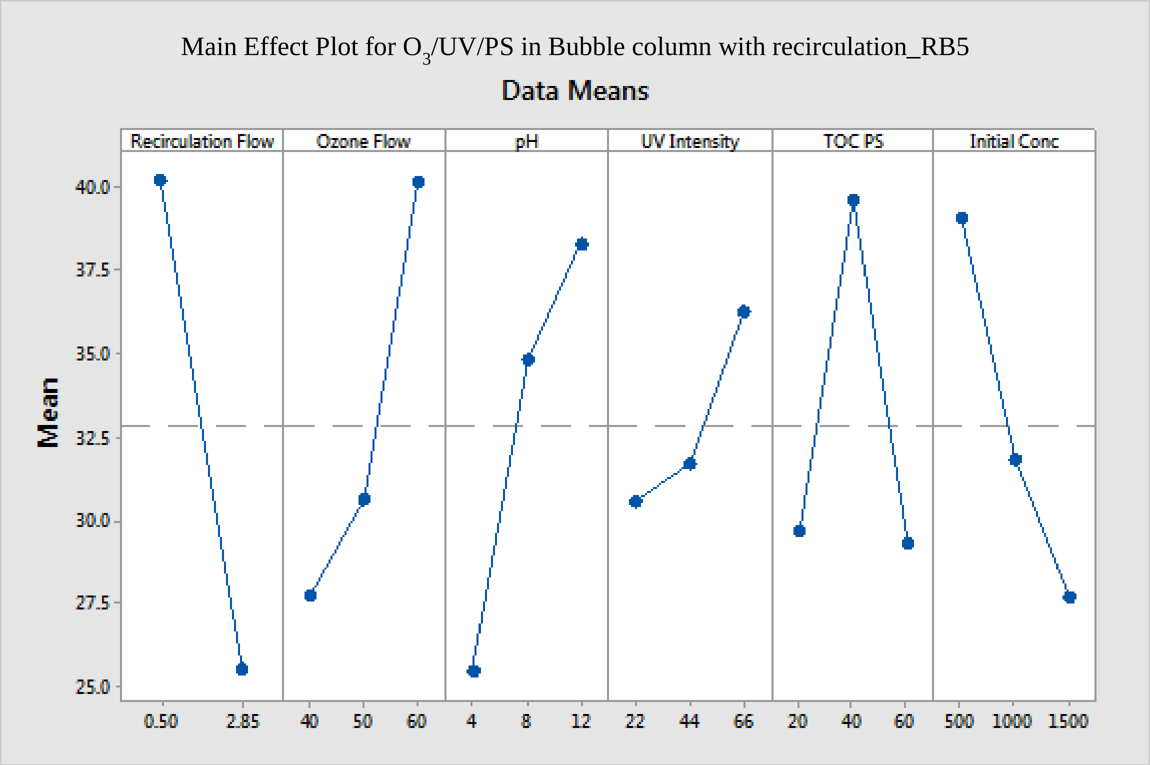
b. Experiments for Venturi and Bubble column with recirculation configuration for individual dye

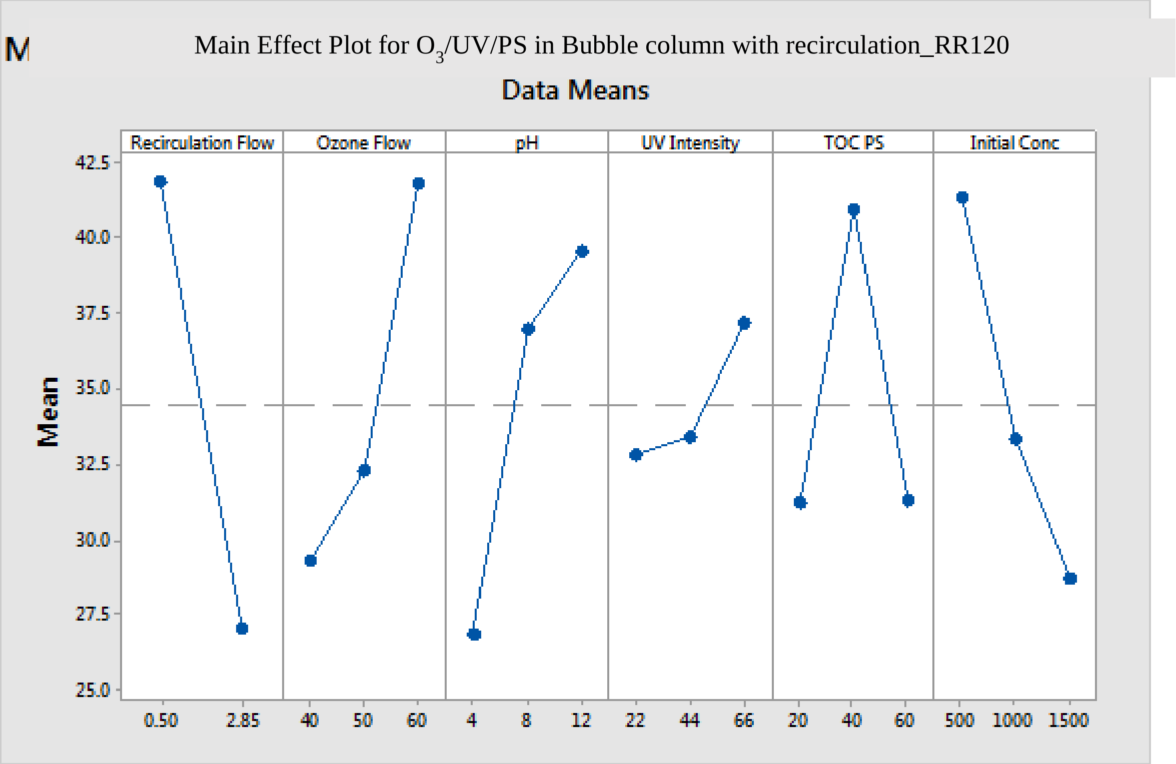
Experiment No.	**Water recirculation Flow**	**Ozone Flow**	**pH**	**UV Intensity**	**TOC PS**	**Initial dye Concentration**
1	1	1	1	1	1	1
2	1	1	2	2	2	2
3	1	1	3	3	3	3
4	1	2	1	1	2	2
5	1	2	2	2	3	3
6	1	2	3	3	1	1
7	1	3	1	2	1	3
8	1	3	2	3	2	1
9	1	3	3	1	3	2
10	2	1	1	3	3	2
11	2	1	2	1	1	3
12	2	1	3	2	2	1
13	2	2	1	2	3	1
14	2	2	2	3	1	2
15	2	2	3	1	2	3
16	2	3	1	3	2	3
17	2	3	2	1	3	1
18	2	3	3	2	1	2

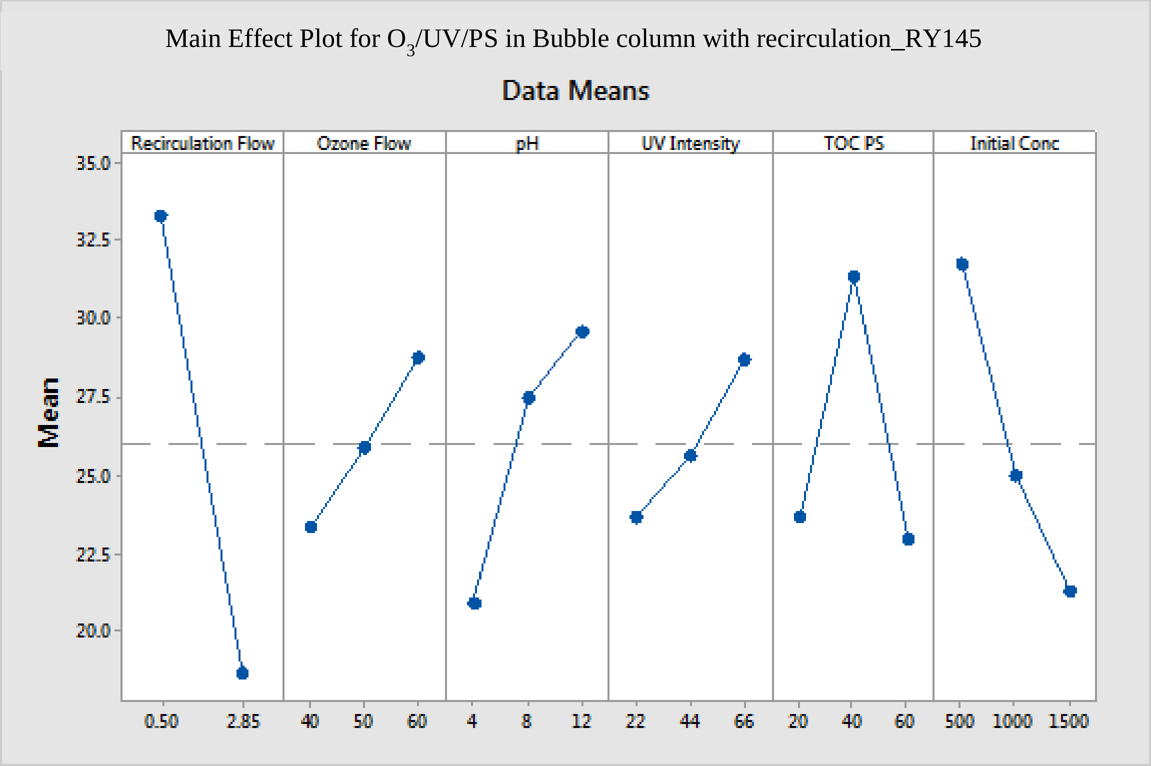
Appendix 3

Main Effect plots for RB5, RR120 and RY145

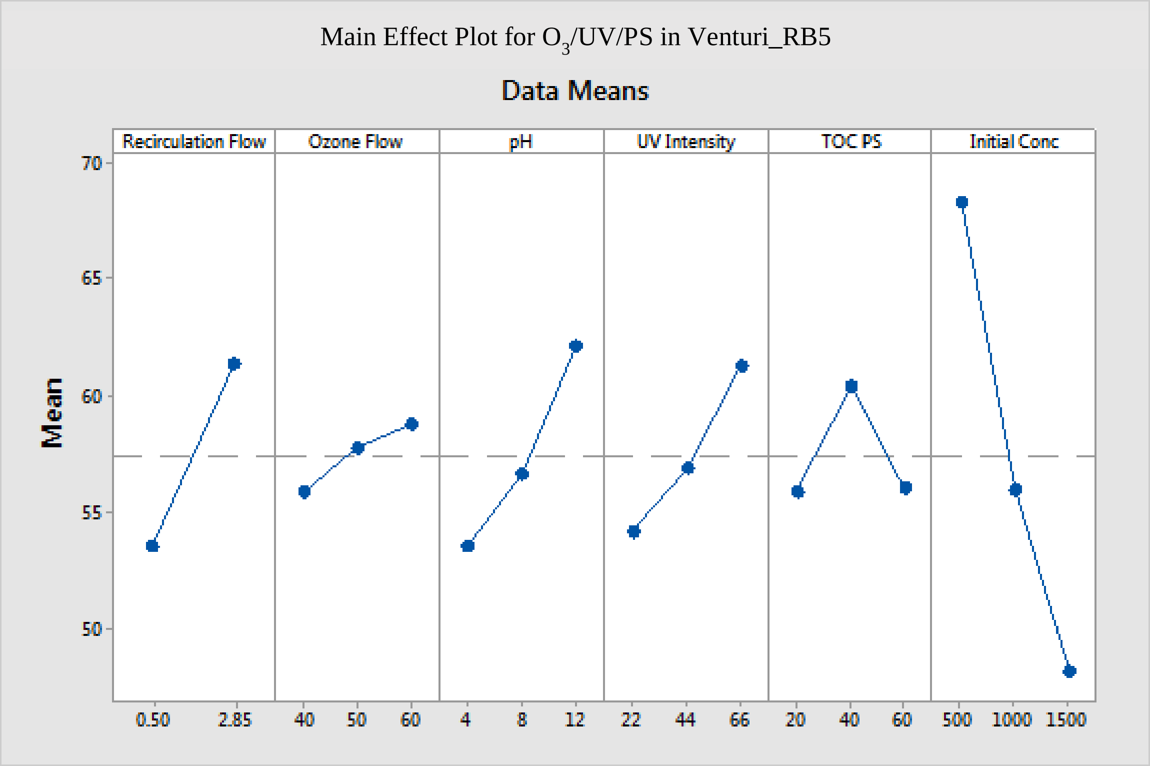
a. Bubble column with recirculation

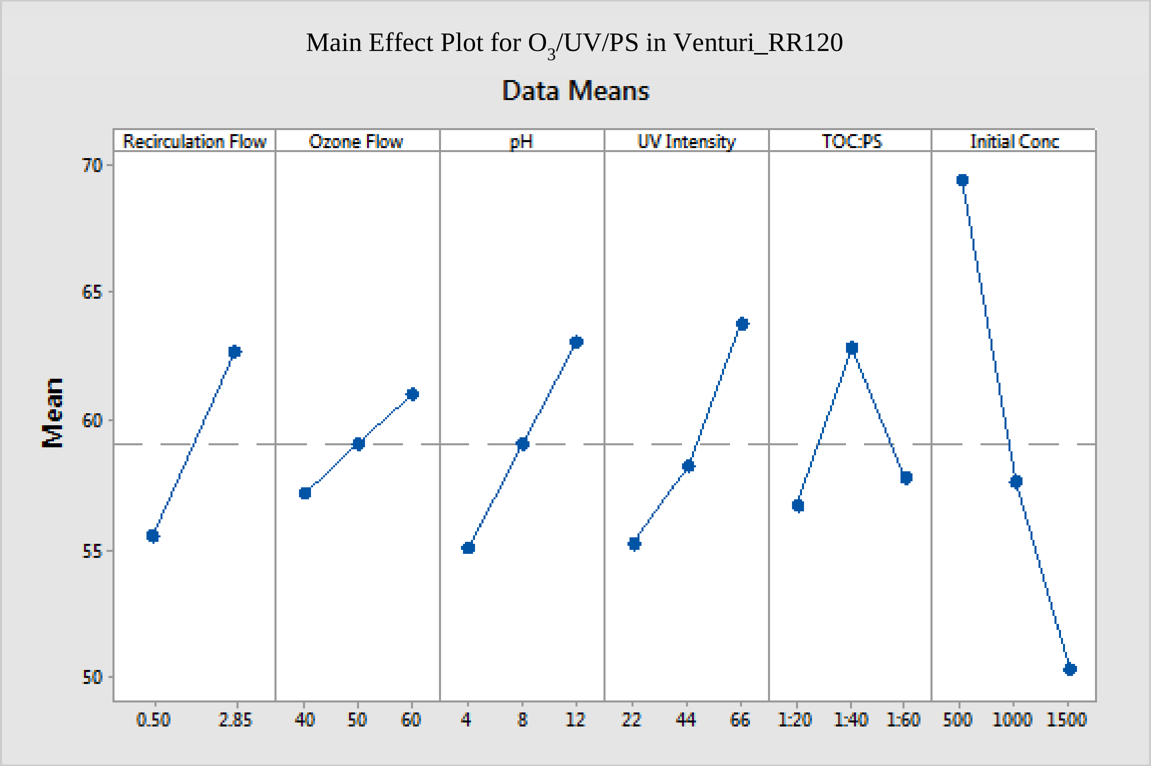


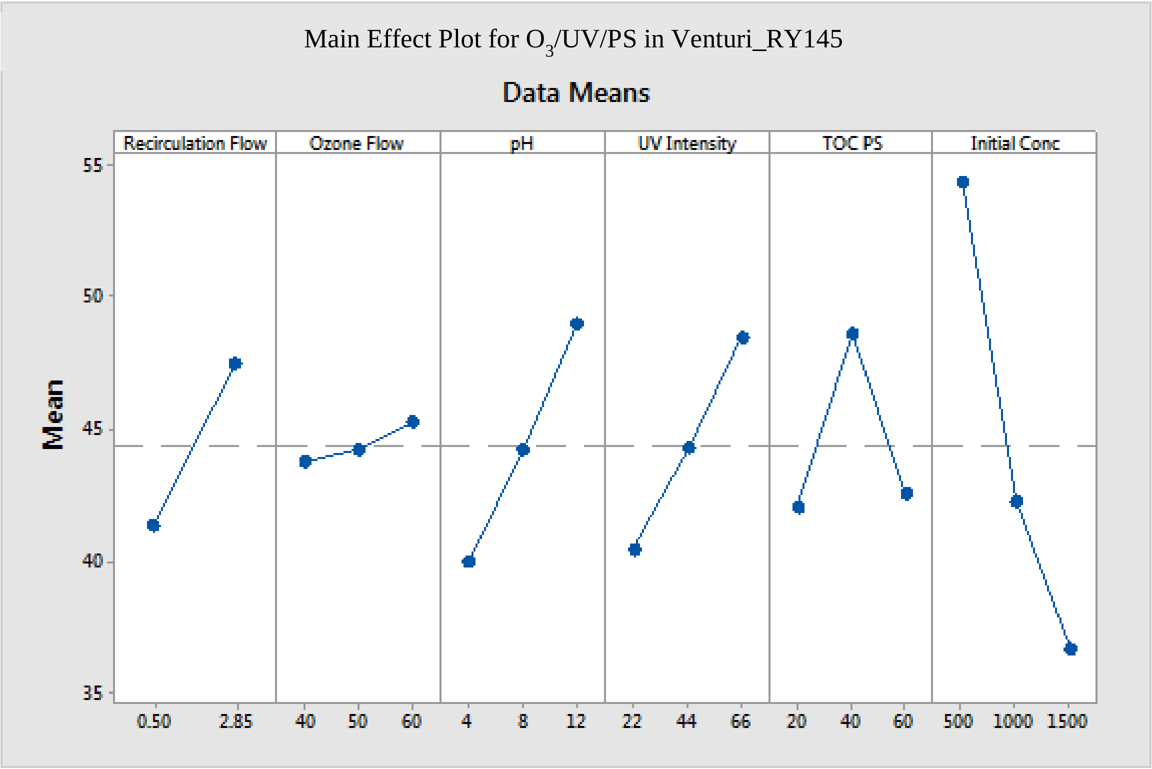



Main Effect Plot for O_3/UV/PS in Bubble column with recirculation_RY145
Data Means
Mean
35.0
32.5
30.0
27.5
25.0
22.5
20.0
Recirculation Flow
Ozone Flow
pH
UV Intensity
TOC PS
Initial Conc
0.50
2.85
40
50
60
4
8
12
22
44
66
20
40
60
500
1000
1500

b. Venturi

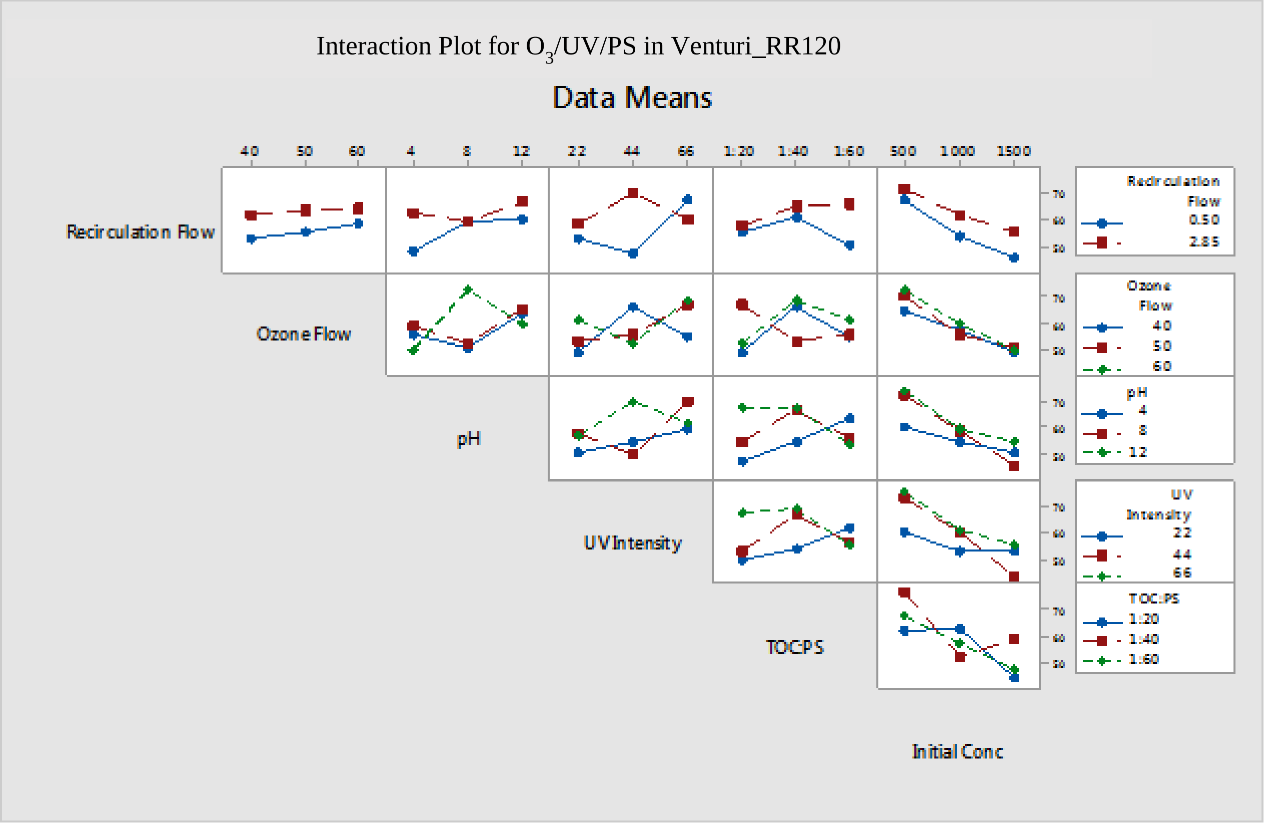

Main Effect Plot for O3/UV/PS in Venturi_RB5
Data Means
Mean
70
65
60
55
50
Recirculation Flow
Ozone Flow
pH
UV Intensity
TOC PS
Initial Conc
0.50
2.85
40
50
60
4
8
12
22
44
66
20
40
60
500
1000
1500

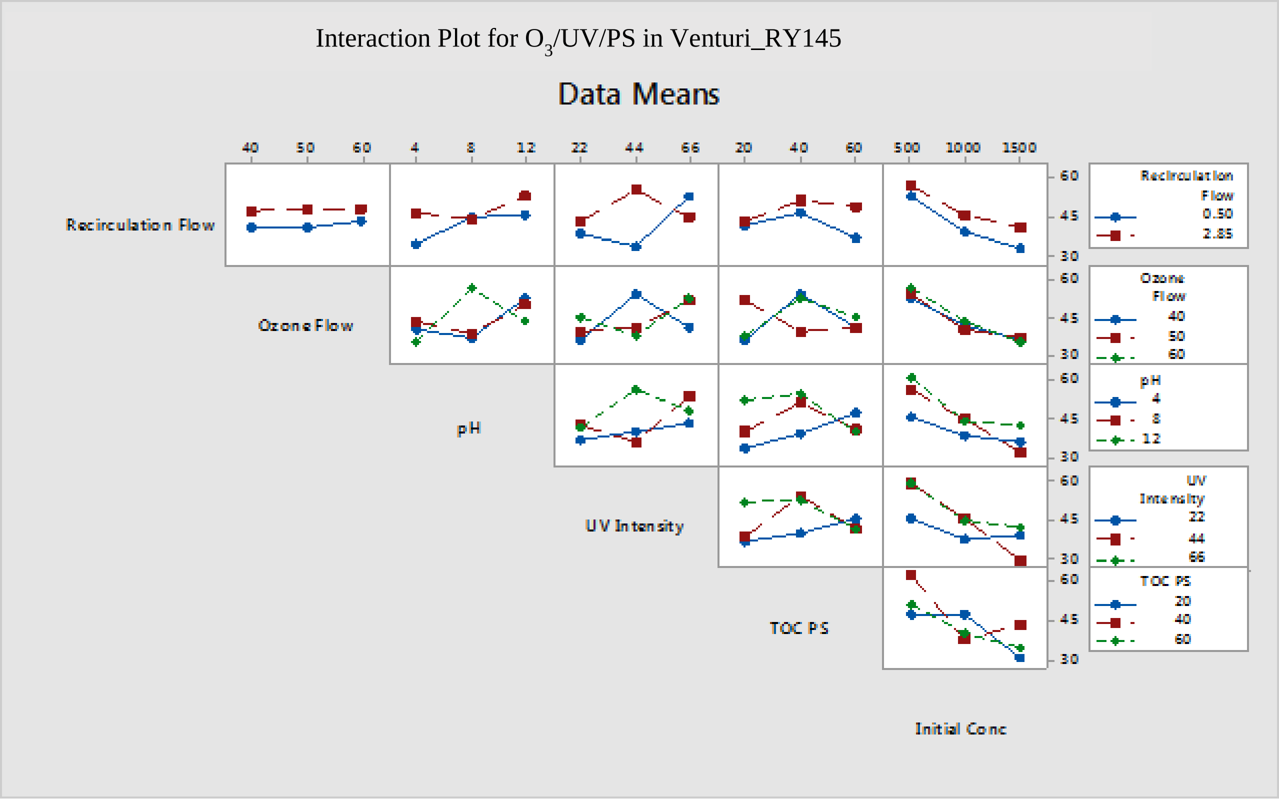

Main Effect Plot for O3/UV/PS in Venturi_RR120
Data Means
Mean
70
65
60
55
50
Recirculation Flow
Ozone Flow
pH
UV Intensity
TOC:PS
Initial Conc
0.50
2.85
40
50
60
4
8
12
22
44
66
1:20
1:40
1:60
500
1000
1500


Main Effect Plot for O_3/UV/PS in Venturi_RY145
Data Means
Mean
55
50
45
40
35
Recirculation Flow
0.50
2.85
Ozone Flow
40
50
60
pH
4
8
12
UV Intensity
22
44
66
TOC PS
20
40
60
Initial Conc
500
1000
1500

Appendix 4

Interaction plots for RR120 and RY145





Appendix 5

Response value for S/N ratio for RB5 in Venturi reactor

Reactive Red 120

Level	Water Recirculation flow	Ozone flow	pH	UV Intensity	TOC:PS ratio	Initial concentration of dye
1	34.71	35.03	34.47	34.77	34.91	36.71
2	35.87	35.29	35.26	35.09	35.84	35.18
3		35.55	35.91	36.01	35..12	33.94
Delta	1.16	0.53	1.21	1.24	0.93	2.81
Rank	4	6	3	2	5	1

Reactive Yellow 145

Level	Water Recirculation flow	Ozone flow	pH	UV Intensity	TOC:PS ratio	Initial concentration of dye
1	32.05	32.61	31.87	32.04	32.22	34.60
2	33.40	32.69	32.66	32.54	33.52	32.46
3		32.87	33.65	33.60	32.43	31.12
Delta	1.35	0.26	1.78	1.57	1.29	3.48
Rank	4	6	2	3	5	1

Appendix 6

OCC Calculations

O_3 Process

1. **Formula:**

$$1\ \mathrm{kg\ O_2 m^{-3}} = \frac{1\ \mathrm{kmol\ O_3}}{48\ \mathrm{kg\ O_3}} \cdot \frac{6\ \mathrm{kmol^{-}}}{1\ \mathrm{kmol\ O_3}} \cdot \frac{1\ \mathrm{kmol\ O_2}}{4\ \mathrm{kmol^{-1}}} \cdot \frac{32\ \mathrm{kg\ O_2}}{1\ \mathrm{kmol\ O_2}} = 1.00\ \left(\frac{\mathrm{kg\ O_3}}{\mathrm{m^3}}\right)$$

$$1\ \mathrm{OCC} = \frac{1\ \mathrm{kg\ O_2}}{\mathrm{m^3}} = 1.00\ \times\ [\mathrm{O_3}]\left(\frac{\mathrm{kg\ O_3}}{\mathrm{m^3}}\right)$$

2. **Sample Calculation:**

Reaction time: 90 min = 1.5 h

Ozone flow: 1.35 g/h

Volume of synthetic wastewater: 3 lit

$$\mathrm{OCC} = \frac{\mathrm{Flowrate}\ \left(\frac{\mathrm{g}}{\mathrm{h}}\right) \times \mathrm{Reaction\ time\ (h)}}{\mathrm{Volume\ of\ wastewater}}$$

$$1\ \mathrm{OCC} = \frac{1.35\ \left(\frac{\mathrm{g}}{\mathrm{h}}\right) \times 1.5\ \mathrm{(h)}}{3\ \mathrm{lit}} = 0.675\ \frac{\mathrm{g}}{\mathrm{L}}\ \mathrm{or}\ \frac{\mathrm{kg}}{\mathrm{m^3}}$$

3. **Table for OCC w.r.t Ozone mass flow**

Sr. No.	**Ozone Mass Flow (g/h)**	**OCC**
1.	1.35	0.675
2.	1.64	0.820
3.	1.8	0.900
4.	1.86	0.930

O$_3$/UV Process

1. Formula

$$1\ \mathrm{OCC} = \frac{1\ \mathrm{kg\ O_2}}{\mathrm{m^3}} = \frac{\mathrm{I_0(cm^{-2}S^{-1}) \times A(cm^2) \times t\ (sec) \times 10^6(cm^3m^{-3})}}{\mathrm{6.023 \times 10^{26}(kmol^{-1}) \times V(cm^3)}} \cdot \frac{\mathrm{1\ kmolO_2}}{\mathrm{4\ kmol^{-1}}} \cdot \frac{\mathrm{32\ kgO_2}}{\mathrm{1\ kmol\ O_2}}$$

$$\mathrm{I_0} = \frac{\mathrm{P\lambda}}{\mathrm{hC}} = \frac{26 \times 10^{-6}\left(\frac{\mathrm{w}}{\mathrm{cm^2}}\right)(254 \times 10^{-7})}{(6.626 \times 10^{-34})(3 \times 10^{10})} = 3.3222 \times 10^{13}$$

$$\mathrm{A} = \pi\mathrm{DH} = 213.2261\ \mathrm{cm^2}$$

$$\mathrm{V} = \frac{\pi}{4}\mathrm{D^2H} = 42.6452\ \mathrm{cm^3}$$

$$1\ \mathrm{OCC} = 0.04621$$

2. Table for OCC w.r.t UV Intensity

Sr. No.	UV Intensity (W)	OCC
1.	11	0.0462
2.	22	0.0924
3.	44	0.1386
4.	66	0.1848

O_3/UV/PS Process

1. Formula

$$1\ \mathrm{OCC} = \frac{1\ \mathrm{kg\ O_2}}{\mathrm{m^3}} = [\mathrm{Na_2S_2O_8}]\left(\frac{\mathrm{kg\ Na_2S_2O_8}}{\mathrm{m^3}}\right)\cdot\frac{1\ \mathrm{kmol\ Na_2S_2O_8}}{238\ \mathrm{kg\ Na_2S_2O_8}}\cdot\frac{2\ \mathrm{kmol^{-1}}}{1\ \mathrm{kmol\ Na_2S_2O_8}}\cdot\frac{1\ \mathrm{kmolO_2}}{4\ \mathrm{kmol^{-1}}}\cdot\frac{32\ \mathrm{kgO_2}}{1\ \mathrm{kmol\ O_2}}$$

$$1\ \mathrm{OCC} = 0.0701 \times [\mathrm{Na_2S_2O_8}]\left(\frac{\mathrm{kg\ Na_2S_2O_8}}{\mathrm{m^3}}\right)$$

2. Sample Calculation

Initial TOC: 100 mg/L

TOC:PS ratio = 1:10

$$\frac{100}{\mathrm{PS}} = \frac{1}{10}$$

PS = 1000 mg/L = 1 g/L

$$192\ \mathrm{gm\ S_2O_8} \approx 238\mathrm{gm\ Na_2S_2O_8}$$

$$= \frac{1.0 \times 238}{192} = 1.2395\,\frac{\mathrm{g}}{\mathrm{L}}\,\mathrm{of\ Na_2S_2O_8}$$

$$= 1.2395\ \frac{\mathrm{kg}}{\mathrm{m^3}}\,\mathrm{of\ Na_2S_2O_8}$$

$$1\ \mathrm{OCC} = 0.0701 \times 1.2395\ \frac{\mathrm{kg}}{\mathrm{m^3}}\,\mathrm{of\ Na_2S_2O_8}$$

$$1\ \mathrm{OCC} = 0.0868$$

Electrical Energy, KWh / order of contaminant /m^3 (EE/O)

1. Formula

$$\frac{\mathrm{EE}}{\mathrm{O}} = \frac{\mathrm{P} \times \mathrm{t} \times 1000}{\mathrm{V} \times 60 \times \log\left(\frac{\mathrm{C}}{\mathrm{C_0}}\right)}$$

where,

EE/O = Electric Energy, KWh or KWh /order of contaminant/m^3.

P = Rate of power of AOP (KW).

t = Treatment time (min).

V = Volume of wastewater treated in time t, (L).

C_O = Initial concentration of contaminant (mol/L).

C = Final concentration of contaminant (mol/L).

2. Sample calculation

Initial TOC, mgL^{-1}	135.47
Final TOC, mgL^{-1}	53.55
log C0/C	0.4031
Time, min	90
Power, kW	0.216754
Volume, L	3
EE/O	268.8702

Publications related to Thesis

Papers published

1. Sandip Sharma, Jimit Buddhdev, Manish Patel, Jayesh P Ruparelia, "Studies on Degradation of Reactive Red 135 Dye in Wastewater using Ozone", *Procedia Engineering* 51 (2013) 451.

2. S. P. Sharma and J. P. Ruparelia, "Integrated Ozonation Process for treatment of Refractory Organic Pollutant – RB5." *International Journal of Advanced Research in Engineering and Technology,* 7(6), (2016): 45–52.

3. S. P. Sharma, J. P. Ruparelia, "Synergistic Effect of O_3/UV/PS Process for oxidation of Reactive Dyes: Effects of operating parameters." *International Journal of Advanced Research in Engineering and Technology,* 8(2),(2017): pp. 49–57.

International conference papers

1. Sandip Sharma, J.P.Ruparelia and M.L.Patel, "A general review on Advanced Oxidation Processes for waste water treatment", *International conference on current trends in technology,* NUiCONE – 2011

2. Sandip Sharma, J.P.Ruparelia, Manish Patel, "Comparison of Fenton and Electro-fenton processes for decolorization of C.I. Acid yellow 23" *4th International Congress of Environmental Research,* SVNIT Surat December 15-17, 2011

3. Sandip Sharma, Jimit Buddhdev, and J. P. Ruparelia, "Treatment of Synthetic Industrial Dyes Wastewater by Ozonation", *International conference on current trends in technology,* NUiCONE – 2013'

4. Sandip Sharma, J. P. Ruparelia, "Comparative study of ozone based AOP's for mineralization of Reactive Red 120", *1st International Conference on Sustainable Water Processing* 11-14 September 2016 Sitges, Spain

Chapters Published in Book

1. Combined catalytic ozonation and UV treatment for removal of reactive red 120 dye from water, Multi-disciplinary Sustainable Engineering: Current and Future Trends, CRC Press 2016, 207-212, ISBN No. 978-1-138-02845-6

2. Feasibility study on degradation of RR120 dye from water by O_3, O_3/UV and O_3/UV/Persulfate, Multi-disciplinary Sustainable Engineering: Current and Future Trends, CRC Press 2016, ISBN No. 978-1-138-02845-6

Papers under communication

1. Sandip P. Sharma, Jayesh P. Ruparelia, “Comparison of Advanced Ozone based oxidation treatment for wastewater containing three different reactive azo dyes” Environmental protection engineering