OXIDATION OF ACID RED 151 SOLUTIONS BY PEROXONE (O_3/H_2O_2) PROCESS

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ABSTRACT

OXIDATION OF ACID RED 151 SOLUTIONS BY PEROXONE (O_3/H_2O_2) PROCESS

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Wastewaters from textile industry contain organic dyes, which cannot be easily treated by biological methods. Therefore, pretreatment by an advanced oxidation process (AOP) is needed in order to produce more readily biodegradable compounds and to remove color and chemical oxygen demand (COD) simultaneously.

In this research, ozone (O_3) is combined with hydrogen peroxide (H_2O_2) for the advanced oxidation of an azo dye solution, namely aqueous solution of Acid Red 151, which is called as "Peroxone process". The aim of the study is to enhance the ozonation efficiency in treating the waste dye solution. The effects of pH, initial dye and initial ozone concentrations and the concentration ratio of initial H_2O_2 to initial O_3 on color and COD removals were investigated. Also, the kinetics of O_3-dye reaction in the presence of H_2O_2 was approximately determined.

As a result of the experimental study, it was seen that an increase in the initial dye concentration at a constant pH and initial ozone concentration did not change the COD % removal significantly, from a statistical analysis of the data. The results obtained at pH values of 2.5 and 7 gave higher oxidation efficiencies in terms of color and COD removals compared to those at pH of 10. The best initial molar ratio of H_2O_2 to O_3 was found to be 0.5, which yielded highest treatment efficiency for each pH value studied. The results of the excess dye experiments suggest that the ozonation of Acid Red 151 follows an average first order reaction with respect to ozone at pH=2.5 and pH=7 whereas it is around 0.56 at pH=10. By Initial Rate Method, the orders with respect to individual reactants of O_3 and dye were determined as one, the total order of the reaction being two for all the studied pH. As a conclusion, a further study of the peroxone process at a pH of 10 can be recommended to determine the reaction kinetics and mechanism at this pH, where radicals play an important role.

Keywords: Peroxone process, Ozonation, Advanced oxidation process (AOP), Acid Red 151, Textile wastewater treatment, Azo dye

ÖZ

ASİT KIRMIZI 151 ÇÖZELTİLERİNİN PEROKSON (O_3/H_2O_2) PROSESİ İLE OKSİDASYONU

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Tekstil endüstrisi atıksuları, biyolojik metodlarla kolaylıkla muamele edilemeyen organik boyalar içerirler. Bu nedenle, biyolojik parçalanmaya daha meyilli bileşiklerin üretilmesi ve renk ile kimyasal oksijen ihtiyacının (KOİ) eşzamanlı giderimi için, kimyasal oksidasyon yolu ile ön muamele gereklidir.

Bu araştırmada, bir azo boya (Asit Kırmızı 151) çözeltisinin ileri oksidasyonu için, ozon (O_3) ve hidrojen peroksitin (H_2O_2) birlikte kullanımına dayanan "Perokson prosesi" ile çalışılmıştır. Bu çalışmanın amacı, atık boya çözeltisinin muamelesinde ozonlama veriminin arttırılmasıdır. pH, başlangıç boya ve O_3 derişimleri ile başlangıç H_2O_2 derişiminin başlangıç O_3 derişimine oranının renk ve KOİ giderimleri üzerindeki etkileri incelenmiştir.

Ayrıca, H_2O_2 varlığında O_3-boya reaksiyonunun kinetiği yaklaşık olarak belirlenmiştir.

Gerçekleştirilen deneysel çalışma sonucunda, sabit başlangıç pH değeri ile O_3 derişiminde, başlangıç boya derişimindeki bir artışın KOİ % giderimini belirgin olarak değiştirmediği istatistiki veri analizi yöntemi ile belirlenmiştir. pH=2.5 ve pH=7 değerlerinde elde edilen renk ve KOİ giderimlerinin pH=10'da elde edilenlere göre daha yüksek olduğu gözlenmiştir. Çalışılan tüm pH değerlerinde, en yüksek proses verimliliği başlangıç H_2O_2 derişiminin başlangıç O_3 derişimine oranının 0.5 olduğu durumda elde edilmiştir. Aşırı miktarda başlangıç boya konsantrasyonu ile gerçekleştirilen deneyler sonucunda (Method of Excess), pH=2.5 ve pH=7 değerlerinde, tepkimenin ozon konsantrasyonuna bağlı derecesi ortalama 1 olarak, pH=10 olduğu durumda ise 0.56 olarak belirlenmiştir. Başlangıç hızı metodu (Initial rate method) ile tepkime derecesi, çalışılan pH aralığında, hem boya hem de ozon konsantrasyonuna göre 1 olarak bulunmuş, toplam tepkime derecesi de 2 olarak belirlenmiştir. Sonuç olarak, ileri bir çalışmada radikallerin önemli bir rol oynadığı pH=10 değerinde perokson prosesindeki reaksiyon kinetiğinin ve mekanizmasının saptanması tavsiye edilebilir.

Anahtar Kelimeler: Perokson prosesi, Ozonlama, İleri oksidasyon prosesi (İOP), Asit Kırmızı 151, Tekstil atıksuyu arıtımı, Azo boya

To my family.....

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LIST OF SYMBOLS

COD	chemical oxygen demand, mg/L
Color	Color of textile wastewater, Pt-Co
TOC	total organic carbon, mg/L
BOD	biochemical oxygen demand, mg/L
M	Molarity
t	time, min
T	temperature, °C
C_b	blank indigo concentration, mM
C_{dye}	dye concentration, mM
C_{O3}	ozone concentration, mM
$C_{dye,i}$	initial dye concentration, mM
C_{ind}	indigo concentration, mM
$C_{O3,i}$	initial ozone concentration, mM
r	$C_{H2O2,i}/C_{O3,i\ ,i}$ concentration ratio
$k^{'}$	reaction rate constant with respect to ozone concentration
k	reaction rate constant with respect to dye concentration
k_{O3}	initial rate constant with respect to initial ozone concentration
k_{dye}	initial rate constant with respect to initial ozone concentration
a	reaction rate order with respect to ozone concentration
b	reaction rate order with respect to dye concentration
r_{O3}	reaction rate with respect to ozone concentration, mM/min
r_{dye}	reaction rate, mM/min
n_b	mols of blank indigo, mol
V_{ind} (s)	volume of sample taken into indigo solution, mL

V_t (s)	volume of sample taken into thiosulphate solution, mL
V_t (T)	total volume in thiosulphate solution, mL
A_b	absorbance of blank indigo, cm^{-1}
A_{dye}	absorbance of dye, cm^{-1}
A_{ind}	absorbance of indigo, cm^{-1}

CHAPTER 1

INTRODUCTION

Wastewater from textile industry is generally characterized by high levels of chemicals, biological oxygen demand (BOD), total suspended solids and color.

Disposal of textile wastewater is an environmental concern since the associated color is noticeable to the public, and some azo dyes may have carcinogenic and/or teratogenic effects on public health [1]. Color, depending on its origin, it is not only a problem of aesthetics but also of toxicity and reduced biodegradability [2-4]. Color is also the primary problem for water reuse and material recovery in dyeing operations [5]. Therefore, it is necessary to find an effective method of wastewater treatment capable of removing color and toxic organic compounds from textile effluents. These less or non-biodegradable compounds, called xenobiotics, cannot be completely removed by biological treatment and wastewater contaminated with these substances must be treated by physical and chemical means.

Because the chemical structures of dyes are rather complicated, biological treatment methods are not efficient for their degradation. These methods do not result in dye degradation. They merely provide the physical removal of the dye material from the effluent, which still creates a waste disposal problem; that is a large amount of sludge or solid waste generated resulting in high operational costs for sludge treatment and disposal [6].

Hence, the use of conventional oxidants has been the standard chemical method for years, for the treatment of dye wastewater, however, these procedures are not always feasible owing to thermodynamic and kinetic limitations of the common reagents to attack refractory compounds. To remedy this situation, advanced oxidation processes or techniques (AOPs, AOTs), which generate powerful hydroxyl radicals ($HO^{\cdot}$, E^{o}= 2.8 V vs. normal hydrogen electrode), have been proposed for color removal and degradation of dyes [7-10]. Particularly, these techniques have been found to be suitable for azo-type dyes, which are the mostly used textile colorants [11-14].

Advanced oxidation processes are defined as those processes which utilize the hydroxyl radical or the primary oxidant and include systems such as combinations of O_3, H_2O_2 and UV [15]. They have been defined broadly as those aqueous phase oxidation processes which are primarily based on the intermediacy of the hydroxyl radical in the mechanism(s) resulting in the destruction of the target pollutant or contaminant compound [16].

Ozone has been shown to be effective in decolorizing industrial dye wastewater, since it quickly reacts with the colored compounds and it achieves high color removal efficiencies [17]. By accelerating the ozone decomposition rate, the hydroxyl radical concentration can be elevated, which increases the oxidation rate of the colored compounds by ozonation. This procedure increases the contribution of indirect oxidation (oxidation by hydroxyl radicals generated via ozone decomposition) over direct ozone oxidation.

Several methods have been used to increase ozone decomposition and produce high concentrations of hydroxyl radicals. The way to produce these radicals in the aqueous phase is to combine two oxidants. One of the most promising processes involves adding hydrogen peroxide to ozonated water, a process commonly referred to as peroxone [18].

In the peroxone process, ozone residual is short lived because the added peroxide greatly accelerates the ozone decomposition. As a result, it can be said that oxidation is expected to be more effective and faster in the peroxone process compared to the molecular ozone process.

Removal of color, taste and pesticide residues from municipal drinking water has been proven with the peroxone process in the U.S.A. and Germany. A municipal plant operated by the city of Los Angeles is being used for the removal of trichloroethylene and tetrachloroethylene [67].

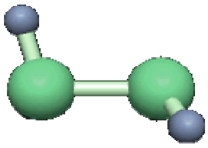
In the literature, there is a lack of information about the oxidation of coloring compounds by the peroxone process. With this in mind, the purpose of the present study is to improve the ozonation efficiency (in terms of color removal and COD reduction percentages) of a synthetic azo dye, Acid Red 151, to observe the effects of the ratio of initial hydrogen peroxide concentration to initial ozone concentration ($[H_2O_2]/[O_3]$), pH, initial dye and initial ozone concentrations and to determine the kinetics of O_3-Dye reactions in the presence of H_2O_2.

CHAPTER 2

BACKGROUND

2.1 Peroxone (O_3 / H_2O_2) Process

2.1.1 Hydrogen Peroxide:



$$2\ H_2O_2 \text{ ----> } 2\ H_2O + O_2$$

(hydrogen peroxide ----> water + oxygen)

Figure 2.1 Chemical structure of Hydrogen Peroxide

H_2O_2 is one of the most powerful oxidizers known. It is stronger than chlorine, chlorine dioxide, and potassium permanganate, and through catalysis, H_2O_2 can be converted into hydroxyl radicals ($OH^{\cdot}$).

Table 2.1 Oxidation potentials of some oxidants

Oxidant	Oxidation Potential, V
Flourine	3.0
Hydroxyl radical	2.8
Ozone	2.1
Hydrogen peroxide	1.8
Potassium permanganate	1.7
Chlorine dioxide	1.5
Chlorine	1.4

Despite its power, H_2O_2 is a natural metabolite of many organisms, which decompose the H_2O_2 into oxygen and water. H_2O_2 is also formed by the action of sunlight on water; aurification system for our environment. Consequently, H_2O_2 has none of the problems of gaseous release or chemical residues that are associated with other chemical oxidants.

H_2O_2 can inhibit microbial growth (as in the biofouling of water circuits) and encourage microbial growth (as in the bioremediation of contaminated groundwaters and soils). Similarly, it can treat both easy-to-oxidize pollutants (iron and sulfides) and difficult-to-oxidize pollutants (solvents, gasolines and pesticides).

The reason why H_2O_2 can be used in such diverse applications is the different ways in which its power can be directed, termed selectivity. By simply adjusting the conditions of the reaction (e.g., pH, temperature, dose, reaction time, and/or catalyst addition), H_2O_2 can often be made to oxidize one pollutant over another, or even to favor different oxidation products from the same pollutant.

Since it was first commercialized in the 1800's, H_2O_2 production has now grown to over a billion pounds per year (as 100%). In addition to pollution control, H_2O_2 is used to bleach textiles and paper products, and to manufacture process foods, minerals, petrochemicals, and consumer products (detergents).

2.1.1.1 Environmental Applications of H_2O_2

H_2O_2 applications span the range of possible media: air, water, wastewater soils and sludges. Depending on the objective, H_2O_2 may be used either alone or in combination with other processes to enhance their performance.

Applications of H_2O_2 alone in wastewater treatment are:

Odor control: Hydrogen peroxide oxidizes hydrogen sulfide, mercaptans, amines and aldehydes. H_2O_2 may be applied directly to aqueous wastes containing these odorants, or to wet scrubbers used to remove them from air streams. If the odors are the result of biological activity, H_2O_2 may instead be added as a preventative to eliminate the anoxic conditions which favor the generation of odors.

Corrosion control: It destroys residual chlorine and reduced sulfur compounds (thiosulfates, sulfites, and sulfides) which form corrosive acids when condensed onto processing equipment and oxidized by air.

*BOD - COD removal: It o*xidizes both organic and inorganic pollutants which contribute to BOD and COD, H_2O_2 may be needed to oxidize the more resistant substances. H_2O_2 may also affect BOD/COD removal ratio by enhancing the performance of other processes.

Inorganic oxidation: It oxidizes cyanides, NO_x/SO_x, nitrites, hydrazine, carbonyl sulfide, and other reduced sulfur compounds mentioned above (odor/corrosion control).

Organic oxidation: It hydrolyzes formaldehyde, carbon disulfide, carbohydrates, organophosphorus and nitrogen compounds, and various water-soluble polymers; and (with catalysis) destroys phenols, BTEX pesticides, solvents, plasticizers, chelants, and virtually any other organic requiring treatment.

Metal oxidation: It oxidizes ferrous iron, manganese, arsenic, and selenium to improve their adsorption, filtration, or precipitation from process waters and wastewaters.

Toxicity reduction - Biodegradability improvement: It chemically digests complex organics into smaller, less toxic and more biodegradable fragments with catalysis.

Disinfection - Biocontrol: It checks excess biogrowth in water supplies and cooling circuits, and (with catalysis) disinfects process waters and biological effluents.

Applications of H_2O_2 to improve/enhance the unit operations and/or processes are listed below:

Flocculation - precipitation: It oxidizes metal complexes and improves the performance of inorganic flocculants.

Air flotation - Releases evenly dispersed microbubbles which entrain emulsified fats, oils and greases to enhance their removal in air flotation units and grease traps.

Biotreatment: It degrades toxic, refractory or bio-inhibitory organics, rendering them more amenable to biodegradation.

Carbon adsorption: It enhances the adsorption of many pollutants while providing dissolved oxygen to support biologically-active carbon beds (improving removal efficiencies still further).

Air scrubbers: It replaces chlorine for deodorizing off-gases and controlling volatile organic compounds (VOC's). Depending on the target pollutant(s), catalytic or advanced oxidation processes may be required.

Incineration: It provides supplemental oxygen to improve combustion efficiencies and lowers operating temperatures.

2. 1.2 H_2O_2 Processes

2.1.2.1 H_2O_2 alone

Most H_2O_2 applications involve its simple injection into wastewater stream with no requirement for additional chemicals or equipment. These include the control of biogrowth (slime), the supply of supplemental oxygen, the removal of chlorine residuals, and the oxidation of sulfides/sulfites, metals, and other easy-to-oxidize components of BOD and/or COD. Activation of H_2O_2 in these applications may be affected by the adjustment/control of pH, temperature, and/or reaction time.

2.1.2.2 Catalytic H_2O_2

The more difficult-to-oxidize pollutants may require the H_2O_2 to be activated with catalysts such as iron, copper, manganese, or other transition metal compounds. These catalysts may also be used to speed up H_2O_2 reactions that may otherwise take hours or days to complete. H_2O_2

catalysis may occur either in solution (using soluble catalysts) or in packed columns (using solid catalysts).

Solution catalysis:

The most commonly used solution-catalyst is iron, which when used with H_2O_2 is referred to as Fenton's Reagent. The reaction requires a slightly acidic pH and results in the formation of highly reactive hydroxyl radicals ($OH^{\cdot}$) which are capable of degrading most organic pollutants. Another solution-catalyst is copper, which is often used to destroy cyanides. Other metals also show catalytic activity with hydrogen peroxide and may be used to selectively destroy specific pollutants.

Packed column catalysis:

Solid catalysts eliminate the need to add soluble metals to the waste stream, and may offer greater flexibility in terms of reaction rates, selectivity, and the need for pH adjustment. This is an active area of research and many new developments are underway for a variety of applications.

2.1.2.3 Advanced Oxidation Processes (AOP's)

AOP's represent the newest development in H_2O_2 technology, and are loosely defined as processes that generate highly reactive hydroxyl radicals without the addition of metal catalysts. Typically, this means combining H_2O_2 with ozone or ultraviolet light. The result is the on-site total destruction of even refractory organics without the generation of sludges or residues. This technology is being widely applied to treat contaminated groundwaters, to purify and disinfect drinking waters and process waters, and to destroy trace organics in industrial effluent

2.1.3 Ozone

Ozone is a strong oxidizing agent that reacts readily with most organic compounds and pathogens found in wastewaters. It is the triatomic form of oxygen (O_3) and is partially soluble in water. It is 10-15 times more soluble than oxygen over the temperature range of 0-60°C [51]. It is a powerful oxidant, with oxidation potential of 2.07 V in alkaline solution. The oxidizing ability of ozone is derived from the third oxygen atom, and ozone attacks electron rich molecules. Ozone is reactive with unsaturated groups and aromatic rings. It produces partial oxidation products such as ketones, aldehydes or acids where oxygen is introduced into many of the carbonaceous sites within the product molecules. It generally does not produce complete mineralization products of CO_2 and H_2O [52].

Although the mechanism of ozone action in aqueous media is complex, it is widely accepted that ozone reacts in two general fashions [53].

- By direct attack of the ozone molecule on the organic compound,
- By an indirect attack, radical-mediated process in which the hydroxyl radical ($OH^{\cdot}$) produced during ozone decomposition in water plays the role of principal oxidizing agent.

The type of process dominating in a given system depends on the physical-chemical conditions: pH, type of substrate, and dissolved salts present. The presence of easily oxidizable substrates and acid conditions favors direct oxidation, whereas oxidation of recalcitrant solutes under alkaline conditions generally takes place by a radical-mediated mechanism.

2.1.4 Peroxone Process

Numerous authors have examined the possibility of increasing ozonation efficiency by associating ozone with various chemical and physical agents. The most thoroughly studied combinations are ozone–catalyst (metal ions, metal oxides, alumina, and activated carbon), ozone–hydrogen peroxide and ozone–UV radiation. One approach that can be used when treating compounds resistant to ozonation is to create conditions favoring indirect oxidation by radical species created by ozone decomposition in water.

Several methods have been used to increase ozone decomposition and to produce high concentrations of hydroxyl radicals. One of the most common of these processes involves adding hydrogen peroxide to ozonated water, a process commonly referred to as peroxone. By adding hydrogen peroxide, the net production of hydroxyl radicals is 1.0 mole of hydroxyl radical per mole of ozone [19].

Oxidation in the peroxone process occurs due to two reactions [20].

- Direct oxidation of compounds by aqueous ozone ($O_{3(aq)}$),
- Oxidation of compounds by hydroxyl radicals produced by the decomposition of ozone.

The two oxidation reactions compete for compounds to be oxidized.

A key difference between the ozone and peroxone processes is that the ozone process relies heavily on the direct oxidation of aqueous ozone while peroxone relies primarily on oxidation with hydroxyl radical. In the peroxone process, the ozone residual is short lived because the added peroxide greatly accelerates the ozone decomposition. However, the increased oxidation achieved by the hydroxyl radical greatly outweighs the reduction in direct ozone oxidation because the hydroxyl radical is much more reactive. The net result is that oxidation is more efficient and much faster in the peroxone process compared to the molecular ozone process.

The peroxone process utilizes oxidation by hydroxyl radicals. The oxidation potential of the hydroxyl radical and ozone are as follows:

$OH^{\cdot} + e^{-} \rightarrow OH^{-}$ ....$E^{o} = + 2.8$ V

$O_3 + 2\,H^{+} + 2\,e^{-} \rightarrow O_2 + H_2O$.....................$E^{o} = + 2.07$ V

$O_3 + H_2O + 2\,e^{-} \rightarrow O_2 + 2\,OH^{-}$....................$E^{o} = + 1.24$ V

The peroxone process requires an ozone generation system and a hydrogen peroxide feed system. The process involves two essential steps: Ozone dissolution and hydrogen peroxide addition. Hydrogen peroxide can be added after ozone (thus allowing ozone oxidation and disinfection to occur first) or before ozone (using peroxide as a pre–oxidant, followed by hydroxyl radical reactions) or simultaneously. The most efficient operation is to add ozone first, followed by peroxide for hydroxyl radical oxidation.

2.1.4.1 Oxidation Reactions

Because the radical oxidation is much more effective than direct oxidation with ozone, it has been used extensively to treat difficult-to-oxidize organics such as taste and odor compounds and chlorinated organics (e.g. geosmin, phenolic compounds, trichloroethylene (TCE) and perchloroethylene (PCE)).

Neither ozone nor peroxone significantly destroys total organic carbon (TOC). Peroxone oxidizes the saturated organic carbons and produces by products similar to those found in ozonation; namely, aldehydes, ketones, peroxides, bromate ion and biodegradable organics [21]. However, with the peroxone process, the biodegradability of the wastewater increases, rendering "a portion of the TOC" amenable to removal in biologically active filters.

Peroxone has found a niche in oxidizing difficult to treat organics, such as taste and odor compounds including geosmin [22]. In addition, peroxone has been shown to be effective in oxidizing halogenated compounds such as 1,1-dichloropropene, trichloroethylene, 1–chloropentane and 1,2-dichloroethane [23-25]. Hydroxyl radicals react with all these compounds plus refractory aliphatics such as alcohols and short–chain acids [26].

Hydrogen peroxide and O_3 reaction mechanism is reported by some authors in the literature; Theoretical and experimental works of Staehelin and Hoigne [27], Tomiyasu et al. [28] and others suggested that in the presence of hydrogen peroxide, the reaction is initiated by the formation of hydroperoxide ion (OH_2^-) in a solution.

$O_3 + OH^- \rightarrow HO_2^- + O_2$.................................. (1)

Since H_2O_2 is a weak acid, its partial dissociation in water produces additional hydroperoxide ions [29].

$H_2O_2 \leftrightarrow HO_2^- + H^+$...................................... (2)

The hydroperoxide ion formed above, reacts with ozone molecules to form hydroxyl free radicals [28].

$O_3 + HO_2^- \rightarrow HO^\cdot + O_2^- + O_2$..........................(3)

Following the above step, a series of chain reactions involving the hydroxyl free radical (O_2^-) and ozonide (O_3^-) ions may occur [30].

The most important reactions are:

$O_3 + HO^\cdot \rightarrow HO_2^\cdot + O_2$................................. (4)

$H_2O_2 + HO^\cdot \rightarrow HO_2^\cdot + H_2O$............................ (5)

$HO_2^- + HO^\cdot \rightarrow HO_2^\cdot + OH^-$............................. (6)

$HO_2^\cdot \leftrightarrow O_2^{-\cdot} + H^+$....................................... (7)

$OH^- + HO^\cdot \rightarrow H_2O + O^-$ ....(8)

$O_3 + O_2^{-\cdot} \rightarrow O_3^- + O_2$ ....(9)

$O_3^- + H^+ \rightarrow HO^\cdot + O_2$ ....(10)

$O^- + H_2O \rightarrow HO^\cdot + OH^-$...............................(11)

In addition to the above steps, dissolved pollutants and/or many other scavengers if present in the solution, can react with the hydroxyl radical [32].

2.1.5 Factors Affecting Peroxone Process

2.1.5.1 $[H_2O_2]$ / $[O_3]$ Ratio

The depletion rate of O_3 is mainly a function of the concentrations of O_3, H_2O_2 and OH^- as it is seen from the reactions of (1)–(3).

Reactions (2) and (5) indicate that the consumption rate of H_2O_2 increases with its concentration. The amount of H_2O_2 utilized effectively in the production of hydroperoxide is limited by the equilibrium relationship given in reaction (2). According to reaction (5), any excessive H_2O_2 present in the solution is likely to act as a scavenger in consuming the hydroxyl radical generated. Although the O_3 depletion rate increases with the concentration of H_2O_2 (because of the interactions between the two reactants), the rate may vary due to the scavenging effect of excessive H_2O_2 (and hydroxyl ion) in reacting with hydroxyl radical.

Experimental results of Kuo et al. [33] suggest that at its concentration below a certain level, the effect of H_2O_2 is insignificant in determining the depletion rate of ozone in the peroxone reactions. In the same study they concluded that the interactions between hydrogen peroxide and ozone are effective in the generation of hydroxyl radical if the concentrations of the two oxidants are of the same order in magnitude. At higher concentrations of hydrogen peroxide, however, the excessive hydrogen peroxide is said to be able to act as a scavenger.

As mentioned earlier, treatment of various pollutants by the peroxone process were carried out by some investigators. On the basis of the oxidants applied and extent of pollutants destructed, the optimum concentration ratios of initial H_2O_2 to initial O_3 ($[H_2O_2]/[O_3]$) were reported to be between 0.5-1 [32, 34, 35, 36].

This optimum ratio for trichloroethylene (TCE) and perchloroethylene (PCE) oxidation in a groundwater system was determined to be 0.5 [18]. Tests showed that TCE required lower ozone doses for the same percentage removal compared to PCE. It was reported that the optimum peroxide to ozone ratio, to maximize the reaction rate of hydroxyl radicals can be determined for a specific oxidation application.

Beltran et al. [50] performed the chemical oxidation of debittering table olive wastewater by using ozone alone and its combination with hydrogen peroxide. Highest oxidation rate was observed with the combined process (O_3/H_2O_2). Negative effect of the presence of hydrogen peroxide at high concentration (10^{-2} M) is observed. However, it is concluded that this is an expected result, since at these conditions the mole ratio between ozone and hydrogen peroxide is likely much higher than the optimum stoichiometry (0.5) of the O_3/H_2O_2 oxidizing system. Both of the processes yielded high COD reductions (90 %), nearly complete disappearance of aromatic content and color (more than 90 %) and moderate TOC reductions (40-60 %).

2.1.5.2 pH

Since the ozone decomposition is enhanced with the increases of pH, many investigators have worked on the effect of pH change in ozonation reactions [37-39].

Kuo et al. [40] studied the kinetics and the mechanism of the reaction between ozone and hydrogen peroxide in aqueous solutions. As a result of the experimental study, they found the rate of hydroxyl radical formation insignificant in acidic solutions and focused on the self-decomposition of dissolved ozone in alkaline solutions. The experimental and calculated results indicated that the increases in the decomposition rate with pH was much more pronounced in alkaline than in acidic solutions. Scavenging reactions of hydrogen peroxide were found to be unimportant at or below the pH of 10, if the concentration ratio is near unity ($[H_2O_2]/[O_3]=1$). Kinetic results showed the negative effects of hydroxyl radical scavenging of peroxide at elevated pH's of 11 and 13. In addition, it is suggested that the adverse scavenging reactions can be minimized only if the concentration ratio is much less than unity. At very low ratio of initial concentrations, however, hydrogen peroxide is said to be ineffective in the formation of hydroxyl radical. Therefore, the results of this study showed that the treatment by hydrogen peroxide and ozone mixtures, it is most desirable to carry out the peroxone oxidation process in alkaline solutions at or below pH of 10 with a ratio of initial concentrations of H_2O_2 to O_3, near unity.

Glaze and Kang [32] examined the effect of pH on the peroxone process in typical groundwater. Experimental data showed that the rate of oxidation was a strong function of pH. The rate of oxidation increased from high to low pH generally, but it was relatively constant in the range of pH 6.6-7.6 and was lowest at pH=10. Negative effects of scavenging reactions on the oxidation efficiency were observed at pH values higher than 7.

Esplugas et al. [41] compared ozonation and peroxone processes for the oxidation of phenol. Results of the experimental work showed that the peroxone process improved ozonation efficiency slightly at neutral pH and at low H_2O_2 concentrations whereas it showed inhibitory effects at concentrations higher than 6.2 mM.

Beltran et al. [42] studied the oxidation of tomato wastewater with ozone and peroxone processes. It was seen that, for a given amount of ozone fed, the increase of pH from 6.3 to 9 led to increases in COD degradation rates both for ozonation alone and for the peroxone process. However a further increase of pH up to 11 reduced the level of oxidation. The highest reduction of COD was achieved at pH 9 by the peroxone process. It was also observed that when hydrogen peroxide was present, increase in ozone consumption occurred with respect to that observed during ozonation alone, and the oxidation system, O_3/H_2O_2, was very effective in the treatment of tomato wastewater.

Rice [43] observed the importance of OH radicals at pH values higher than 5. On the other hand, Saupe and Wiesmann [44] observed a critical pH of 7 to get radical reactions for the oxidation of 2,4–dinitrotoluene and 4–nitroaniline. At pH=2, dinitrotoluene removal was slow whereas it increased with the increase of pH to 7.

Koyuncu and Afşar [44] found higher ozonation rates for three different synthetic dyes (N-Rot-Gre, Indisol-Rubinol, N-Orange) at pH=9 than those at pH=2. Oxidation rates of all the dyes increased above pH of 7.

2.1.6 Other Factors Affecting Ozonation

Chen studied [46] the important factors (pH, T, initial dye and ozone concentrations and agitation speed) of the ozonation reactions of Methyl Orange dye. After the statistical analyses, the most important factors for the ozonation rate of the methyl orange were the initial ozone and initial dye concentrations. Agitation speed was found to have no significant effect on the oxidation rate. There was an interaction between the temperature and the initial O_3 concentration.

Xu et al. [47] stated that the ozone dose transferred to the aqueous phase is the critical parameter for the design of wastewater disinfection. In the same study, they ozonated dyestuff effluent to observe the change of biodegradability by ozonation and to observe the effects of pH and dyestuff concentration on the COD removal. COD removal of 60-75 % was obtained whereas color removal increased to 86 % at an initial pH of 11. Instead, increasing the dyestuff concentration (100 to 1000 mg/l) had a negative effect upon COD removal at pH=11.

Balcıoğlu and Arslan [48] studied the ozonation of a concentrated dye bath effluent. They concluded that applying higher ozone doses might not be advantageous for the enhancement of biodegradability.

Calvosa et al. [49] studied ozone oxidation of nonyl phenol ethoxylate (NPE) at two different initial concentrations (25, 50 mg/l) of NPE, and found that the rate of disappearance of NPE did not change with the initial concentration of NPE.

2.2 Advantages and Disadvantages of Peroxone Use

The following list highlights selected advantages and disadvantages in usage of peroxone as a disinfection method for drinking water. Because of the wide variation of system size, water quality, and dosages applied, some of these advantages and disadvantages may not apply to a particular system [54].

Advantages:

- Oxidation is more reactive and much faster in the peroxone process compared to the ozone molecular process.
- Peroxone is effective in oxidizing difficult-to-treat organics, such as taste and odor compounds.
- Peroxone processes have been shown to be effective in oxidizing halogenated compounds.
- The tendency to transform organic carbon compounds to a more biodegradable form may be increased with the addition of hydrogen peroxide.
- Pumps used to house peroxide are not very large; so space requirements are not significant in peroxone process.

Disadvantages

- Peroxide is a strong oxidant and its contact with personal is extremely dangerous.
- Peroxide can be stored on site, but deteriorates gradually even when stored correctly.
- Peroxone as a disinfection process does not provide a measurable disinfectant residual.
- Peroxone's ability to oxidize iron and manganese is less effective than that of ozone.

2.3 Comparison Between Ozone and Peroxone Oxidations

The key difference between ozone and peroxone is in the primary oxidation mode; that is, direct oxidation or hydroxyl radical oxidation. The reactivities of these compounds create different effects in the reactions with water constituents and, thus, disinfection effectiveness. Table 2.2 summarizes the key differences between ozone and peroxone as they relate to their applications in drinking water treatment [55].

Table 2.2. Comparison between ozone and peroxone oxidation

Process	Ozone	Peroxone
Ozone decomposition rate	Normal decomposition, producing hydroxyl radical	Accelerated ozone decomposition above that of ozone alone
Ozone residual	5-10 minutes	Very short lived due to rapid reaction
Oxidation Path	Usually direct aqueous molecular ozone oxidation	Primarily hydroxyl radical oxidation
Ability to oxidize iron and manganese	Excellent	Less effective
Ability to oxidize taste and odor compounds	Variable	Good, hydroxyl radical is more reactive than ozone.
Ability to oxidize chlorinated organics	Poor	Good, hydroxyl radical is more reactive than ozone.
Disinfection ability	Excellent	Good

CHAPTER 3

EXPERIMENTAL

In the peroxone-dye experiments, Acid Red 151 was selected as a model dye compound since it is an azo dye and due to the fact that azo dyes are mostly used ones in textile industry.

3.1 Acid Red 151

During experimental study, Acid Red-151 is used. Acid Red 151 is an azo dye, which contains two nitrogen to nitrogen double bonded groups (N=N) and a sulfonic group (NaO_3S). This sulfonic group makes it soluble in the aqueous medium [56]. The structure of Acid Red 151 dye is given in Figure 3.1:

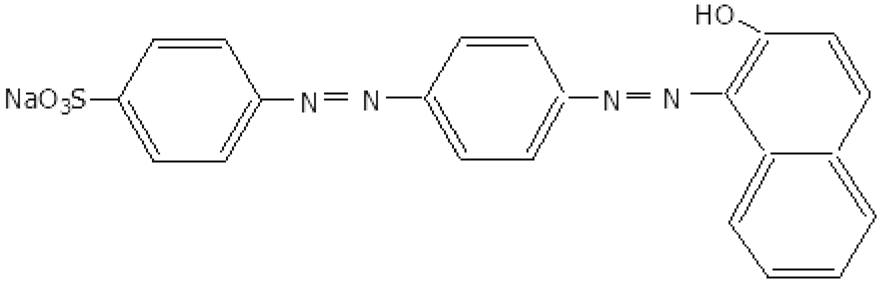


Figure 3.1 Structure of Acid Red 151 dye.

Properties of Acid Red 151 :

Type: Azo Dye
Color Index Number: 26900
Color Index Name: Acid Red 151
Molecular Weight: 454.44 g/mol
Maximum Absorbance Wavelength of Dye:λ_{max} : 512 nm

Shang and Yu [57] reported that at any pH, azo bond (-N=N-) is very reactive with ozone in solutions and after ozonation the nitrogen in the azo group is partly released as nitrogen gas, consequently reducing nitrate ion concentration in solution. In addition, Rajeswari et al. [58] stated that water soluble structure of azo dyes makes them more amenable to oxidation and to color removal by ozone.

3.2 Experimental Apparatus

Experimental apparatus is given in Figure 3.2. Ozone gas is produced from dry air (O_2+N_2) by using a Fischer OZ-502 type ozone generator (Meckenheim, Bonn). Gas flow rate (140 L/h) is monitored by a flow meter incorporated with the ozone generator. Generated ozone is fed to a 1 L volume Gallenkamp Modular type glass reactor through a sparger at its bottom, for 10 min of ozonation time (t_{O_3}). Temperature of the reactor medium is kept constant as 25°C by using a Memmert WBU-45 type water bath around the reactor. A WTW-310 pH meter is used to control the pH of the solution during reaction period. To collect the unreacted ozone, potassium iodide (KI) traps are used at the inlet and outlet of the reactor.

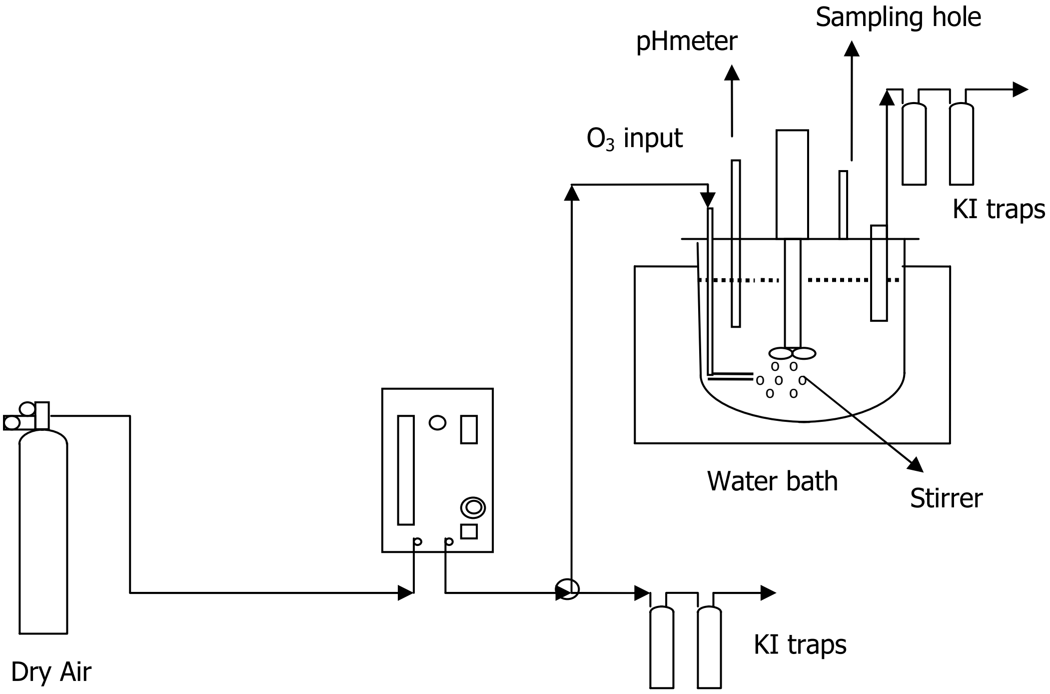


Figure 3.2 Schematic diagram of the experimental apparatus

Distilled-deionized water is used in all the experiments for solution preparations. Peroxone oxidation experiments are conducted at pH values of 2.5, 7 and 10. The solution pH is regulated by using buffer solutions (HCl/KCl, KH_2PO_4/NaOH and H_3BO_3-KCl/NaOH) throughout the ozonation of the distilled-deionized water. No significant decrease of pH (~0.1) was observed during experimental runs at each pH value.

3.3 Experimental Parameters

Possible Independent Experimental Parameters:

Initial O_3 , initial dye concentration and r ratio of initial concentrations of H_2O_2 to O_3 ($[H_2O_2]/[O_3]$)
pH
Temperature
Gas flow rate (GFR)
Ozonation time, t_{O3}
Stirrer speed (SS)

Experimental Parameters Selected:

at T=25°C, t_{O3}=10 min, GFR=140 L/min, SS=400 rpm,

r= $[H_2O_2]/[O_3]$; (0.3, 0.5, 0.75 and 1)
Initial dye concentration, $C_{dye,i}$; (0.0220, 0.0275, 0.033, 0.0440 and 0.0880 mM)
Initial O_3 concentration, $C_{O3,i}$; (0.0140, 0.030, 0.0360 mM)
pH; (2.5, 7, 10)

Dependent Experimental Parameters:

Chemical Oxygen Demand (COD) & Color values
Residual O_3 and effluent dye concentrations with respect to ozonation time.

3.4 Experimental Strategy

Experimental strategy followed can be summarized as follows;

- O_3 absorption and decomposition experiments at different pH values,

- Peroxone-dye oxidation experiments,

  Peroxone-dye experiments at different "r" concentration ratios for each pH value,

  Peroxone-dye experiments at different initial dye concentrations for each pH value,

  Peroxone-dye experiments at different initial ozone concentrations for each pH value,

- Peroxone experiments at excess initial dye concentrations for each pH value to determine the reaction kinetics.

3.4.1 O_3 Absorption and Decomposition Experiments

These experiments are conducted before the dye and hydrogen peroxide additions at each pH value (2.5, 7 and 10). Firstly, the pH of distilled-deionized water is adjusted to the desired pH value by using buffer solutions and making final volume 1 L. Then, this solution is ozonated at 25°C until maximum possible ozone concentration is attained to eliminate the mass transfer effects of the ozone into the water solution during experimentation. To reach to the maximum attainable ozone concentration at a specific pH value, 10 min of ozonation time is found to be enough at the studied experimental conditions. Ozone concentration data with respect to time is collected until a stable maximum value is reached. This sequence of the study is named as “ozone absorption experiments” part.

At the end of 10 min of ozone absorption part, ozonation is stopped and the necessary amount of hydrogen peroxide (in order to reach to the desired “r” initial concentration ratio) is added to the ozonated water, simultaneously. After that, ozone concentration in the solution is measured with time to obtain the ozone decomposition data. Ozone concentration is rapidly decreased as it is reported in the literature [59]. Ozone decomposition data is used in the dye-peroxone oxidation experiments to get the different initial ozone concentrations as the experimental parameter.

3.4.2 Peroxone-Dye Oxidation Experiments

In these experiments, 1 L of buffered solution at the desired pH was ozonated at T=25°C as in the case of ozone absorption experiments until the maximum attainable ozone concentration is reached and initial dissolved O_3 concentration is measured. Then, ozonation is stopped. At the start of the experimental run, necessary amount of H_2O_2 in the liquid form to provide the desired “r” ratio, and necessary amount of dye (10-20 mg) to provide the desired initial dye concentration are added to the ozonated water, simultaneously. In the following part of the experimental run, liquid samples from the reactor are collected during 50 minutes. At each definite time, two liquid samples are withdrawn from the reactor, simultaneously, into two glass sampling bottles, one of which contains 10 ml of 0.01 M sodium thiosulphate ($Na_2S_2O_3$) solution in order to measure the dye concentration and COD in the reaction medium at that time. $Na_2S_2O_3$ is used due to the fact that it stops the reaction between the remaining dye molecules and the dissolved ozone. The possible interference of the excess

$Na_2S_2O_3$ solution with the COD analysis is accounted for. For this purpose, COD value corresponding to the amount of added excess $Na_2S_2O_3$ is determined from the calibration data of $Na_2S_2O_3$-COD curve (Figure B.3), which is substracted from the measured total COD of the sample containing $Na_2S_2O_3$. Sample calculation related to the COD correction is given in Appendix A.3. Second sampling bottle contains 1 ml indigo reagent and 10 ml of pH=2 buffer solution to determine the residual ozone concentration in the aqueous medium. All the samples are withdrawn from the reactor under vacuum in order to prevent the escape of ozone into the gas phase. Also two samples (25 ml each) were withdrawn from the reactor to the empty sampling bottles for measuring the color of the dye solution, both at the beginning and the end of the reaction.

The procedure described is followed for different "r" ratios (0.30, 0.50, 0.75 and 1.00), at different nominal initial dye (0.0220 mM, 0.0275 mM, 0.0330 mM and 0.0440 mM) and initial O_3 concentrations (determined from the ozone decomposition experiments) at each pH value (2.5, 7 and 10). Table 3.1 shows the summary of the experimental parameters.

Table 3.1 Experimental conditions for peroxone-dye experiments

Gas flow rate (GFR)	140 L/h		
Stirrer speed (SS)	400 rpm		
Nominal Initial dye concentration ($C_{dye,i}$)	0.0220, 0.0275, 0.0330, 0.0440 mM		
Temperature (T)	25°C		
pH	$C_{O3,i}$ (mM)	$C_{O3,i}$ (mM)	$C_{O3,i}$ (mM)
2.5	0.0170	0.0260	0.0360
7	0.0070	0.0120	0.030
10	0.0036	0.0042	0.0140

3.4.3 Peroxone Experiments at Excess Initial Dye Concentrations

These experiments are performed to determine the reaction kinetics of the ozone-Acid Red 151 reactions in the peroxone process. The same procedure with the peroxone–Acid Red 151 dye oxidation experiments is followed. But in this case, excess initial dye concentrations are used. Initial ozone concentrations are the maximum attainable concentrations at each pH value. Table 3.2 shows the conditions applied for these experiments.

Table 3.2. Experimental parameters for excess dye experiments.

Gas flow fate (GFR)	140 L/h
Stirrer speed (SS)	400 rpm
Nominal initial dye concentration ($C_{dye,i}$)	0.551, 0.881, 1.321 mM
Temperature (T)	25°C
pH	$C_{O3,i}$ (mM)
2.5	0.036
7	0.030
10	0.014

3.5 Analytical Methods

Indigo method is used [60-62] to determine the residual O_3 concentrations in the visible region by using a Hitachi U-3010 spectrophotometer at a wavelength of λ=600 nm. Dye concentrations in the solution are measured by using the same spectrophotometer at λ=512 nm. COD analyses are carried out with a WTW Cr-3000 thermoreactor and a Hach DR-2010 spectrophotometer. Calibration curves (absorbance vs. concentration) of indigo and dye are obtained by measuring the absorbance values of the standard samples prepared at the known concentrations of the indigo and dye (Figure B.1 and Figure B.2). For color measurements, the same spectrophotometer is used. Indigo, COD and color analyses are given in Appendix A.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Ozone Absorption and Decomposition Experiments

Firstly, three experiments are performed to determine the maximum attainable ozone concentrations in water at three different pH values of 2.5, 7 and 10. In these experiments, water is ozonated until the maximum ozone concentration is attained in order to eliminate the mass transfer effects of O_3 before the addition of the dye solution in the oxidation experiments. In the ozone absorption experiments, 10 min of ozonation is found to be enough to reach the maximum ozone concentration in water at T=25°C for each pH value as shown in Figure 4.1. Data are given in Table C.1.

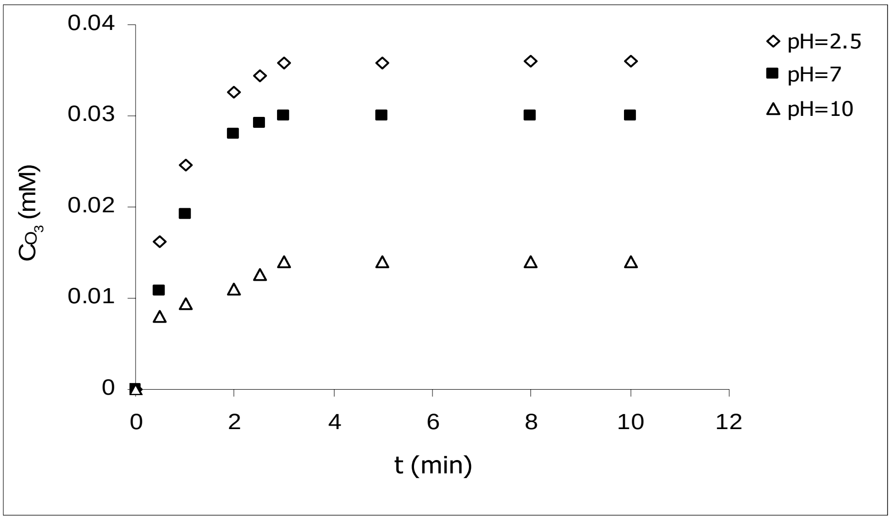


Figure 4.1 Absorption of ozone in water at different pH values, at T=25°C

Maximum attainable ozone concentrations are found to be 0.036 mM, 0.030 mM and 0.014 mM for pH values of 2.5, 7 and 10, respectively. It is highest at pH 2.5 whereas it is lowest at pH 10, as it is expected. This is a result of the ozone decomposition to some radicals at pH=10, therefore its concentration decreases at higher pH values in the aqueous medium.

After the maximum attainable ozone concentration is reached, ozonation is stopped and then, the change in dissolved ozone concentration due to the decomposition of ozone at different pH values is followed with respect to time without adding any H_2O_2, as it is seen in Figure 4.2. The related data are presented in Table C.2.

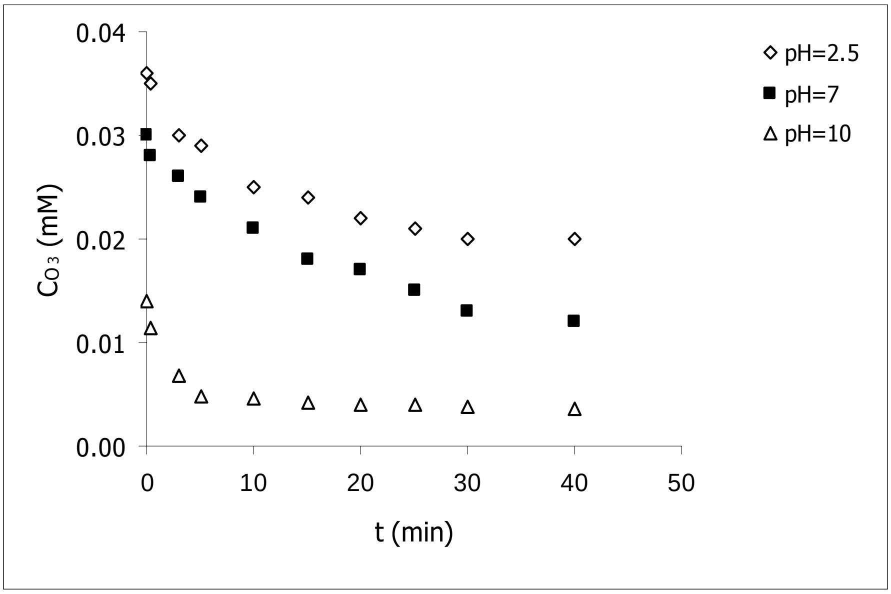


Figure 4.2 Decomposition of O_3 in aqueous medium at different pH values and at T=25 °C, r=0

As it can be seen in Figure 4.2, ozone decomposition rate is increased with the increases in the pH of the solution, as it is expected [69]. This is because at high pH values ozone decomposes to some radicals/molecules appreciably and ozone concentration decreases in the aqueous medium. Since the initial maximum attained O_3 concentration in solution is least at pH=10, therefore, the dissolved O_3 concentrations are lowest at that pH after the decomposition of O_3.

According to Staehelin and Hoigne [27], rate of ozone decomposition with hydrogen peroxide is twice of the primary initiation. H_2O_2 addition rapidly initiates the chain reactions of ozone decomposition, and this changes the reaction pathway with organic compounds when they are added to the medium. To see the effects of H_2O_2 addition on the ozonation of the Acid Red-151, remaining experiments will include it.

In order to observe the effects of H_2O_2 on the ozone decomposition, previous decomposition experiments in the absence of organic dye, are repeated with the addition of H_2O_2 to the reaction medium at "r" ratio of 0.5 (mM H_2O_2/mM O_3) for each pH value as it is seen in Figure 4.3. The data are presented in Table C.3.

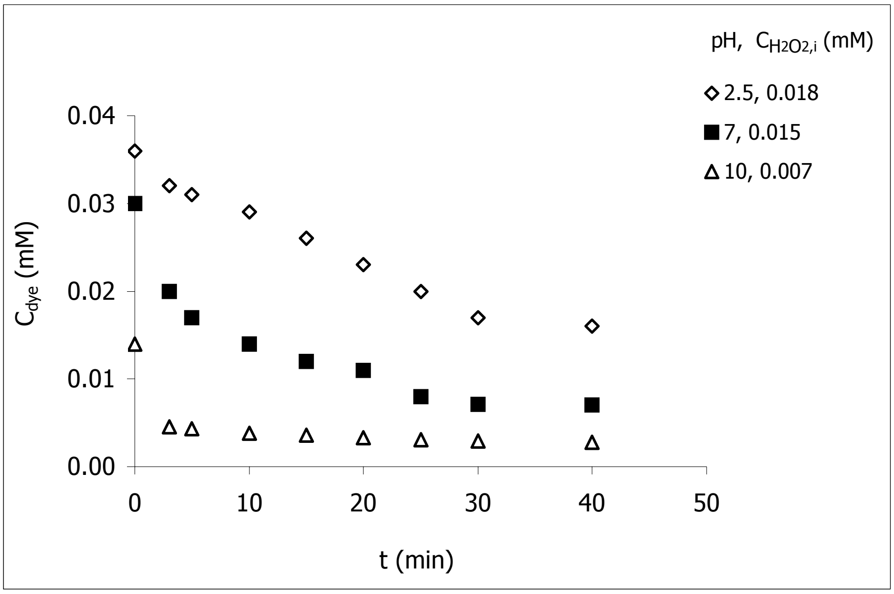


Figure 4.3 Decomposition of O_3 in aqueous medium at different pH values and at T=25°C , r=0.5

When the results in the Figures 4.2 and 4.3 are compared, it can be said that the ozone decomposition increases when H_2O_2 is added to the ozonated water, as it is concluded by Staehelin and Hoigne [27]. Figures 4.2 and 4.3 also show that H_2O_2 addition is more effective on ozone decomposition at pH values of 2.5 and 7 compared to that at pH=10. This result can be a key point to guess the efficieny of the peroxone process on the dye oxidation at these pH values. Probably, the peroxone process will increase the ozonation efficiencies at pH values of 2.5 and 7 much more than it will at pH of 10.

4.2 Peroxone-Dye Experiments

In this part of the study, ozone absorption experiments are repeated at three different pH values (2.5, 7 and 10). After the maximum attainable ozone concentration is reached, ozonation is stopped and the necessary amount of hydrogen peroxide and dye solution are added to the reactor. Firstly, the effect of initial dye concentration on the efficiency of peroxone is aimed to be observed. For this reason, 15 experiments are performed at five different nominal initial dye concentrations at three different pH values. The change in the dye concentration is measured with respect to time at different nominal initial dye concentrations as they can be seen in Figures 4.4, 4.5 and 4.6. The related data are given in Tables C.5, C.7, C.9, C.11 for Figure 4.4, in Tables C.13, C.15, C.17, C.19 for Figure 4.5 and in Tables C.21, C.23, C.25,C.27 for Figure 4.6.

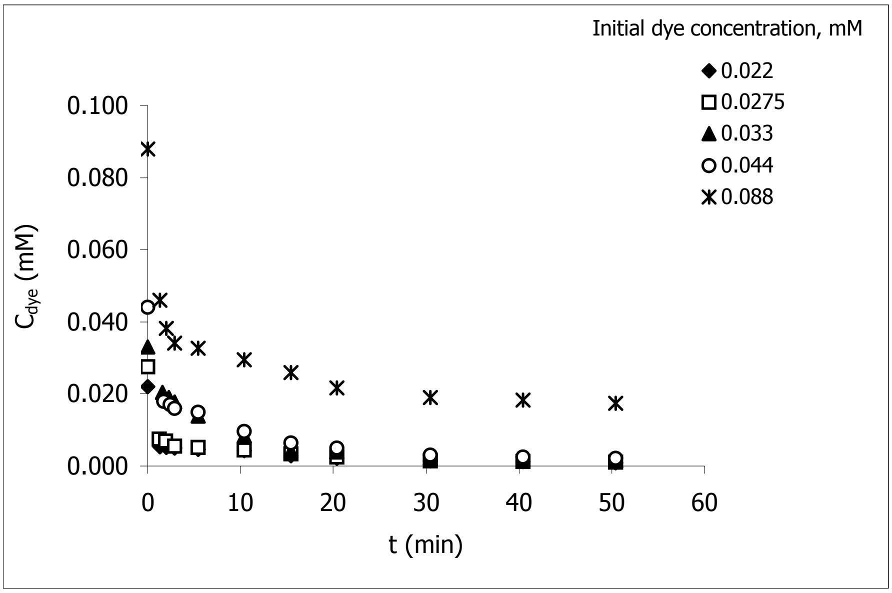


Figure 4.4 Effect of nominal $C_{dye,i}$ on C_{dye} vs. t graphs at pH=2.5, T=25°C, $C_{O3,i}$=0.036±0.0005 mM, r=0.5

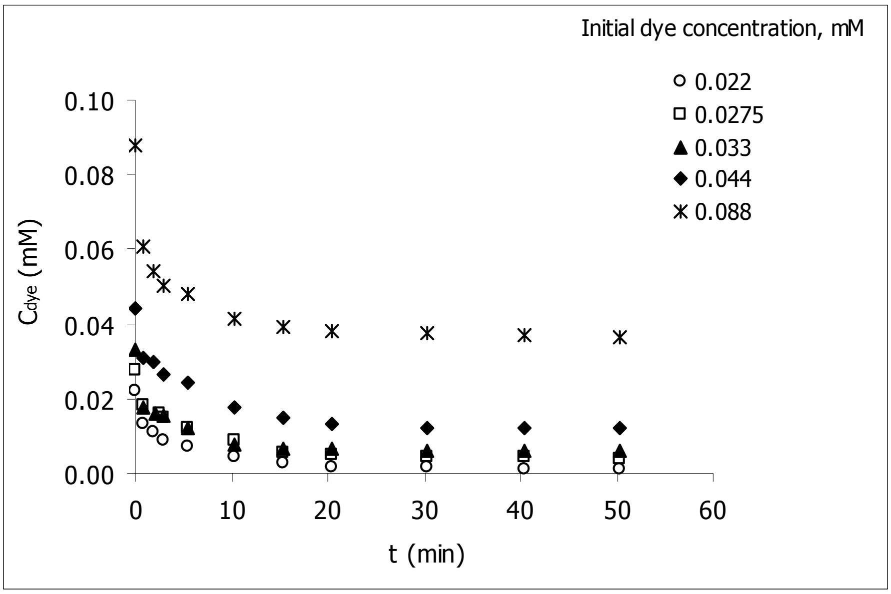


Figure 4.5 Effect of nominal $C_{dye,i}$ on C_{dye} vs. t graphs at pH=7, T=25°C, $C_{O3,i}$=0.030±0.001 mM, r=0.5

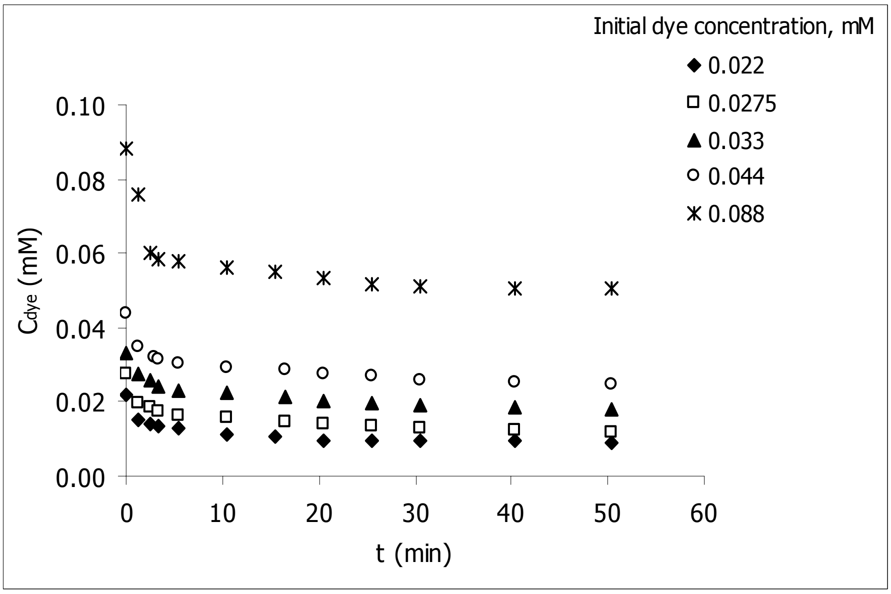


Figure 4.6 Effect of nominal $C_{dye,i}$ on C_{dye} vs. t graphs at pH=10, T=25°C, $C_{O3,i}$=0.014±0.001 mM, r=0.5

Figures 4.4, 4.5 and 4.6 show that dye oxidations are nearly completed in the first 10 min of the peroxone-dye reactions. After a rapid decrease in the dye concentrations, reactions seem to be slower after around 10 min as a result of the decreases in the concentrations of the reactants, namely dye, ozone and hydrogen peroxide. Initial rate of disappearance of the dye ($r_{dye,i}$) is increased with the increases in the pH and initial dye concentration (Figure 4.7). The rate of decrease in the dye concentration gives an idea about the Acid Red 151 oxidation efficiency of the peroxone process at different pH values. It can be concluded that the peroxone process seems to be more efficient at pH values of 2.5 and 7 for the dye degradation compared to that at pH=10. Perhaps, scavenging reactions of H_2O_2 might decrease the oxidation performance of peroxone process at pH=10, being insignificant below the pH of 10, as it is reported by Kuo et al. [40].

Another approach to explain the low oxidation efficiency obtained at pH=10 can be done by using the half-life ($t_{1/2}$) of the organic matter (dye, in this case) in the solution, within the reaction time at different pH values. Gunten [69] emphasized that determination of the half-life to decrease the concentration of an organic compound to 50% of its initial value during the ozonation shows the effectiveness of this process. In addition, it was concluded that, in the case of short half-lives ($t_{1/2}<5$ min), ozonation is very efficient for the degradation of an organic compound, because it mainly occurs via the direct ozone reaction whereas for slower processes ($t_{1/2}>5$ min), OH radicals play an important role; this indirect pathway is said to cause a loss of oxidation capacity in the system due to the fast scavenging of OH radicals by many compounds of the water matrix. Half-lives of the organic dye at different pH values are also determined in this study. Results show that $t_{1/2}$ values are changing in the ranges of 0.5-5 min and 1.8-5 min for pH values of 2.5 and 7, respectively. These small values indicate that more efficient direct reactions of ozone are observed at these pH values. At pH=10, half-life of the dye is greater than 10 min even in the smallest dye concentration of 0.022 mM. This shows that at pH=10, OH radical-based slow reaction mechanism is dominant. Since ozone is the limiting reactant for the production of OH radicals from the reaction of HO_2^- and O_3 [27], and since the initial dissolved ozone concentration is the smallest at pH=10, therefore necessary amounts of HO radical and O_3 for the effective oxidation can not be provided at this pH value [69].

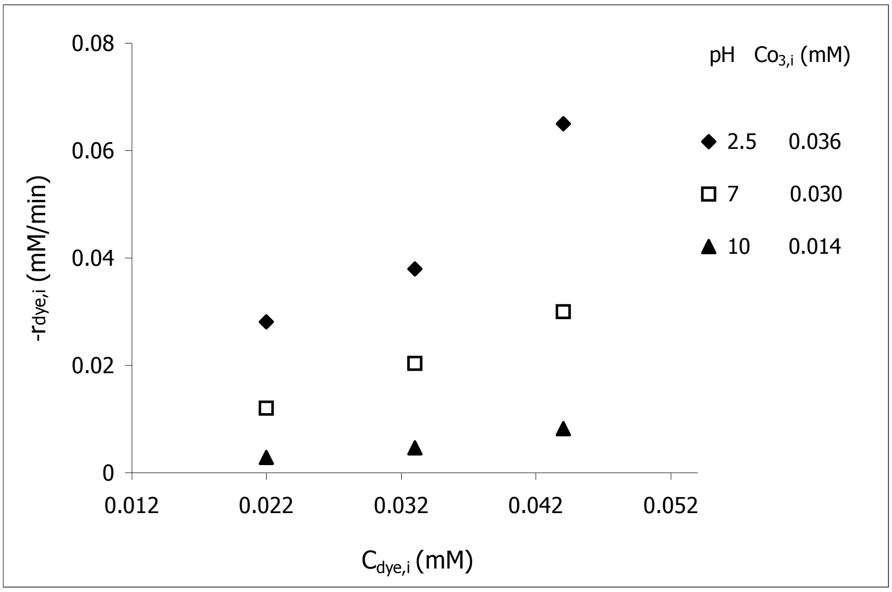


Figure 4.7 Effects of nominal $C_{dye,i}$ and pH on the initial rates at T=25°C and r=0.5

In order to see the decreases in O_3 concentrations more clearly, C_{O3} vs. time graphs are drawn on the semi-logarithmic scale. Changes of ozone concentrations with time are given in Figures 4.8, 4.9 and 4.10. Related data are given in Tables C.4, C.6, C.8, C.10 for Figure 4.8, in Tables C.12, C.14, C.16, C.18 for Figure 4.9 and in Tables C.20, C.22, C.24, C26 for Figure 4.10. Residual O_3 concentration decreases rapidly in the O_3/H_2O_2-dye experiments during the first few minutes of the reaction time. In the case of ozone concentration changes, similar trends are observed at each pH. The rate of decrease in residual O_3 concentration increases with the increasing initial dye concentration, since it is the major reactant to spend dissolved O_3 in the reaction medium, for all the studied pH values. Lower final residual O_3 concentrations are observed at pH values of 7 and 10 as it can be a result of the relatively lower initial dissolved O_3 concentrations and higher ozone decomposition rates at these conditions compared to those at pH=2.5.

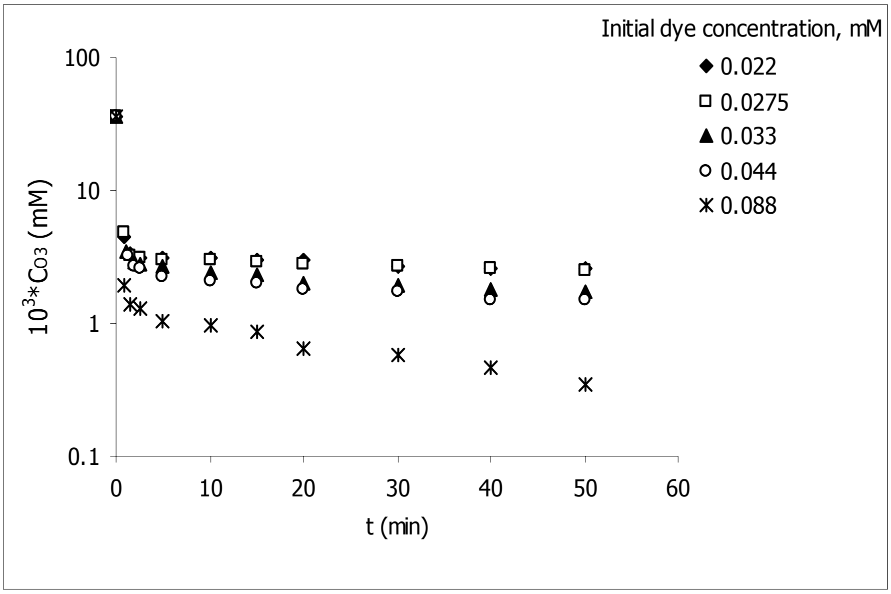


Figure 4.8 Effect of $C_{dye,i}$ on the variation of C_{O3} vs. time at pH=2.5, T=25°C, $C_{O3,i}$=0.036±0.0005 mM, r=0.5

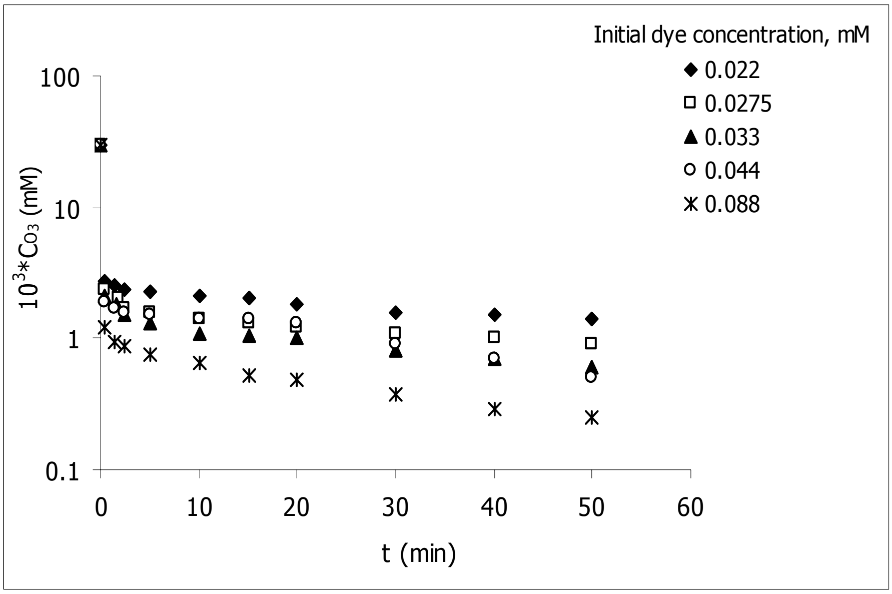


Figure 4.9 Effect of $C_{dye,i}$ on the variation of C_{O3} vs. time at pH=7, T=25°C, $C_{O3,i}$=0.030±0.001 mM, r=0.5

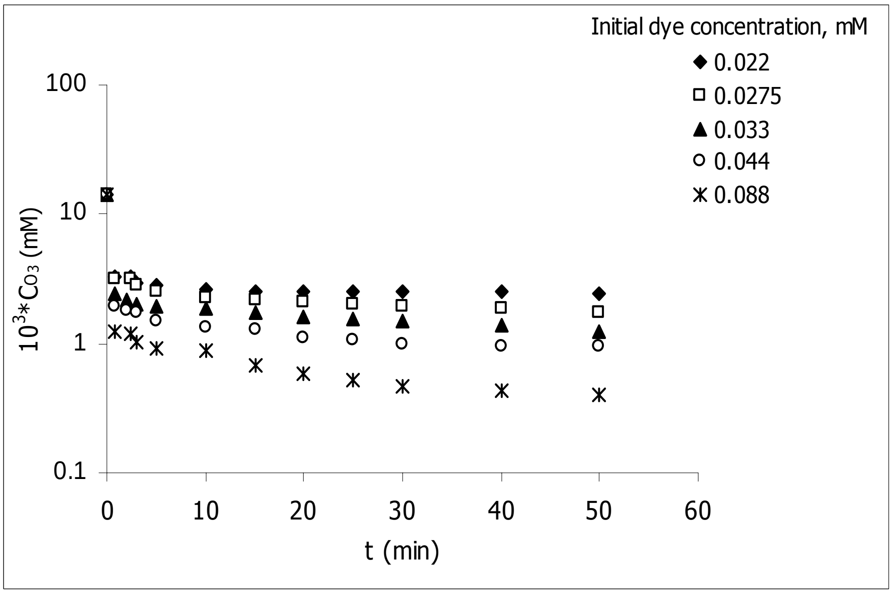


Figure 4.10 Effect of $C_{dye,i}$ on the variation of C_{O3} vs. time at pH=10, T=25°C, $C_{O3,i}$=0.014±0.001 mM, r=0.5

Peroxone-dye experiments, at pH values of 2.5 and 7, were repeated at the nominal initial dye concentrations of 0.0220, 0.0275, 0.0330 and 0.0440 mM to analyze the experimental error. One way to analyze the experimental error is to calculate the percent error (% error). The term, percent error is useful when there is a single experimental result that is wished to be compared with a standard value, or when there are two experimental results obtained by the repetition of the same run at exactly the same conditions. In the latter case, it is often called as percent difference (% difference) since there is no standard to compare [68]. In this study, the term, % difference is used to give an idea about the experimental error in the reproducibility of the results.

Percent experimental differences are calculated by using the following formula;

$$\% \text{ Difference}=100\text{x}(\text{Run1}-\text{Run2})/\text{Run2}$$

where;
Run1: Result of the first run
Run: Result of the repeated run with the same initial conditions as in the first run.

Results of % differences for the experiments at pH=2.5 are given in Tables 4.1-4.4. Results for pH=7 are given in Tables C.28 and C.29.

Table 4.1 Percent differences in C_{dye} at each specific time for the repeated runs at pH=2.5, T=25°C, $C_{O3,i}$=0.036±0.0005 mM, r=0.5

t (min)	$C_{dye,i}$=0.022 mM	$C_{dye,i}$=0.0275 mM	$C_{dye,i}$=0.033 mM	$C_{dye,i}$=0.044 mM
	% difference	% difference	% difference	% difference
0.00	0.00	0.00	0.00	0.00
1.32	-1.82	-1.20	3.54	-2.17
2.00	1.96	-1.41	4.40	-1.45
2.92	2.08	2.23	4.73	-4.76
5.42	2.17	-1.14	-0.72	-3.23
10.42	2.38	2.04	-2.35	-3.03
15.42	3.70	1.19	-2.44	-1.54
20.42	4.76	2.46	2.09	-2.53
30.42	1.35	2.74	-4.55	-3.23
40.42	4.00	4.35	-3.41	-4.21
50.42	2.27	3.77	3.68	-3.51

Table 4.2 Percent differences in the C_{O3} at each specific time for the repeated runs at pH=2.5, T=25°C, $C_{O3,i}$=0.036±0.0005 mM, r=0.5

	$C_{dye,i}$=0.022 mM	$C_{dye,i}$=0.0275 mM	$C_{dye,i}$=0.033 mM	$C_{dye,i}$=0.044 mM
t (min)	% difference	% difference	% difference	% difference
0	0.00	0.00	0.00	0.00
0.90	-1.32	-1.01	2.94	-3.32
1.58	1.85	-2.14	2.84	-3.23
2.50	1.61	2.31	1.82	-4.04
5.00	2.99	2.72	-0.37	-3.91
10.00	3.02	-1.64	-2.04	-2.78
15.00	3.41	2.84	-1.71	-3.38
20.00	3.16	2.55	2.56	-2.70
30.00	2.28	2.71	2.09	-3.41
40.00	3.17	2.00	-1.62	-4.43
50.00	2.82	4.17	3.64	-1.96

Tables 4.1 and 4.2 show that % difference values for the repeated experiments are lower than 5%, and this shows that there is no significant difference between the two runs performed at exactly the same conditions.

To observe the effects of concentration ratio of initial hydrogen peroxide to initial ozone ($r=[H_2O_2]/[O_3]$) on the peroxone-Acid Red 151 oxidation, previous peroxone-dye oxidation experiments for r=0.5 were repeated for the ratios of 0.30, 0.75 and 1.00 at $C_{dye,i}$= 0.0330 mM. For this purpose, nine experiments were performed at three different pH values (2.5, 7 and 10) for three different "r" values of 0.30, 0.75 and 1.00. Comparison of the variation in dye concentration with time at different "r" values can be seen in Figures 4.11, 4.12 and 4.13, for the pH values of 2.5, 7 and 10, respectively. Data for these graphs are given in Tables C.30-32.

The lowest effluent dye concentration, in other words, the highest dye degradation of 96% is observed at r=0.5 value for pH=2.5. This ratio seems to be the best value for this pH. pH=7 is better than pH=10 for the dye degradation. The best "r" value for these conditions is r=0.5 with the highest dye degradations of 95.9% and 58.2% for pH=7 and pH=10, respectively.

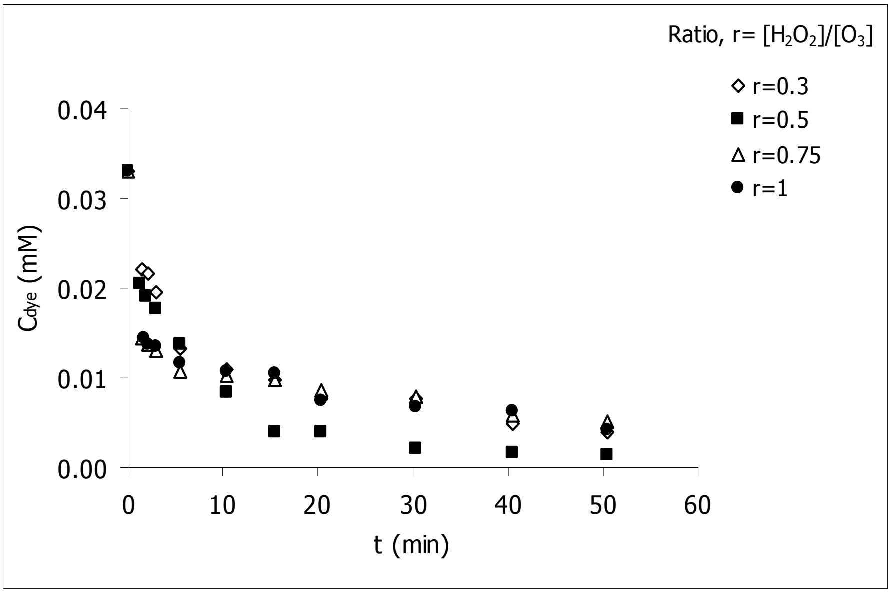


Figure 4.11 Effect of "r" value on C_{dye} vs. t graphs at pH=2.5, T=25°C, $C_{dye,i}$=0.033 mM, $C_{O3,i}$=0.036 mM

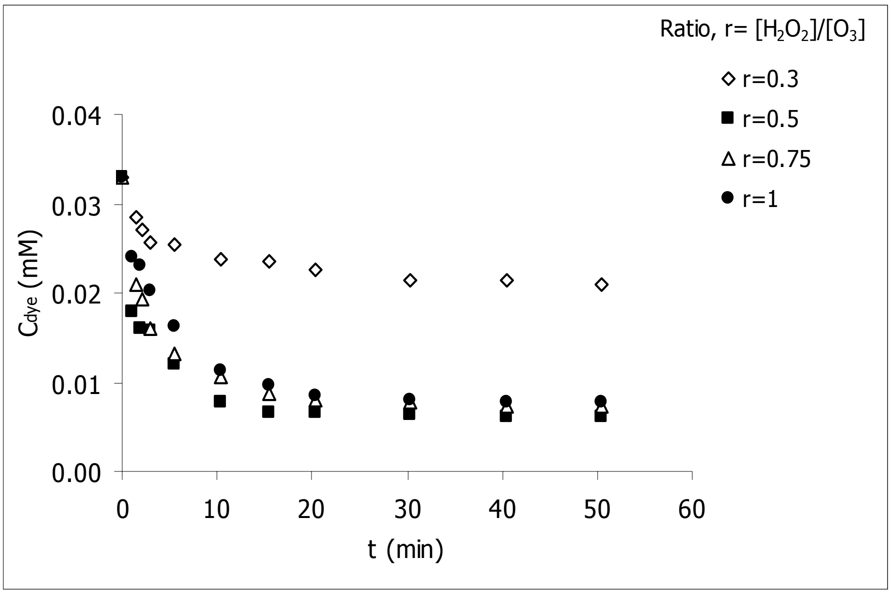


Figure 4.12 Effect of "r" value on C_{dye} vs. t graphs at pH=7, T=25°C, $C_{dye,i}$=0.033mM, $C_{O3,i}$=0.030 mM

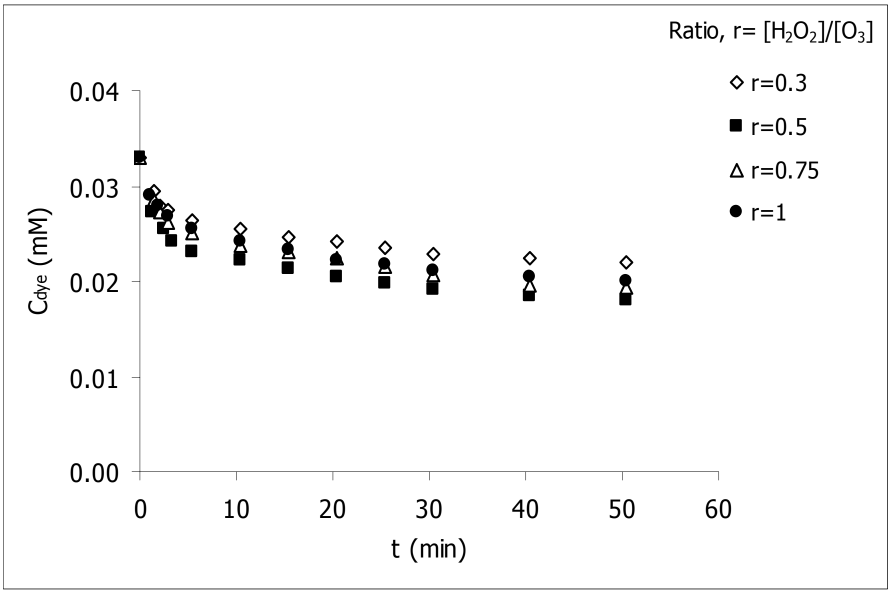


Figure 4.13 Effect of "r" value on C_{dye} vs. t graphs at pH=10, T=25°C, $C_{dye,i}$= 0.033 mM and $C_{O3,i}$=0.014 mM

The changes in the dissolved ozone concentrations with time at different "r" ratios for pH values of 2.5, 7 and 10 are given in Figure 4.14, Figure 4.15 and Figure 4.16, respectively. Data for Figures 4.14-4.16 are given in Tables C.33-C.35, respectively. These results show that higher decreases in ozone concentration occur at pH=7 and pH=10 when compared with those at pH=2.5. This is an expected result due to the higher ozone decomposition rates and radical mediated reactions at pH values of 7 and 10 compared to those at pH=2.5. As it is seen in Figures 4.14-4.16, ozone consumption is highest at "r" ratio of 0.5 for each pH value studied. This is an expected result since maximum dye degradations are also observed at this ratio for all these pH conditions.

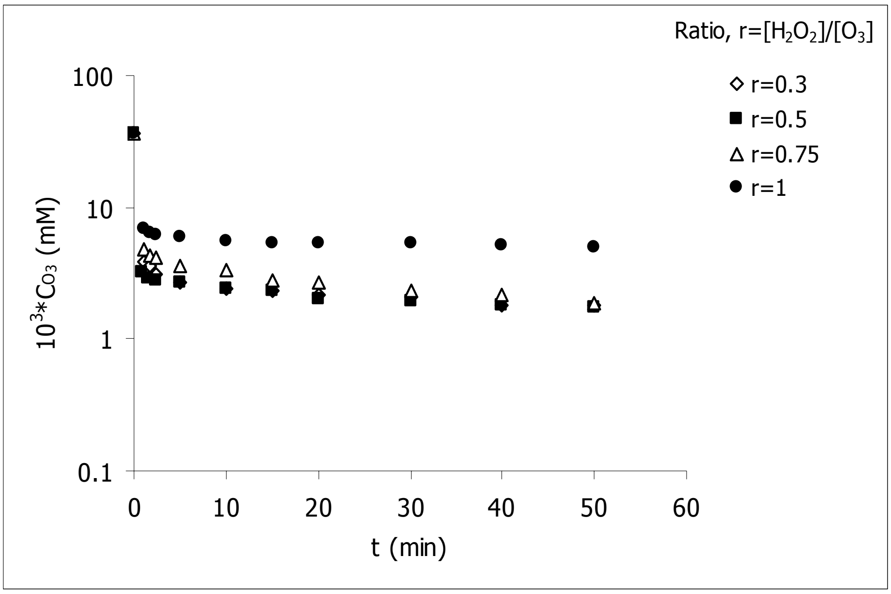


Figure 4.14 Effect of "r" ratio on C_{O3} vs. t graphs at pH=2.5, T=25°C, $C_{dye,i}$=0.033 mM and $C_{O3,i}$=0.036 mM

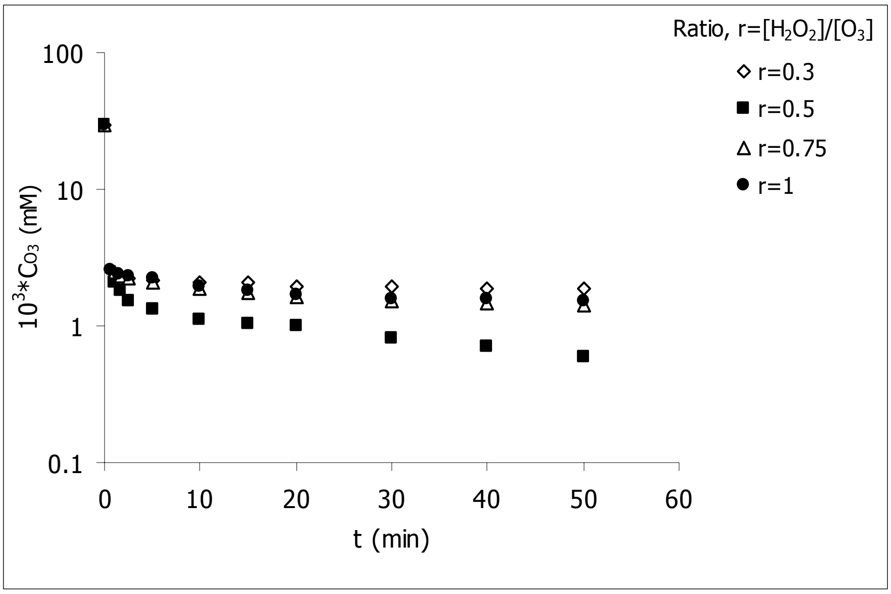


Figure 4.15 Effect of "r" ratio on C_{O3} vs. t graphs at pH=7, T=25°C, $C_{dye,i}$=0.033 mM, $C_{O3,i}$=0.030 mM

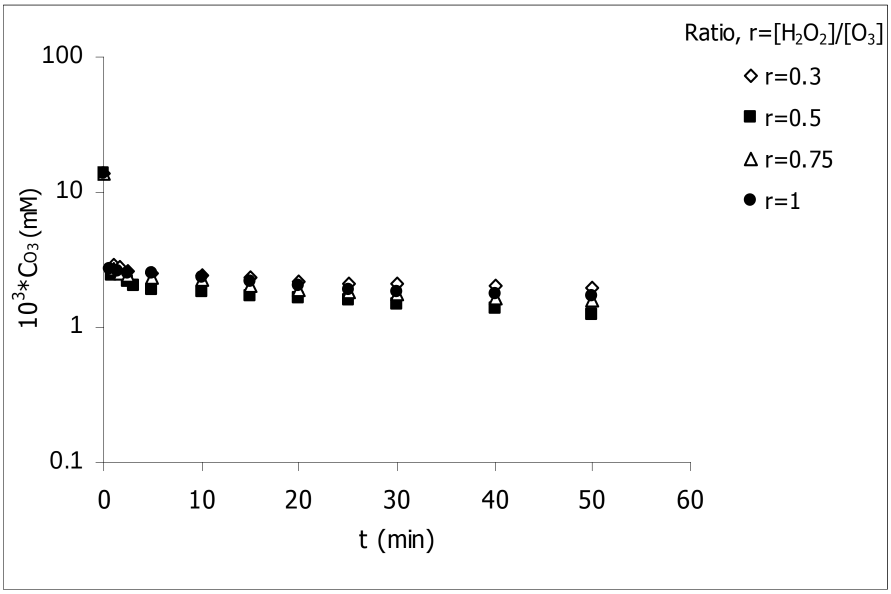


Figure 4.16 Effect of "r" ratio on C_{O3} vs. t graphs at pH=10, T=25°C, $C_{dye,i}$=0.033 mM, $C_{O3,i}$=0.014 mM

Peroxone-dye experiments at different “r” values were repeated at pH values of 2.5 and 7. Percent difference values in dye and ozone concentrations at each specific time are given in Tables 4.3 and 4.4, respectively, for pH=2.5. The results for pH=7.0 are given in Table C.36. Results of the repeated runs do not seem to have significant differences. The differences between the repeated run and the previous run might be due to some small fluctuations (in temperature, pressure, gas flow rate etc.) that were unavoidable in these types of experiments.

Table 4.3 Percent differences in C_{dye} with “r” ratio at each specific time for the repeated runs at pH=2.5, T=25°C, $C_{O3,i}$=0.036±0.0005 mM, $C_{dye,i}$=0.033 mM

t (min)	r=0.30	r=0.50	r=0.75	r=1.00
	% difference	% difference	% difference	% difference
0.00	0.00	0.00	0.00	0.00
1.32	2.33	1.49	0.55	0.49
2.00	3.85	1.60	0.66	0.37
2.92	3.16	1.72	0.38	0.60
5.42	-4.32	0.58	0.66	2.63
10.42	-1.79	1.22	0.99	3.88
15.42	2.11	2.56	0.82	2.97
20.42	4.05	2.09	0.82	4.17
30.42	2.70	3.96	1.04	1.19
40.42	2.08	1.80	-1.02	1.12
50.42	2.56	-2.10	-0.57	1.69

Table 4.4 Percent differences in C_{O3} with "r" ratio at each specific time for the repeated runs at pH=2.5, T=25°C, $C_{O3,i}$=0.036±0.0005 mM, $C_{dye,i}$=0.033 mM

t (min)	r=0.30	r=0.50	r=0.75	r=1.00
	% difference	% difference	% difference	% difference
0.00	0.00	0.00	0.00	0.00
0.90	2.63	2.56	1.48	1.19
1.58	2.86	3.57	1.90	1.40
2.50	3.33	2.56	2.44	0.99
5.00	3.85	3.05	1.69	1.87
10.00	4.35	2.56	1.85	1.48
15.00	3.14	2.68	3.32	0.75
20.00	2.80	1.52	2.66	1.73
30.00	2.44	0.52	2.68	3.11
40.00	4.05	-1.09	2.33	1.19
50.00	2.86	0.29	3.83	1.03

Peroxone-dye experiments were performed at different nominal initial ozone concentrations, and its effects on the oxidation efficiency of Acid Red 151 at different pH values (2.5, 7 and 10) were observed keeping the $C_{dye,i}$ at 0.033 mM. The results of these experiments are given in Figures 4.17, 4.18 and 4.19. Tabulated data for these graphs are given in Tables C.37, 38 and 39, respectively. These figures imply the importance of initial ozone concentration on the oxidation efficiency of Acid Red 151 aqueous solutions. The results show that an increase in the initial ozone concentration positively affects the dye degradation efficiency at all the studied pH values, keeping the initial dye concentration constant.

Peroxone-dye experiments were also performed at approximately the same $C_{O3,i}$ values of 0.017 mM, 0.014 mM and 0.014 mM for pH values of 2.5, 7 and 10, respectively , at $C_{dye,i}$=0.0330 mM to compare the dye degradation efficiencies at different pH values. These results can be seen in Figure 4.20. This figure also shows the lower oxidation efficiency of peroxone process on the dye degradation at pH=10, as it was explained for Figures 4.4-4.6, before.

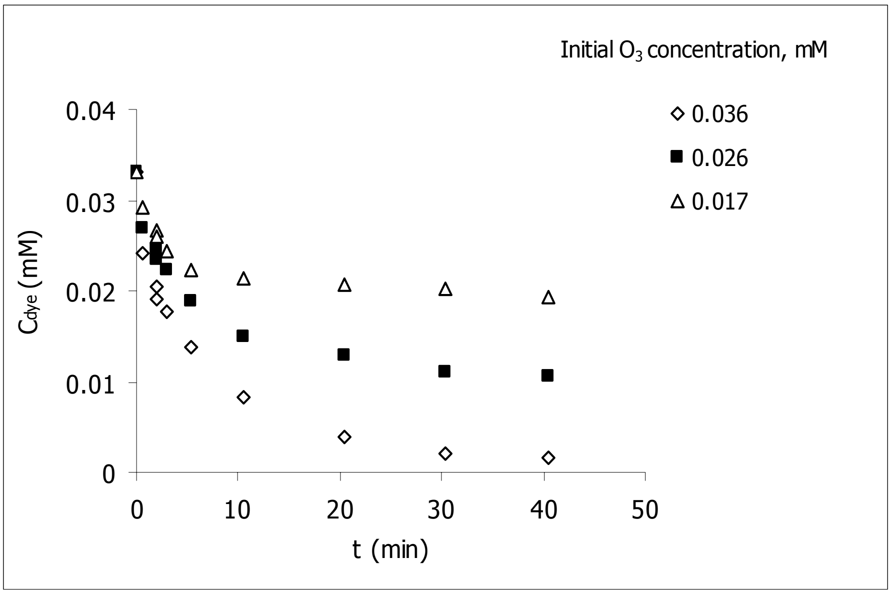


Figure 4.17 Effect of $C_{O3,i}$ on C_{dye} vs. t graphs at pH=2.5, T=25°C, $C_{dye,i}$=0.033 mM, r=0.5

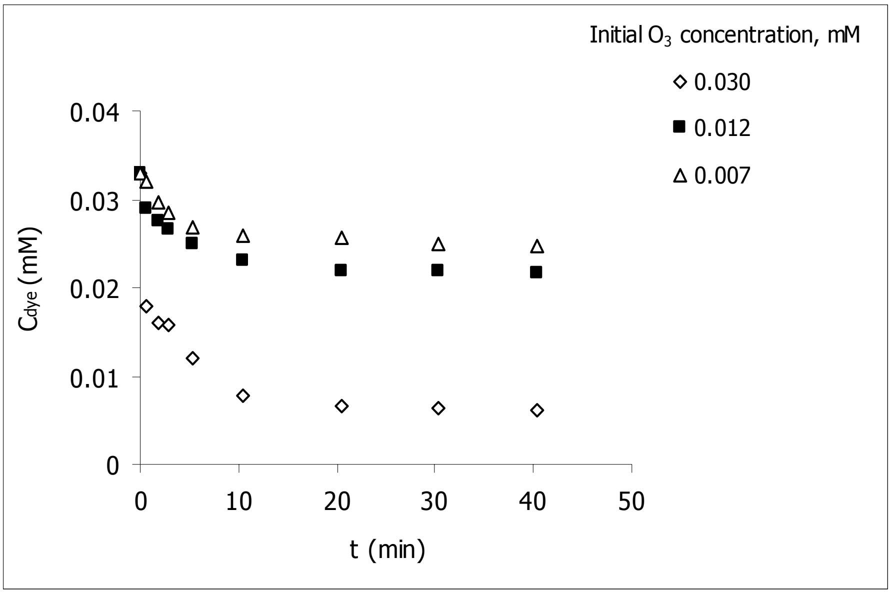


Figure 4.18 Effect of $C_{O3,i}$ on C_{dye} vs. t graphs at pH=7, T=25°C, $C_{dye,i}$=0.033 mM, r=0.5

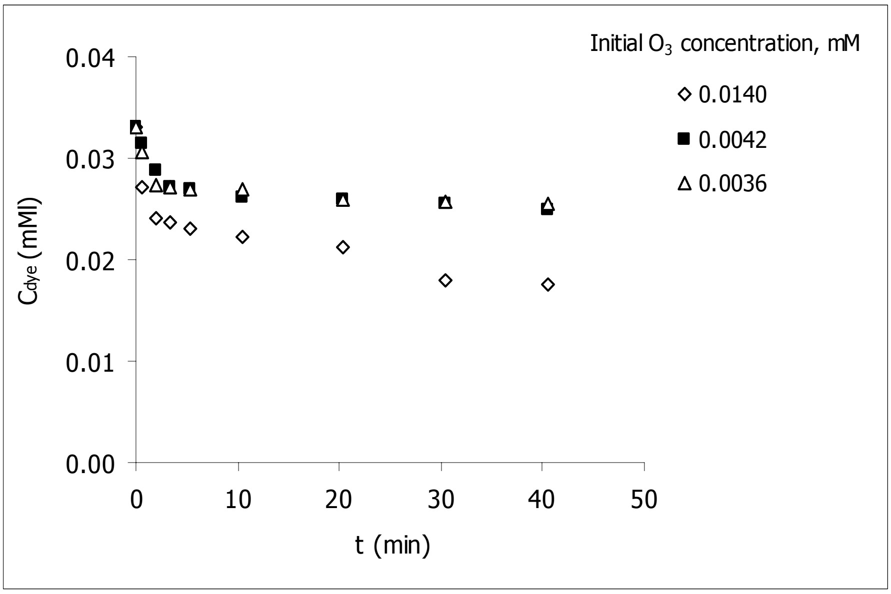


Figure 4.19 Effect of $C_{O3,i}$ on C_{dye} vs. t graphs at pH=10, T=25°C, $C_{dye,i}$=0.033 mM, r=0.5

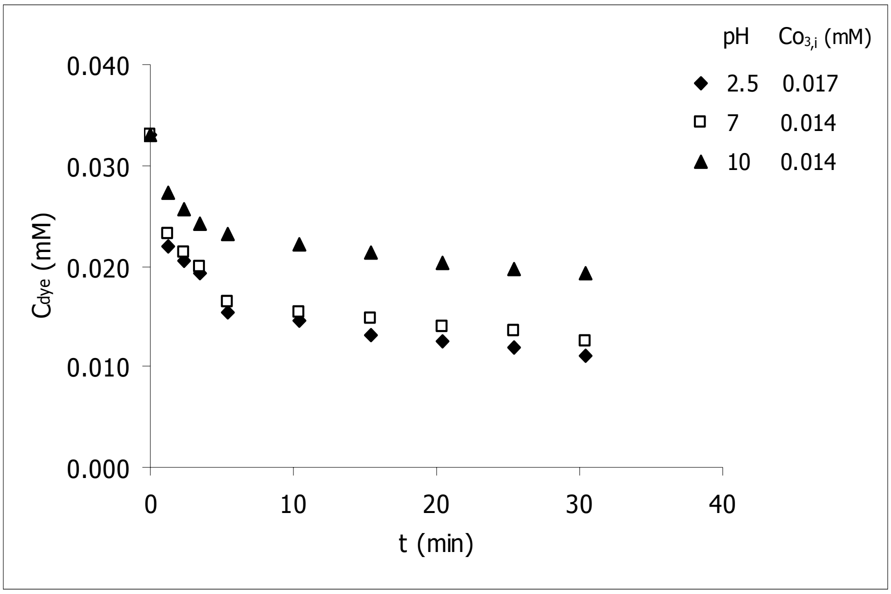


Figure 4.20 Effect pH on C_{dye} vs. t graphs at T=25°C, $C_{dye,i}$=0.033 mM, r=0.5, Reaction time=30 min

4.3 Color Removal

In the ozonation of the coloring materials, the most important thing is known to be the percent color reduction in the wastewater [63-64]. There are two methods for color removal determination; one of them is the percent decolorization calculated from the change of color units (measured by Pt-Co Method), and the other one is based on the concentration change of the coloring material which can be found if the solution contains only one type of coloring material. In this study, percent decolorization of Acid Red 151 solution is obtained by using both of these methods. Percent decolorization values were obtained at pH=2.5, pH=7 and pH=10 for the nominal initial dye concentrations of 0.0220, 0.0275, 0.0330, 0.0440 and 0.0880 mM. Effects of pH and initial dye concentration on the color removal (%) are given in Figure 4.21, and the effects of pH and "r" ratio on the color removal (%) are given in Figure 4.22. It should be noted that the $C_{O3,i}$ values at each pH correspond to the maximum attained ozone concentration in the solution, in Figures 4.21-4.22. Related data for these graphs are presented in Tables C.40 and C.41, respectively. In order to compare the color removal percentages at different pH values more accurately, peroxone-dye experiments were performed at approximately the same $Co_{3,i}$ values of 0.017 mM, 0.014 mM and 0.014 mM for pH values of 2.5, 7 and 10, respectively, in order to eliminate the effect of initial ozone concentration at $C_{dye,i}$=0.0330 mM. Results can be seen in Figure 4.23.

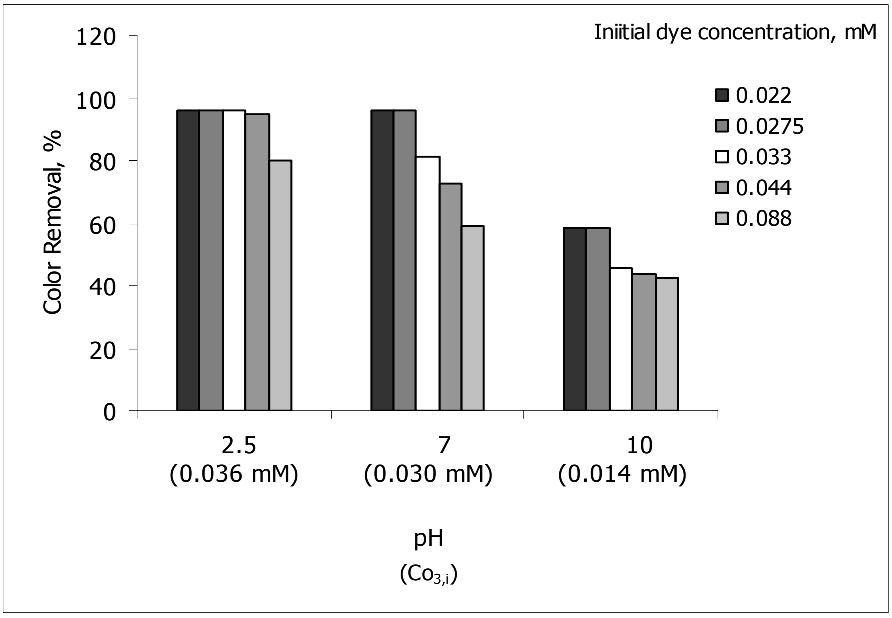


Figure 4.21 Effects of $C_{dye,i}$ and pH on the Color Removal (%) of Acid Red 151 at T=25°C, r=0.5, Reaction time=50 min

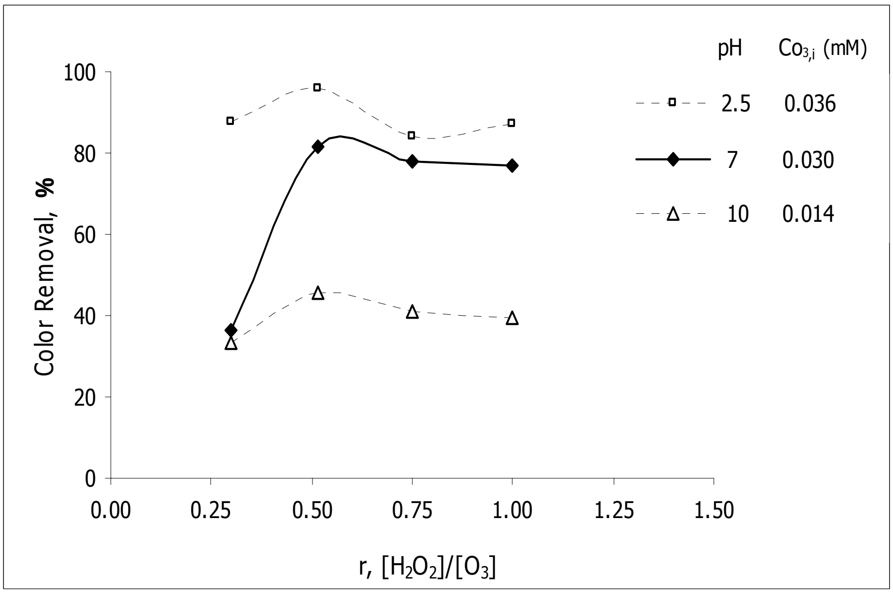


Figure 4.22 Effects of pH and "r" ratio on the Color removal (%) of Acid Red 151 at T=25°C, $C_{dye,i}$=0.033 mM, Reaction time=50 min

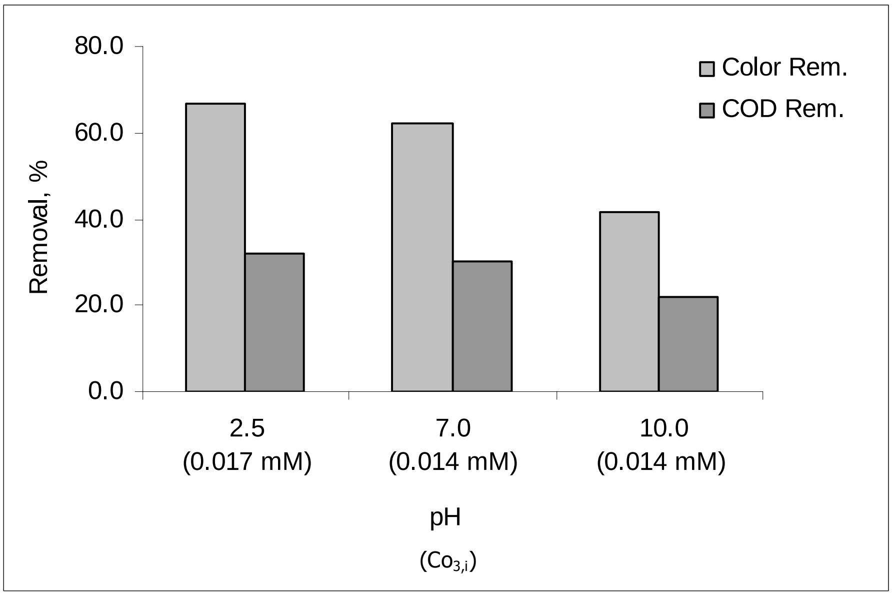


Figure 4.23 Effect of pH on Color and COD removals (%) at T=25°C, $C_{dye,i}$=0.033 mM, r=0.5, Reaction time=50 min

Figures 4.21 and 4.22 show the important effects of pH, initial dye concentration and the "r" value on the color removal. An increase in the initial dye concentration adversely affects the color removal. The maximum color removal is observed as 96% at pH=2.5. For decolorization, it can be concluded that at pH=10, peroxone process seems to be less efficient when it is compared with pH=2.5 and pH=7. As mentioned before, Kuo et al. [40] studied the kinetics and the mechanism of the reaction between ozone and hydrogen peroxide in aqueous solutions. As a result of the experimental work, they concluded that the scavenging reactions of hydrogen peroxide were found to be important (means the decrease in oxidation performance by hydroxyl radicals) at elevated pH values (at or above pH of 10). Figure 4.23 also implies that the lowest color removal percentage was achieved at pH=10 even at the same $Co_{3,i}$ value of 0.014 mM at both of the pH values of 7 and 10. Since oxidation performance of the process in terms of dye degradation is smallest at pH=10 (Figure 4.6), this was an expected result in agreement with the results of Kuo et al. [40] and the statement that was made in a previous study [69].

On the other hand, "r" value also affects the process efficiency. From Figure 4.22 it can be concluded that the best "r" value for peroxone-dye oxidation is r=0.5 for all the studied pH values at a nominal initial dye concentration of $C_{dye,i}$=0.0330 mM.

As mentioned earlier, the treatments of various pollutants by the peroxone process were carried out by some investigators [32, 34, 35, 36]. On the basis of the oxidants applied and the destruction extent of the pollutants, the optimum "r" ratios were reported to be about 0.5 to unity. The results seem consistent with the requirement of hydrogen peroxide and ozone concentrations with an "r" ratio of 0.5 for effective generation of hydroxyl radical with minimum effects of the scavenging reactions, as concluded in the work of Kuo et al. [40]. Result of this work is also in agreement with the results in literature. In conclusion, color removal, depending on the initial conditions is changed from 42.7%-96%. Therefore, the effects of the initial conditions are crucial for the process efficiency.

4.4 COD Removal

Chemical Oxygen Demand (COD) is the amount of oxygen from chemical oxidants required for the complete oxidation of substances dissolved or suspended in water. By COD determination it is possible to quantitatively evaluate substances which can be oxidized by strong oxidants like potassium dichromate in highly acidic solutions. COD is an important parameter for water quality determination. In this work, COD of the samples, taken from the reactor at definite time intervals, were measured. The results of the COD removal (%) are given in Table 4.5.

Table 4.5 Results of COD removal (%) at T=25°C, at different pH values and nominal initial dye concentrations for r=0.5

pH	**$C_{dye,i}$ (mM)**	**COD Removal (%)**
2.5 $C_{O3,i}$=0.036 mM	0.0220	40.5
	0.0275	36.5
	0.0330	36.8
	0.0440	31.2
7 $C_{O3,i}$=0.030 mM	0.0220	33.8
	0.0275	34.6
	0.0330	36.4
	0.0440	37.4
10 $C_{O3,i}$=0.014 mM	0.0220	23.1
	0.0275	22.0
	0.0330	24.6
	0.0440	24.9

The highest COD removal was observed at pH=2.5 and $C_{dye,i}$=0.0220 mM as 40.5% and the lowest one was determined at pH=10 and $C_{dye,i}$=0.0275 mM as 22.0%. COD removal at a specific pH value does not change significantly with the change in the initial dye concentration, the significance level from the F-table being determined as 16%. The statistical ANOVA (Analysis of Variance) table and related calculations are given in Appendix E. From the ANOVA table (Table E.2), it can also be observed that the significance level for the variability among % COD removals obtained at different pH values is very small and it is almost 0.1%. Thus, the null hypothesis of no pH-to-pH variation is discredited. This indicates that pH is a very important parameter in the present experimental study. Since pH fixes the maximum attainable ozone concentration in the reaction medium, therefore accordingly initial ozone concentration ($C_{O3,i}$) is an extremely important parameter affecting the % COD and color removals and the % dye degradation.

The results show that the COD of the dye solution is reduced with time as expected, but the total COD reductions could not reach to the values that can be achieved by the simple conventional methods. The lower percentage removal in the total COD compared to that in the color can be explained by the production of smaller organic molecules instead of CO_2 and H_2O [23]. Ozonation combined with the other treatment methods would be more effective and feasible, and can be recommended at this point.

Effect of pH at $Co_{3,i}$ values of 0.017 mM, 0.014 mM and 0.014 mM at pH values of 2.5, 7 and 10, respectively, on COD removal (%) is given in Figure 4.23. Effects of pH (at different $Co_{3,i}$) and "r" value on the COD removal (%) are given in Figure 4.24. Data of this figure are given in Table C.42.

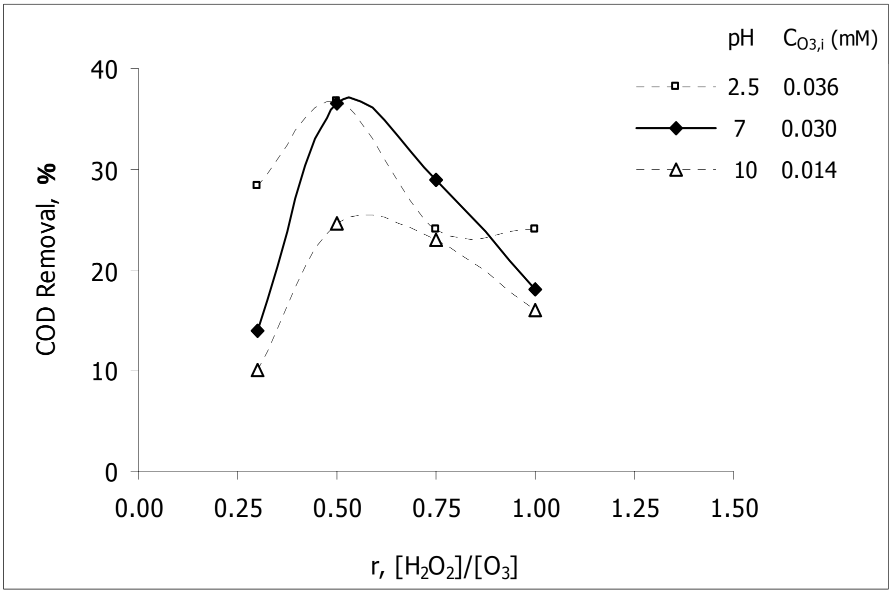


Figure 4.24: Effects of pH and "r" value on COD removal (%) at each pH value, at T=25°C

Figures 4.23 and 4.24 show the importance of pH value and "r" ratio on the COD removal by the peroxone process. The best "r" value for COD removal is also found to be 0.5 as it was for the color removal experiments. Increase in the pH to 10 decreases the COD removal (%) significantly, the significance level being 0.1% (see Table E.2).

The results obtained in this experimental batch study show that at pH=10, peroxone process is not sufficiently capable for the efficient oxidation of Acid Red 151 solutions. At pH=2.5 and pH=7, better results are obtained in terms of both the color and COD removals.

4.5 Kinetics of Ozone-Acid Red 151 Reactions

The ozonation reaction between the Acid Red 151 dye and ozone is;

$$\text{Dye} + a\, O_3 \rightarrow \text{Products}$$

The reaction temperature was kept constant at 25°C in all the experiments. For the determination of reaction kinetics, the rate equation is taken to be a function of dye and ozone concentrations for each pH value:

$$-r = -r_{dye} = -r_{O3} / a = k_1\, C_{dye}^{m}\, C_{O3}^{n}$$

$$-r_{O3} = k_1\, a\, C_{dye}^{m}\, C_{O3}^{n} = k_{O3}\, C_{dye}^{m}\, C_{O3}^{n}$$

In this study, the reaction order and rate constants are found according to Method of Excess [65] by taking initial dye concentration excessively (0.551 mM, 0.881 mM and 1.321 mM). However, because of very fast reaction between Acid Red-151 and ozone, initial rate of the reaction is very high and it cannot be used in excess dye experiments. Therefore, for the determination of the reaction kinetics at the first few seconds of the reaction, Initial Rate Method is applied to all the experimental data obtained without using any excess of the reactants.

4.5.1 Method of Excess [65]

In this part of the study, the initial dye concentration is used in excess; its change with respect to time is assumed so small that the dye concentration throughout the reaction remains nearly constant. Therefore, the reaction rate becomes only a function of dissolved ozone concentration:

$$-dC_{O3}/dt = -r_{O3} = k\, C_{dye,i}^{m}\, C_{O3}^{n} = k'\, C_{O3}^{n} \quad (1)$$

$$\log_{10}(-dC_{O3}/dt) = \log_{10}(k') + n \log_{10}(C_{O3}) \quad (2)$$

The reaction rates are determined differentially from C_{O3} versus time data as shown in Figure 4.25. By using this procedure (Differential Method), a polynomial equation is obtained for each set of data in an experiment that gives C_{O3} as a function of time. Differentiation of this equation with respect to time yields rate equation $-dC_{O3}/dt$ as a function of time. Thus, $-dC_{O3}/dt$ values at each time value or at each residual ozone concentration in the aqueous phase corresponding to that time value are calculated from the rate equation. The logarithmic plots of $-dC_{O3}/dt$ versus C_{O3} are prepared in order to obtain the reaction order with respect to O_3 concentration (n) from the slope and the rate constant (k′) from the intercept of the straight line according to equation (2). Figure 4.26 shows the graphical determination of the reaction order with respect to ozone concentration and rate constant at pH=2.5 and $C_{dye,i}$=0.551 mM. The rates at the very beginning of the reaction (initial rates) are very high. Therefore, the data point at t=0 is not included at this stage of the kinetic study. Tables 4.2, 4.3 and 4.4 show the results of the kinetic study for pH values of 2.5, 7 and 10, respectively.

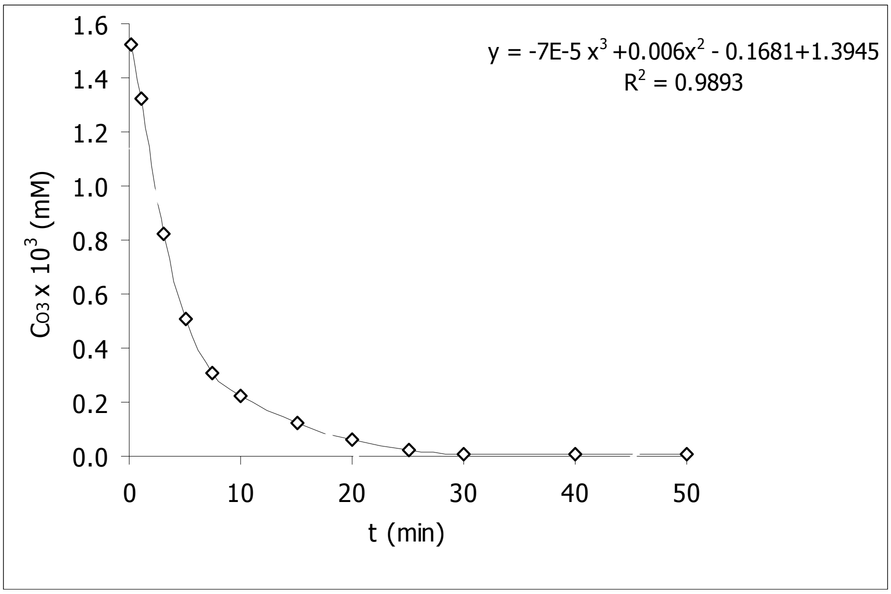


Figure 4.25 Polynomial fit to C_{O3} vs. t data at T=25°C, pH=2.5, $C_{dye,i}$=0.551 mM, $C_{O3,i}$=0.036 mM, r=0.5

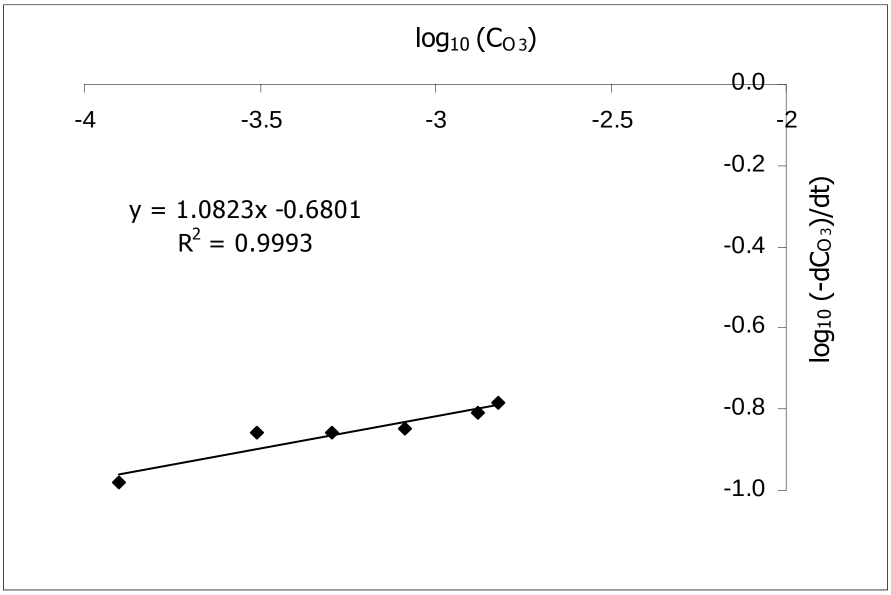


Figure 4.26 $\log_{10}(-dC_{O3}/dt)$ vs. $\log_{10}(C_{O3})$ graph at pH=2.5, $C_{dye,i}$=0.551 mM, $C_{O3,i}$=0.036 mM, r=0.5

In the Method of Excess experiments three different excess initial dye concentrations (0.551 mM, 0.881 mM and 1.321 mM) were used at each pH value. At every initial dye concentration, $k^{'}$ values, calculated from the C_{O3} vs. t graph and equation (2), were used to find the reaction order with respect to dye concentration (m) and the reaction rate constant (k) at each pH value according to equation (3). Since;

$k' = k\,[C_{dye,i}]^m \rightarrow \log_{10}(k')=\log_{10}(k)+m\,\log_{10}[C_{dye,i}]$.....................(3)

By using least square regression analysis and the plots of $\log_{10}(k')$ vs. $\log_{10}(C_{dye,i})$ as shown in Figures 4.27, 4.28 and 4.29 for pH values of 2.5, 7 and 10, respectively, reaction order with respect to dye concentration (m) and log(k) were found from the slope and the intercept of the straight line, respectively.

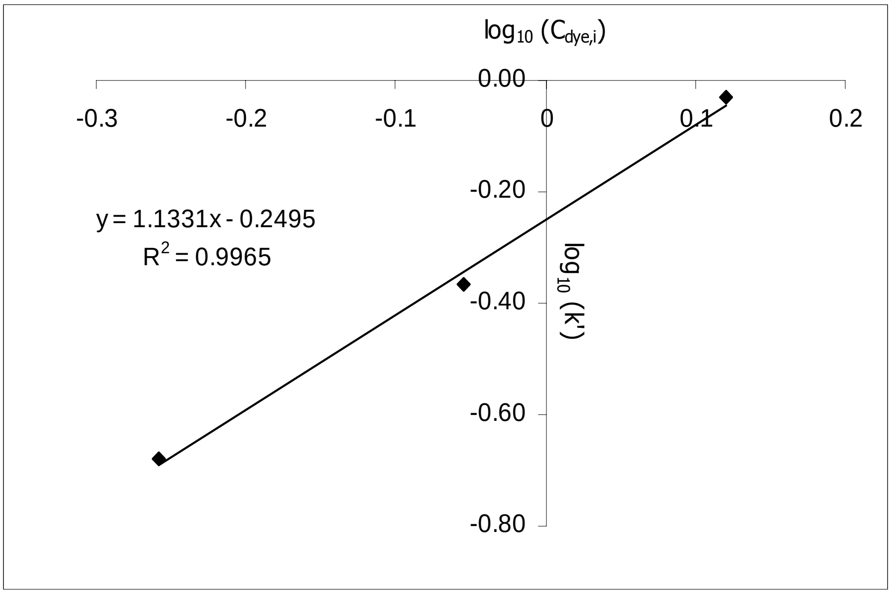


Figure 4.27 Determination of m and k values at pH=2.5 and r=0.5 with the Method of Excess.

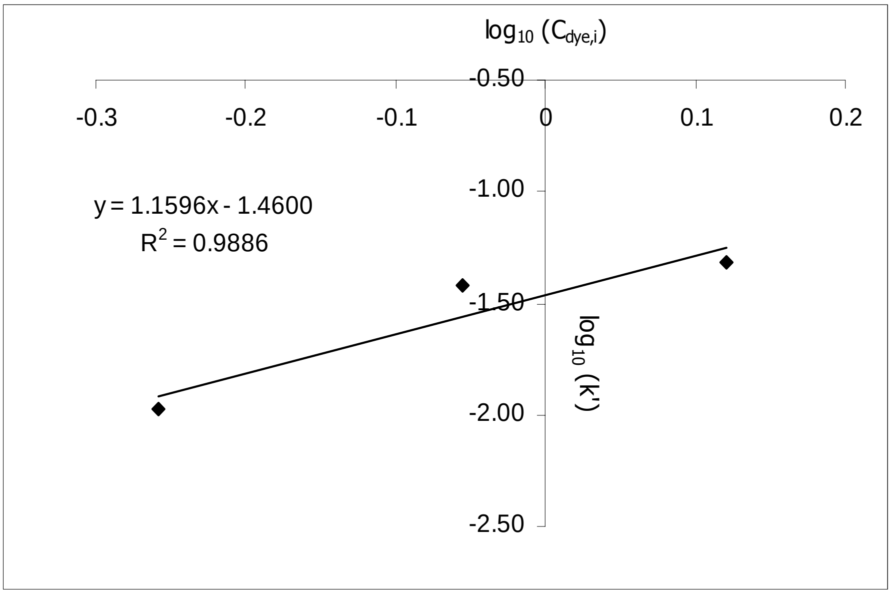


Figure 4.28 Determination of m and k values at pH=7 and r=0.5 with the Method of Excess.

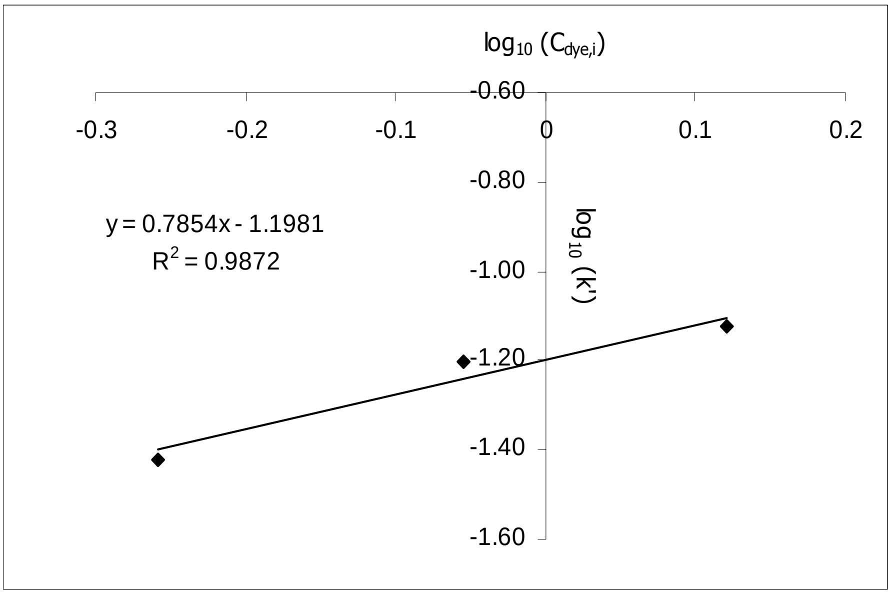


Figure 4.29 Determination of m and k values at pH=10 and r=0.5 with the Method of Excess.

Table 4.6 Rate constants and orders calculated by the Method of Excess at pH=2.5, r=0.5

pH	$C_{dye,i}$ **(mM)**		
	0.551	0.881	1.321
2.5	n=1.08 k′=0.21	n=0.99 k′=0.54	n=0.97 k′=0.93
$-r_{O_3}$	$0.21 \times [C_{O3}]^{1.08}$	$0.54 \times [C_{O3}]^{0.99}$	$0.93 \times [C_{O3}]^{0.97}$

$k' = k.\,[C_{dye,i}]^m \rightarrow m = 1.13 \qquad k = 0.56$

Table 4.7 Rate constants and orders calculated by the Method of Excess at pH=7, r=0.5

pH	$C_{dye,i}$ **(mM)**		
	0.551	0.881	1.321
7	n =1.27 k′=0.010	n =1.00 k′=0.038	n=0.82 k′=0.048
$-r_{O_3}$	$0.01 \times [C_{O3}]^{1.27}$	$0.038 \times [C_{O3}]^{1.00}$	$0.048 \times [C_{O3}]^{0.82}$

$k' = k.\,[C_{dye,i}]^m \rightarrow m = 1.15 \qquad k = 0.035$

Table 4.8 Rate constants and orders calculated by the method of excess at pH=10, r=0.5

pH	**$C_{dye,i}$ (mM)**		
	0.551	0.881	1.321
10	n=0.73 k′=0.038	n=0.49 k′=0.063	n=0.47 k′=0.075
$-r_{O_3}$	$0.038 \times [C_{O3}]^{0.73}$	$0.063 \times [C_{O3}]^{0.49}$	$0.075 \times [C_{O3}]^{0.47}$

$k' = k.\ [Cdye_{,i}]^m \rightarrow m = 0.78 \qquad k = 0.063$

During ozone-dye oxidation reactions, ozone reacts with the dye molecule and decomposes in the aqueous phase at the same time. Obtained rate values from the calculations by using the Method of Excess are determined by substracting the decomposition rate of ozone from the total ozone consumption rate for each pH value studied. By this way, the reaction rate used in the Method of Excess analyses is the net rate of ozone-dye oxidation reaction. Since the ozone decomposition rate is very slow at pH=2.5, its effect on the total reaction rate after t=0 min is insignificant. Detailed data related to the kinetic study with the Method of Excess are given in Tables D.1-3.

The results of the excess-dye-experiments as presented in Tables 4.6-4.8 show that the ozonation of Acid Red 151 follows approximately first order reaction with respect to ozone concentration at pH=2.5 and pH=7, whereas average reaction order with respect to ozone concentration is around 0.56 at pH=10. Reaction orders with respect to dye concentrations are found to be 1.13, 1.15 and 0.78 at pH=2.5, pH=7 and pH=10, respectively. Results show that ozone concentration and initial dye concentration are both found as important parameters for reaction kinetics.

Results of the kinetic study with the Method of Excess show that when the initial dye concentration is increased, the reaction order with respect to ozone concentration is decreased at each pH value. As mentioned earlier, in this part of the kinetic study, initial rates at the first few seconds of the reaction time are not included since they are expected to be very high. Therefore, increases in the initial dye concentrations cause the faster decreases in the initial ozone concentrations in the first few seconds of the reaction time. Since the initial dye concentration is in excess, a rapid decrease in ozone concentration at the first few seconds probably affects the reaction rate with respect to ozone concentration in the proceeding reaction time. As mentioned before, this kinetic study is based on the direct reaction of ozone-Acid Red 151 dye, but it is known that the radical mediated reactions also play a role in the oxidation of the dye molecules [27].

4.5.2 Initial Rate Method

Initial rates are determined by using the experiments in which none of the reactants are in excess. The initial rates at t=0 are found from the initial slopes of the concentration vs. time curves. This is done at a set of different initial ozone and initial dye concentrations. In the first set of these experiments, three different runs were performed at different initial O_3 concentrations while the initial dye concentrations were kept at the same value ($C_{dye,i}$=constant). In the second set, three more experiments were performed at different initial dye concentrations, while initial O_3

concentration being kept at the same chosen value ($C_{O3,i}$=constant). The related data are given in tables D.4-D.6. The desired $C_{O3,i}$ values are provided by starting the reaction at the time value corresponding to that initial ozone concentration from the decomposition curves of O_3 with respect to time (Figure 4.3).

The orders and rate constants based on ozone concentrations are calculated from the logarithm of initial rates, $\log_{10}(-dC_{O3}/dt)_i$, vs. the logarithm of the initial ozone concentration, $\log_{10}(C_{O3,i})$ for each pH value studied, as seen in Figures 4.30, 4.32 and 4.34. Orders and rate constants based on dye concentrations are calculated by the same way for each pH value, as seen in Figures 4.31, 4.33 and 4.35. Summary of the orders and rate constants based on the initial ozone and dye concentrations are given in Table 4.9.

at $C_{dye,i}$ = constant

$-r_{O3,i} = (-dC_{O3} / dt)_i = k\, C_{dye,i}^{a}\, C_{O3,i}^{b} = k_{O3}\, C_{O3,i}^{b}$……………………………………(4)

at $C_{O3,i}$ = constant

$-r_{dye,i} = (-dC_{dye} / dt)_i = k_1\, C_{O3,i}^{b}\, C_{dye,i}^{a} = k_{dye}\, C_{dye,i}^{a}$………………………………(5)

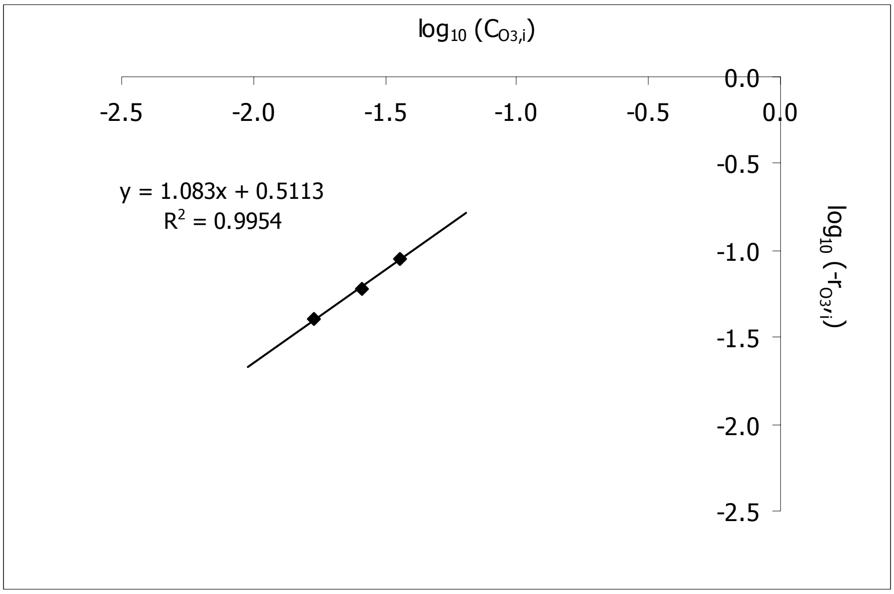


Figure 4.30 Determination of the reaction order and rate constant with respect to $C_{O3,i}$ at pH=2.5, $C_{dye,i}$=0.0330 mM, r=0.5

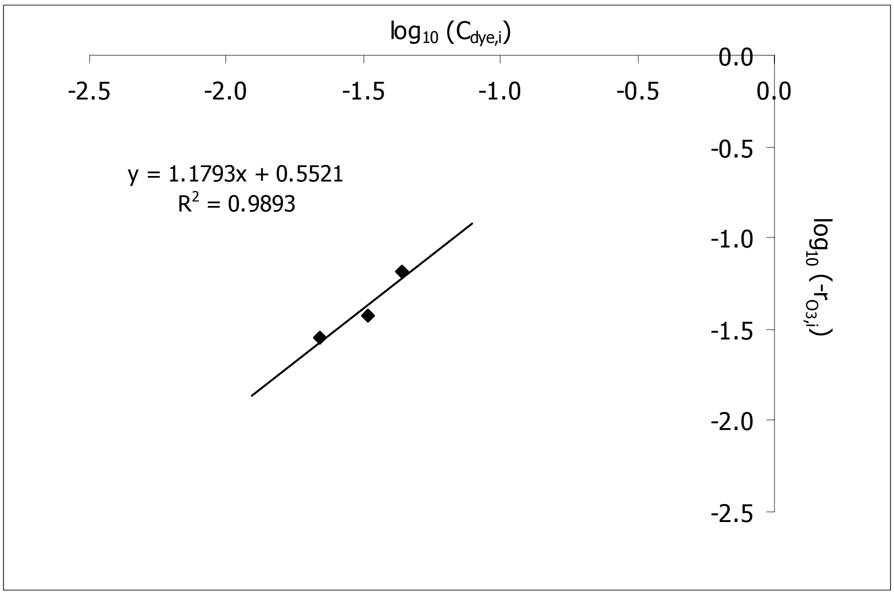


Figure 4.31 Determination of the reaction order and rate constant with respect to $C_{dye,i}$ at pH=2.5, $C_{O3,i}$=0.0360 mM, r=0.5

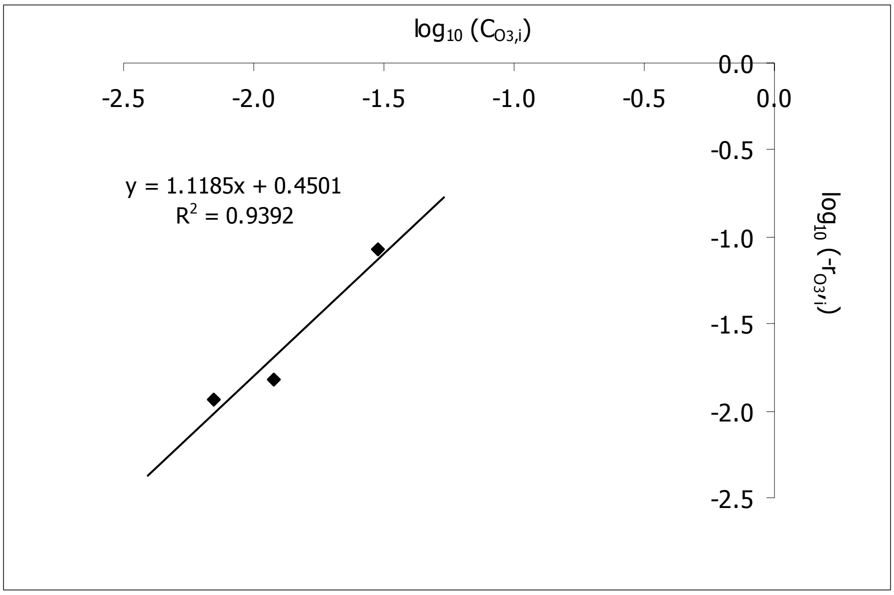


Figure 4.32 Determination of the reaction order and rate constant with respect to $C_{O3,i}$ at pH=7, $C_{dye,i}$=0.0330 mM, r=0.5

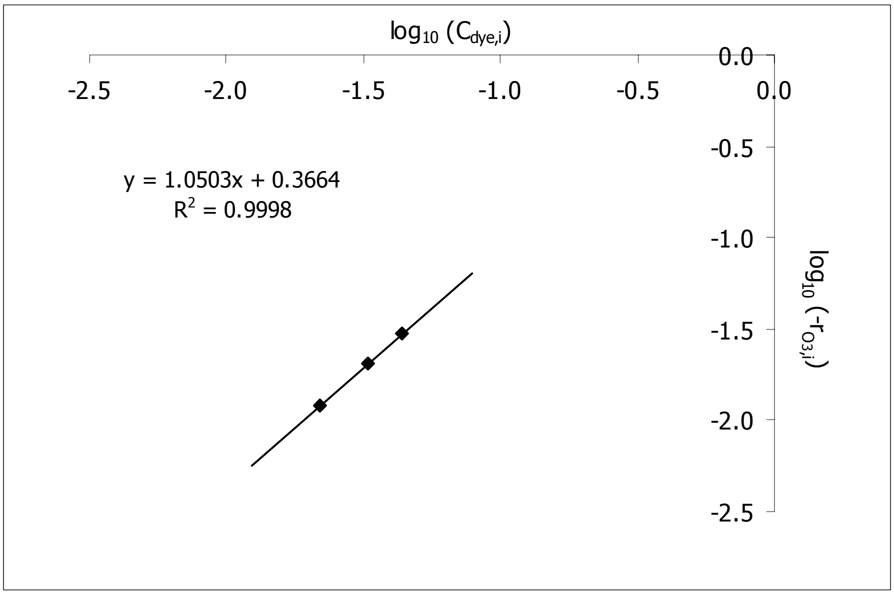


Figure 4.33 Determination of the reaction order and rate constant with respect to $C_{dye,i}$ at pH=7, $C_{O3,i}$=0.030 mM, r=0.5

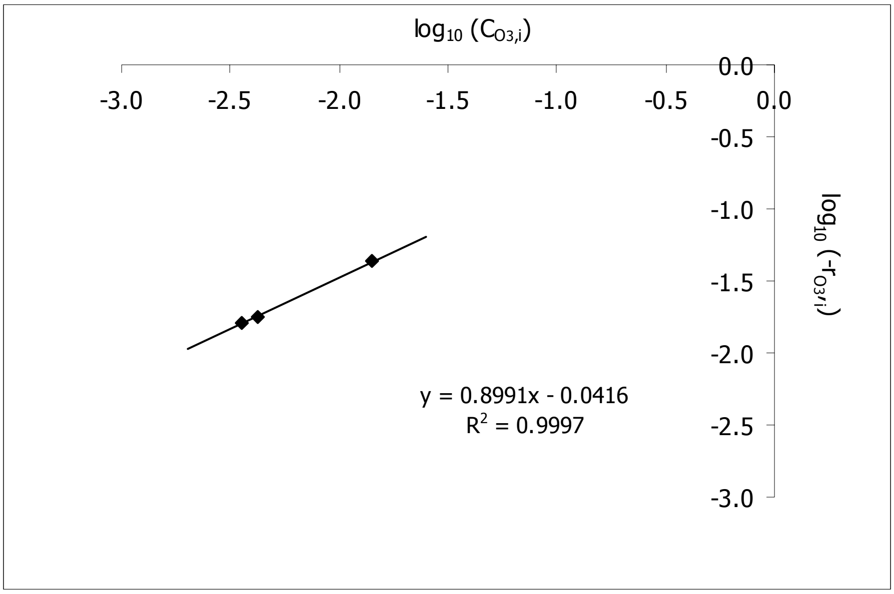


Figure 4.34 Determination of the reaction order and rate constant with respect to $C_{O3,i}$ at pH=10, $C_{dye,i}$=0.0330 mM, r=0.5

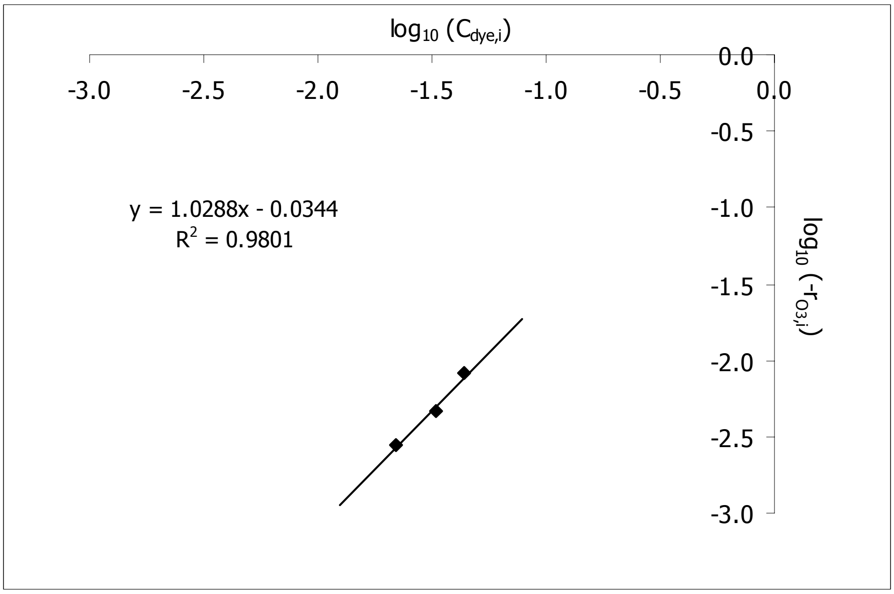


Figure 4.35 Determination of the reaction order and rate constant with respect to $C_{dye,i}$ at pH=10, $C_{O3,i}$=0.014 mM, r=0.5

Table 4.9 Summary of reaction orders and rate constants from the Initial Rate Method at r=0.5

pH	a	b	k_{O3}	k_{dye}
2.5	1.18	1.08	3.25	3.56
7	1.05	1.12	2.82	2.32
10	1.03	0.90	0.91	0.92

The reaction kinetics was determined as first order both in ozone and in dye by the Initial Rate Method, the total order being 2. With the Initial Rate Method, higher rate constants were obtained, when compared with those found by the Method of Excess, due to taking the initial rates into account in the former. The highest rate constant was found as 3.56 at pH=2.5, whereas the lowest one was 0.92 at pH=10. This is an expected result since the direct reaction of ozone with Acid Red 151 is expected to be the dominant step for the ozonation of organics at acidic pH values instead of radical mediated reactions that most probably occur when pH>7.

It is thought that the results of the Initial Rate Method are more reliable compared to those of the Method of Excess. The reason is that this method takes initial rates into account and O_3-dye reaction is very fast and it occurs in the first few minutes of the reaction time.

In order to see the first order reaction rate with respect to C_{O3} and C_{dye} values, separately, design equation of a batch reactor for a first order reaction (given in equation (6)) is used and hand drawing of ln (C/C_i) vs. t graph is done for each C_{O3} vs. t and C_{dye} vs. t data, between the 1st and 15th minute of reaction time, at different experimental conditions, on a natural-semi -logarithmic-scale paper.

$dC/C= k_1\ dt$...(6)

By integrating equation (6) from initial time of t_i=0 min to a final time value, t min, we obtain equation (7) as;

$\ln(C/C_i)=k_1\ t$..(7)

Equation (7) can also be written in the logarithmic form as ;

$\log_{10}(C/C_i)= (k_1/2.303)\ t= k_2\ t$..(8)

Equations (7) and (8) imply that if the reaction order in C is one, the plot of ln (C/C_i) vs. t should be a straight line. As a result of the drawn ln (C/Ci) vs. t graphs, straight lines were observed with the data at different initial experimental conditions. Representative plots of drawn ln (C/Ci) vs. t for ozone and dye concentrations at pH values of 2.5 and 7 are given in Figures 4.36-38.

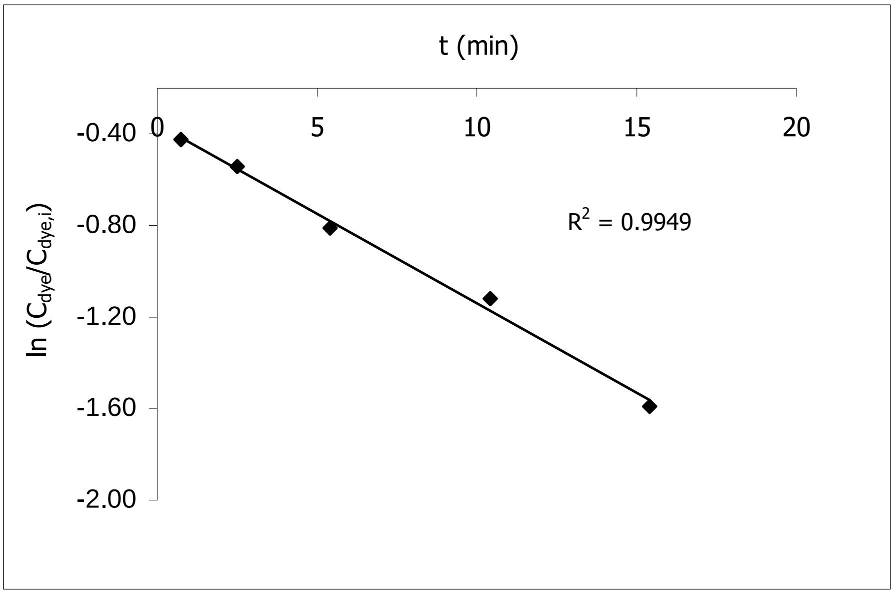


Figure 4.36 ln ($C_{dye}/C_{dye,i}$) vs. t graph at pH=7, $C_{dye,i}$=0.0275 mM, $C_{O3,i}$=0.030 mM and r=0.5

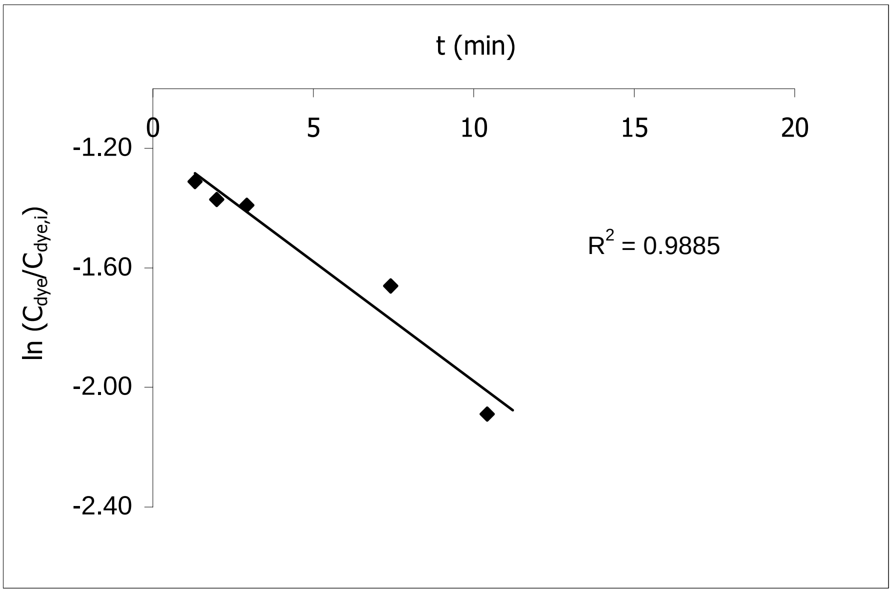


Figure 4.37 ln($C_{dye}/C_{dye,i}$) vs. t graph at pH=2.5, $C_{dye,i}$=0.0275 mM, $C_{O3,i}$=0.036 mM and r=0.5

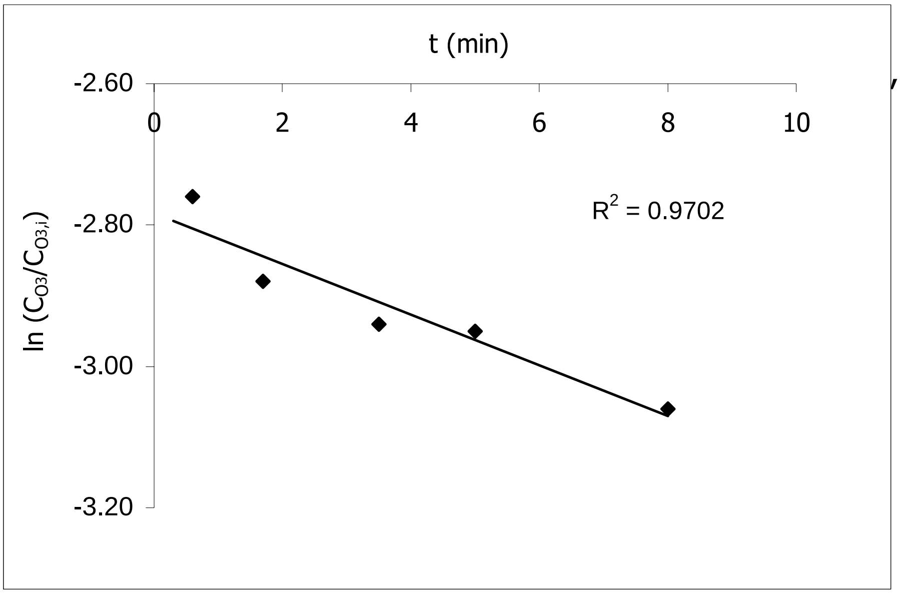


Figure 4.38 ln($C_{O3}/C_{O3,i}$) vs. t graph at pH=7, $C_{dye,i}$=0.044 mM, $C_{O3,i}$=0.030 mM and r=0.5

Rate constants for the data given in Figures 4.36-4.38 were also determined and k_1 values were found to be as 0.080 min^{-1}, 0.053 min^{-1} and 0.023 min^{-1} and k_2 values were calculated as 0.035 min^{-1}, 0.023 min^{-1} and 0.010 min^{-1} for Figures 4.36-4.38, respectively.

4.6 Comparison of Peroxone Process with a Previous Study of Ozonation

Oxidation of Acid Red 151 solution by ozonation process was studied by Özbelge et al. [66]. In order to compare the ozonation and peroxone processes for the oxidation of Acid Red 151, experiments at the same conditions are repeated with the peroxone process, in this study. Comparison of the results is given in Table 4.10.

Table 4.10 Comparison of Ozonation and Peroxone Processes

pH	Removal (%)	$C_{dye,i}$ (mM)							
		0.0220		0.0275		0.0330		0.0440	
		1*	2**	1	2	1	2	1	2
2.5	Color R.	95.9	99.1	96.0	98.7	95.8	96.8	95.0	97.7
	COD R.	40.5	51.1	36.5	52.8	36.8	54.3	30.2	58.2
7	Color R.	95.9	69.7	85.5	64.8	81.5	56.0	72.7	59.7
	COD R.	33.8	17.9	34.6	19.2	36.4	22.4	37.4	26.8
10	Color R.	58.2	53.2	56.7	40.8	45.5	31.2	43.9	25.1
	COD R.	23.1	18.9	22.0	17.6	24.6	21.7	24.9	24.4

* First columns show the results of this work with the Peroxone Process

** Seconds columns show the results of the previous study with Ozonation only [66]

It can be observed in Table 4.10 that the overall color removal percentages in the oxidation of Acid Red 151 yield similar values by both of these processes at pH=2.5. The highest color and COD removals at pH=2.5 for ozonation process are 99.1% and 58.2% whereas they are 96.0% and 40.5% for the peroxone process, respectively.

At pH=7 and pH=10, as it is expected, peroxone process gives higher % removals of color and COD, when it is compared with the ozonation process. The highest color removal at pH=7 is 95.9% with the peroxone process, whereas it is 69.7% with the ozonation process.

At pH values of 7 and 10, color and COD removals with the peroxone process are higher than those obtained with the previous study of the ozonation process.

CHAPTER 5

CONCLUSIONS

In this study, O_3 is mixed with H_2O_2 for the oxidation of a textile dye solution, namely, Acid Red 151. The aim of this study is to improve the process efficiency in the oxidation of the dye solution (in terms of color removal, COD reduction and dye degradation), to observe the effects of pH, initial dye concentration, initial ozone concentration, the ratio of initial concentrations of H_2O_2 to O_3 on the oxidation efficiency and to determine the reaction kinetics of the O_3-dye reactions in the presence of H_2O_2.

From this experimental work, the following conclusions can be drawn:

- Ozone decomposition experiments in the presence of H_2O_2 show that ozone decomposition is enhanced at all the studied pH values (pH=2.5, 7 and 10), but it is more significant at the pH values of 7 and 10.

- Ozone-Acid Red 151 reaction is a very fast reaction and almost overall reaction occurs in the first ten minutes of the reaction time.

- Although the initial dye degradation rates increased with the increasing initial dye concentrations, the average oxidation efficiency over a reaction time of 50 min (may be defined as overall efficiency) seemed to decrease due to the insufficient amount of dissolved ozone in the present batch reactor at some of the experimental conditions.

- In the peroxone process, it was statistically shown that pH and initial dissolved ozone concentration are the important parameters affecting the color and COD removals significantly. At a certain pH and initial ozone concentration, the change in initial dye concentration did not have a significant effect on the COD removal.

- For O_3/H_2O_2 treatment of the dye solution, pH is the most important factor affecting the color and COD removals. pH=2.5 and pH=7 give higher color and COD removals compared with those at pH=10. As a conclusion, depending on the initial conditions, color removal of 42.9% to 96.0% and COD reduction of 23.1% to 40.5% are achieved with the peroxone oxidation of the Acid Red 151 solution. Therefore, the effects of the initial conditions are crucial for the process efficiency.

- The observation of moderate COD reductions compared with the high color removals show that by the peroxone process, dye molecules are reduced to small organic molecules instead of complete mineralization to CO_2 and H_2O.

- The best "r" ratio of 0.5 was determined at all the studied pH values, in agreement with the literature value.

- When the results of this study are compared with the previous study [66] for the ozonation of Acid Red 151 dye solution at the same conditions, it is seen that at pH=7, there is a significant increase in the color and COD removals in the peroxone process.

- The results of the excess dye experiments show that the ozonation of Acid Red 151 follows an average first order reaction with respect to ozone concentration at pH=2.5 and pH=7 whereas average reaction order with respect to ozone concentration is around 0.56 at pH=10.

- By Initial Rate Method, a first order reaction rate with respect to initial ozone concentration, and first order reaction rate with respect to initial dye concentration were found for the studied pH values.

- Results of the Initial Rate Method are more reliable compared to those of the Method of Excess, since this method takes initial rates into account and O_3-dye reaction mainly occurs in the first 10 min of the reaction time.

CHAPTER 6

RECOMMENDATIONS

- Continuous ozonation experiments may be recommended to achieve steady state concentrations of OH radicals, thus the scavenging of these radicals by some compounds in the water matrix can be minimized [69]. This is important especially in the advanced oxidation processes used to treat the industrial textile wastewater. By using a continuous feed of O_3, it will not be the limiting reactant, thus the oxidation process may be more efficient. In addition, continuous system, leading to higher initial ozone and dye concentration usages, decreases the possibility of experimental errors for concentration and COD analysis.

- In this study, to eliminate the effects of mass transfer of ozone to aqueous phase, dye-peroxone experiments are conducted after maximum dissolved ozone concentration is attained. This study is limited to only chemical reaction kinetics of ozonation process. Therefore, it can be useful to spread out the study in a manner that mass transfer of ozone is included in the kinetics. Continuous experiments can be performed for this purpose.

- On-line concentration monitors for hydrogen peroxide and dissolved ozone can be used to minimize the experimental errors that might occur during spectrophotometric analysis, and to have more data. It can be useful to determine the concentrations of ozonation by-products, and to measure the concentration of hydroxyl radicals, in order to understand the mechanism of the reactions occurring in the peroxone-dye process, clearly.

- In the industrial application of the peroxone process to real textile wastewater, peroxone treatment before a conventional biological treatment step can be a recommended study in order to have higher COD removal. By this way, biodegradability of the wastewater will be enhanced and thus the overall treatment efficiency will be higher.

- O_3+H_2O_2+UV combination for the advanced oxidation of Acid Red 151 solution can be a recommended study for improvement of the ozonation efficiency further.

- A previous study [70] performed by preliminary experiments and computer simulations showed that two-port ozone injection, by using two continuous reactors in series, was advantageous for the ozone-hydrogen peroxide treatment of a synthetic sodium acetate wastewater than the conventional one-port ozone injection method, under the condition of same ozone dose. In this work, amount of ozone for the hydroxyl radical formation and the amount of hydroxyl radical reacting in the oxidation reactions increased with the two-port injection method. This method can be used for the peroxone–textile wastewater treatment process.

- It can be a recommended study for the peroxone-textile wastewater treatment to be performed with a series of continuous reactors in order to improve process effectiveness. By using a process control system, in order to control the concentration of outlet stream from the final treatment reactor, a feedback stream from that outlet can be sent to the first treatment reactor in order to improve process effectiveness in terms of color and COD removals.

REFERENCES

[1] Mishra, G. (1993). "Critical review of the treatment for decolorization of textile effluent" Colourage 40, 35-38.

[2] Stahr, R.W., Boepple, C.P. and Knocke, W.R. (1980) "Textile waste treatment colour removal and solids handling characteristics" In: Proc. of the 35th Industrial Waste Conference, Purdue University, West Lafayette, Indiana, U.S., 187-199.

[3] Geronszy, M.C. and Tomas, H. (1992) "Characterization and biological treatibility of textile dyehouse wastewater" In: Proc. of the 47th Industrial Waste Conference, Purdue University, West Lafayette, Indiana, U.S., 743-764

[4] Gahr, F., Hermanutz, F. and Oppermann, W. (1994) "Ozonation-An important technique to comply with new German Laws for textile wastewater treatment" Wat. Sci. Tech., 30 (3), 255-263.

[5] Perkins, W.S., Judkins, J.F. and Perry, W.D. (1980) "Removation of dye bath water by chlorination or ozonation" Textile Chemist and Colorist, 12 (8), 27/182-32/187.

[6] Lin, S.H. and Lin, C.N. (1993) "Treatment of textile waste effluents by ozonation and chemical coagulation" Wat. Res., 27 (2), 1743-1748.

[7] Glaze, W.H., (1987) "Drinking water treatment with ozone" Environ. Sci. Technol. 21 (3), 224-230.

[8] Glaze, W.H., Kang, J.W., Chapin, D.H., (1987) "The chemistry of water treatment processes involving ozone, hydrogen peroxide and UV radiation" Ozone Sci. Eng. 9, 335-352.

[9] Huang, C.P., Dong, C.H., Tang, Z., (1993) "Advanced chemical oxidation: its present role and potential future in hazardous waste treatment" Waste Manag. 13, 361-377.

[10] Legrini, O., Oliveras, E., Braun, A.M., (1993) "Photochemical processes for water treatment" Chem. Rev. 93, 671-698.

[11] Ince, N.H., Stefan, M.I., Bolton, J.R., (1997) "UV/H_2O_2 degradation and toxicity reduction of textile azo dyes: Remazol Black-B, a case study" J. Adv. Oxid. Technol. 2 (3), 442-448.

[12] Chun, H., Yizhong, W., (1999) "Decolorization and biodegradability of photocatalytic treated azo dyes and wool textile wastewater" Chemosphere 39 (12), 2107-2115.

[13] Rott, U., Minke, R., (1999) "Overview of wastewater treatment and recycling in textile processing industry" Water Sci. Technol. 40 (1), 137-144.

[14] Stock, N.L., Peller, J., Vinodgopal, K., Kamat, P.V., (2000) "Combinative sonolysis and photocatalysis for textile dye degradation" Environ. Sci. Technol. 34, 1747-1750.

[15] Ledakowicz, S., Solecka, M. and Zylla, R., (2001), "Biodegradation, decolorization and detoxification of textile wastewater enhanced by advanced oxidation processes", J. of Biotech. 89, 175-184.

[16] Ollis, D. (1993) "Comparative aspects of advanced oxidation processes" Emerging Technologies in Waste Management II, ACS Symposium Series 518. Washington DC, 18-34.

[17] Saunders, F., Gould, J.P. and Southerland, C.R. (1983) "The effect of solute competition on ozonolysis of industrial dyes" Wat. Res. 17 (10), 1407-1419.

[18] Paillard, H., Bunet, R., Dore, M. (1988) "Optimal conditions for applying an Ozone-Hydrogen peroxide oxidizing system" Wat. Res. 22 (1), 91-103.

[19] Roques, H. (1995) """Chemical Water Treatment: Principals and Practice", New York.

[20] Hoigne, J. and Bader, H. (1978) "Ozone initiated oxidations of solutes in wastewater: A reaction kinetic approach" Progress Water Technol. 10 (516): 657.

[21] MWDSC and JMM (Metropolitan Water District of Southern California and James M. Montgomery Consulting Engineers), (1992) "Pilot scale evaluation of ozone and peroxone" AWWARF and AWWA, Denver, CO., 432-436.

[22] Pereira, G., Huck, P.M. and Anderson, W.A. (1996) "A simplified kinetic model for predicting peroxone performance for geosmin removal in full-scale processes" Conference Proceedings, AWWA Quality Technology Conference; Part I. New Orleans, LA.

[23] Masten, S.J and Hoigne, J. (1992) "Comparision of ozone and hydroxyl radical-induced oxidation of chlorinated hydrocarbons in water" Ozone Sci. Eng. 14 (3): 197-214.

[24] Aieta, E.M., Reagen, K.M., Lang, J.S., Mc Reynolds, L., Kang, J. W. and Glaze, W.H. (1988) "Advanced oxidation processes for treating groundwater contaminated with TCE and PCE: Pilot scale evaluations" J. AWWA. 88 (5), 64-72.

[25] Glaze, W.H. and Kang, J.W. (1988) "Advanced oxidation processes for treating groundwater contaminated with TCE and PCE: Laboratory Studies" J. AWWA. 88 (5), 57-63.

[26] Chutny, B. and Kucera, J. (1974) "High energy radiaton-induced synthesis of organic compounds. I. Introduction isomerization and carbon-skeleton changes, radiation synthesis in aqueous solutions" Rad. Res. Rev. 5, 1-54.

[27] Staehelin, J. and Hoigne, J. (1982) "Decomposition of ozone in water: Rate of initiation by hydroxide ions and by hydrogen peroxide" Env. Sci. Technol., 19 (12), 1206-1213.

[28] Tomiyasu, H., Fukutomi, H. and Gordon, G. (1985) "Kinetics and mechanism of ozone decomposition in basic aqueous solution" Inorg. Chem. 24, 2962-2966.

[29] Taube, H. and Bray, W.C. (1940) "Chain reactions in aqueous solutions containing ozone, hydrogen peroxide and acid" J. Am. Chem. Soc. 62, 3357-3373.

[30] Hong, A., Zappi, M., Kuo, C.H. and Hill, D. (1996) "Modelling the kinetics of illuminated and dark advanced oxidation processes" J. Env. Eng. 122, 58-62.

[31] Christensen, H.S., Sehested, H., Corfitzan, H. (1982) "Reactions of hydroxyl radicals with hydrogen peroxide and ambient and elevated temperatures" J. Phys. Chem. 86, 15-88.

[32] Glaze, W.H. and Kang, J.W. (1989) "Advanced Oxidation process" Ind. Eng. Chem. Res. 28, 1573-1580, 1580-1587.

[33] Kuo, C.H., Zhong, L., Zappi, E. and Hong, A.P. (1996) "The role of hydrogen peroxide-ozone reactions in the advanced oxidation of hazardous pollutants" in emerging technologies in hazardous waste management VI, Am. Academy of Env. Eng. 77, 177-190.

[34] Brunet, R., Bourbigot, M.M. and Dore, M. (1984) "Oxidation of organic compounds through the combination ozone-hydrogen peroxide" Ozone Sci. and Eng. 6, 163-183.

[35] Paillard, H., Brunet, R. and Dore, M. (1988) "Optimal conditions for applying on ozone-hydrogen peroxide oxidizing system" Water Res. 22, 91-103.

[36] Zappi, M.E. (1995) "Peroxone oxidation treatment of 2,4,6-trinitrotoluene contaminated water with and without sonolytic catalyzation" Ph.D. Dissertation, Mississippi State University.

[37] Snider, E.H. and Porter, J.J. (1974) "Ozone treatment of dye waste", J.WPCF, 46 (5), 886-894.

[38] Hsu, Y., Yen, C., and Huang, H. (1998) "Multistage treatment of high strength dye wastewater by coagulation and ozonation", J. Chem. Technol. Biotechnol., 71, 71-76.

[39] Kornmuller, A., Karcher, S., Jekel, M. (2001) "Cucurbituril for water treatment. Part II: Ozonation and oxidative regeneration of Cucurbituril" Wat.Res. 35 (IV), 3317-3324.

[40] Kuo, C.H., Zhang, L., Zappi, M.E., Hang, .A.P (1999) "Kinetics and mechanisms of the reactions between ozone and hydrogen peroxide in aqueous solutions" Can. J. of Chem. Eng. 77, 473-482.

[41] Esplugas, S., Gimenez, J., Contreras, S., Pascual, E., Rodriguez, M. (2002) "Comparison of different advanced oxidation processes for phenol degradation" Wat.Res. 36, 1034-1042.

[42] Beltran, J.F., Encinar, J.M., Gonzalez, J.F. (1997) "Industrial wastewater advanced oxidation. Part II. Ozone combined with hydrogen peroxide or UV radiation" Wat. Res. 31 (10), 2415-2428.

[43] Rice, R.G. (1997) "Application of ozone for industrial wastewater treatment: A review" Ozone Sci. Eng. 18, 477-515.

[44] Saupe, A. and Wiesmann, U. (1998) " Ozonation of 2,4-Dinitrotoluene and 4-Nitroaniline as well as Improved dissolved organic carbon removal by sequental ozonation-biodegradation", Wat. Environ. Res. A31 (2), 146-154.

[45] Koyuncu, I., and Afşar, H., (1996) "Decomposition of dyes in the textile wastewater with ozone" J. Environ. Sci. Health A31 (5), 1035-1041.

[46] Chan, L., (2000) "Effects of factors and interacted factors on the optimal decolorization process of methyl orange by ozone" , Wat. Res. 34 (3), 974-982.

[47] Xu, P., Janex, M., Savoye, P., Cockx, A. and Lozarova, V. (2002) "Wastewater disinfection by ozone: Main parameters for process design", Wat.Res. 36 (4), 1043-1055.

[48] Balcıoğlu, I.A. and Arslan, İ. (2001) "Partial oxidation of reactive dyestuffs and synthetic textile dye-bath by the O_3 and O3/H2O2 processes", Wat. Sci. and Technol. 43 (29), 221-228.

[49] Calvosa, L., Monteverdi, A., Rindone, B., Riva G. (1991) "Ozone oxidation of compounds resistant to biological degradation", Wat. Res. 25, 985-993.

[50] Beltran, J.F., Garcia, A.J.F., Frades, J., Alvarez, P., Gimero, O. (1998) "Effects of single and combined ozonation with hydrogen peroxide or UV radiation on the chemical degredation and biodegradability of debittering table olive industrial wastewaters", Wat. Res. 33 (3), 723-732.

[51] Rice, R.G., and Netzer, A. (1982) "Handbook of Ozone Technology and Applications" Vol.1, 15-25, Ann Arbor Science, Michigan.

[52] Masschelein, W.J., (1982) "Ozonation Manual for Water and Wastewater Treatment", John Wiley and Sons Ltd., New York.

[53] Hoigne, J., and Bader, H., (1976) "The role of hydroxyl racidal reactions in ozoation process in aqueous solutions", Wat. Res. 10, 377-385.

[54] Duguet, J., Brodard, E., Dussert, B., and Malevialle, J., (1985) "Improvement in the effectiveness of ozoation of drinking water through the use of hydrogen peroxide", Ozone Sci. Eng., 7 (3), 241-258.

[55] Ferguson, D.W., McGuire, M.J., Koch, B., Wolfe, R.L., and Aieta, M.E., (1990) "Comparing peroxone and ozone for controlling taste and odor compounds, disinfection by products and microorganisms", J. AWWA, 82 (4), 181-189i

[56] Venkataraman, K. (1997) "The analytical chemistry of synthetic dyes", John Wiley Sons, New York.

[57] Shang, N.C., Yu, Y.H., (2002) " Toxicity and color formation during ozonation of monosubstituted aromatic compounds", Env. Tech. 23, 43-53

[58] Rajeswari, R.K., Noorsaadah A.R., Wong C.S. (2001) "Effect of temperature on the ozonation of textile waste effluent", Color.Technol. 117, 95-97.

[59] Hoigne, J. and Bader, H. (1983) "Rate constants of reactions of ozone with organic and inorganic compounds in water-I", Wat. Res. 17, 173-183.

[60] Bader, H., and Hoigne, J. (1981) "Determination of ozone in water by the Indigo Method", Wat.Res. 15, 449-455.

[61] Standard Methods for the examination of water and wastewater, (1995) 19th edition, APHA-AWWA-WPCF.

[62] Shechter, H. (1973) "Spectrophotometric method for determination of ozone in aqueous solutions" Water Res. 7, 729-739.

[63] Gurol, M. D., (1985) "Factors controlling thr removal of organic pollutants in ozone reactor", J. Am. Wat. Works Assoc. 77 (8), 55-63.

[64] Langlais, B., Reckhow, D. A. and Brink, D. R. (1991) "Ozone in water treatment: Application and engineering" Lewis Publishers.

[65] Levenspiel, O. (1999), "Chemical Reaction Engiineering", 3rd Edition, John Wiley & Sons, New York.

[66] Özbelge, T. A., Erol, F., Özbelge, Ö. H. (2003), "A kinetic study on the decolorization of aqueous solutions of Acid Red 151 by ozonation", J. of Env. Sci. and Health, A38 (8), 1607-1623.

[67] http://www.epa.gov/safewater/mdbp/pdf/alter/chapt_7.pdf

[68] http://www2.volstate.edu/tfarris/PHYS2110/experimental_error.
htm

[69] Gunten, U. V., (2002), "Ozonation of drinking water: Part I. Oxidation kinetics and product formation", Water Res., 37 (2003), 1443-1467.

[70] Furukawa, S., Yasunaga, N., Kawaai, Y., Hirotsuji, J., (1997), "Highly efficient ozone-hydrogen peroxide reactor with multiple injection ports", Proceedings of 13th Ozone World Congress, 1, 499-503.

[71] Hach Dr/2010 Spectrophotometer Handbook, Hach Company, 1996-2000, U.S.A.

[72] Box, G. E. P., Hunter, W. G., Hunter, J. S. (1978), "Statistics for experimenters", 3rd Edition, 208-214, John Wiley & Sons, New York.

APPENDIX A

ANALYTICAL PROCEDURES

A.1 O_3 Analysis with Indigo Method [60]

Indigo is a well known blue vat dye. It contains only one C=C double bond which can react with ozone rapidly, and thus decolorization of the blue dye solution occurs in acidic solutions. The concentration of aqueous ozone can be best determined by the decolorization of indigo trisulfonate at $\lambda=600$ nm and $pH<4$ [60]. Precision of the analysis is 2 % if a spectrophotometer is used and the sensitivity of the method is eight times higher than the other colorimetric methods. The method is recommended for kinetic measurements, for studies of ozonation processes and for visual field methods. Oxidants that are used in water treatment methods including hydrogen peroxide or chlorite do not interfere. In order to measure dissolved ozone concentration in the solution with the Indigo Method [60], sample from the reactor at definite time value is withdrawn to sampling bottle which contain 1 mL of indigo solution and 10 mL of pH=2 buffer solution. pH=2 buffer solution is used to lower the pH of the sample below 4. Difference between the absorbance of the sample solution and the blank indigo solution give the absorbance of the dissolved ozone in the liquid sample from the reactor. In this study ozone concentration in the aqueous phase was determined by this method.

Apparatus

A Hitachi U-3010 UV Spectrophotometer at the maximum wavelength of the Indigo (600 nm) and 100 mL glass flasks with flat bottoms are used.

Reagents

Indigo reagent:

600 mg of potassium indigo trisulfonate is dissolved in 1 L of 20 mM phosphoric acid solution. The obtained reagent, when diluted by a factor of 100, has an absorbance of 0.16 to 0.18 cm^{-1} at 600 nm. This solution can be stored up to four months or until the native absorbance decreases below 80% of its initial value. This reagent should be stored in a dark place.

Buffer reagent of pH=2:

28 g NaH_2PO_4 (H_2O) and 35 g 85% (20.5 mL) H_3PO_4 are dissolved in 1 L distilled water.

Procedure

Before starting the ozonation experiments, 1 mL of Indigo reagent and 10 mL of pH=2 buffer reagent are added to each of a series of 100 mL volumetric flasks. For blank Indigo measurement, two new flasks are filled up to the 100 mL mark with distilled water after the addition of the above mentioned reagents. During ozonation, samples are withdrawn from the reactor to the sampling bottles under vacuum which contain 1 mL of Indigo and 10 mL of pH=2 buffer solution to measure the residual ozone concentrations. Then the volume of each sample is measured, and it was transferred to the volumetric test-flask with a capacity of 100 mL. After adding the test samples, a slightly blue color should remain. Otherwise, it is understood that the amount of added Indigo is not sufficient to react with all O_3 in the solution. Each of the test flasks is then filled up to the 100 mL mark with the distilled-deionized water. Then UV-Spectrophotometer is turned on and UV-Solutions 1.2 Program is started by the computer connected to the spectrophotometer. From the Edit menu, wavelength is adjusted to 600 nm. At the same time, test-flasks, diluted to 100 mL, are shaked in order to obtain mixing between the distilled-deionized water and the sample. Then, residual absorbance of the ozone-containing sample is measured at 600 nm and substracted from the value that is measured for the blank. Absorption measurements can be performed up to approximately 4 h after the samples are mixed. The concentration of the residual Indigo is then found from the calibration curve of Indigo Concentration vs. Absorbance (cm^{-1}) graph that is given in Appendix B.

Calibration equation is used for the determination of ozone concentration.

$$C_{ind}\ (mM) = 0.0551 \times A_{ind}$$

Blank concentration is calculated:

$$C_b\ (mM) = 0.0551 \times A_b$$

Indigo solution is diluted to 100 mL (0.1 L) and number of mols Indigo blank is found.

$$n_b\ (mmol) = C_b \times V_b = 0.0551 \times A_b \times 0.1 = 5.51 \times 10^{-3} \times A_b$$

In the sample, number of mols Indigo remained after the reaction with ozone is calculated by the same way:

$$n_{ind}\ (mmol) = 5.51 \times 10^{-3} \times A_{ind}$$

number of mols indigo used by O_3 = $n_b - n_{ind} = 5.51 \times 10^{-3} \times (A_b - A_{ind})$

1 mol indigo reacts with 1 mol of ozone.

number of mols dissolved O_3 in the sample = $n_{O3} = 5.51 \times 10^{-3} \times (A_b - A_{ind})$

The concentration of ozone in the reactor is found after dividing number of mols by sample volume:

$$C_{O3} = \frac{5.51 \times 10^{-3} \times (A_b - A_{ind})}{V_{ind}\,(s)\,(mL) \times 10^{-3}} = \frac{5.51 \times (A_b - A_{ind})}{V_{ind}\,(s)\,(mL)}$$

Sample calculation:

At pH=2.5, T=25°C, T_{room}=23.2°C and P_{atm}=679 mmHg

Absorbance Blank= 0.154 cm^{-1}

Absorbance Sample= 0.022 cm^{-1}

V_{sample}= 31.2 mL

$V_{ind\,(s)}$= 31.2-11 =20.2 mL

From the calibration data given in Figure B.1;

C_{O3} (mM) = 0.0551 x A (cm^{-1})

$$C_{O3} = \frac{5.51 \times (0.154 - 0.022)}{20.2\ mL}$$

$$= 0.0360\ mM$$

A.2 Dye Concentration Measurement

Dye concentration is determined from the sample which is taken from the reactor at definite times. The absorbance of the dye solution is measured at the maximum wavelength of the Acid Red 151, namely at 512 nm, in a spectrophotometer, in order to calculate the dye concentration.

Apparatus

Hitachi U-3010 Spectrophotometer and two precision cells are used.

Procedure

One of the precision cells is filled with the sample from the reactor and the other is filled with the distilled-deionized water as blank. Then, these two cells are placed into the cell hole in the spectrophotometer. After that, absorbance of the sample is read at the wavelength of 512 nm.

Sample Calculation:

Dye concentration in the sampling bottle is found from the calibration curve of the Dye Concentration (mM) vs. Absorbance (cm^{-1}) graph that is given in Figure B.2.

$$C_{dye}\,(mM) = 0.073 \times A_{dye}\,(cm^{-1})$$

Total number of moles of dye is calculated from the total volume of the solution.

$$n_{dye} = C_{dye} \times V_t(T) = 0.073 \times A_{dye} \times [V_t(s) + 10] \times 10^{-3}$$

$$= 7.3 \times 10^{-5} \times A_{dye} \times [V_t\ (s)\ (mL) + 10]$$

The concentration of the dye in the reactor is determined after dividing n_{dye} by sample volume:

$$C_{dye} = \frac{7.3 \times 10^{-5} \times A_{dye} \times [V_t\ (s)\ (mL) + 10]}{V_t\ (s)\ (mL) \times 10^{-3}}$$

$$= \frac{7.3 \times 10^{-2} \times A_{dye} \times [V_t\ (s)\ (mL) + 10]}{V_t\ (s)\ (mL)}$$

At pH=2.5, T=25°C, T_{room}=23.2°C and P_{atm}=679 mmHg

$A_{dye} = 0.060\ cm^{-1}$
$V_t\ (T) = 31.5\ mL$
$V_t\ (s) = 21.5\ mL$

$$C_{dye} = \frac{7.3 \times 10^{-2} \times 0.060 \times [21.5 + 10]}{21.5} = 0.0064\ mM$$

A.3 Chemical Oxygen Demand (COD) Analysis

COD is measured by the Standard Dichromate Method that is accepted by Standard Methods [61]. A sample taken from the reactor to an empty sampling bottle is used in the COD analysis.

Apparatus

A WTW COD thermoreactor, Hach DR-2010 Spectrophotometer, magnetic stirrer, COD vials are used.

Reagents

COD reagent: 4.9 g of potassium dichromate, $K_2Cr_2O_7$, 6.4 g of silver sulfate, $AgSO_4$ and 6.4 g of mercuric sulfate, $HgSO_4$, are added to 500 mL of concentrated sulfuric acid (95-98%) H_2SO_4. Then, the solution is stirred more than 2 days until no precipitate remains.

Procedure

2 mL of sample solution taken from the reactor, and 3 mL of COD reagent are added to each of a series of glass vials. Into the blank bottle, 2 mL of distilled-deionized water and 3 mL of COD reagent are added. Then, vial cap is closed and the vial is inverted several times, the solution in the vial is mixed, and all the vials are placed in the COD thermoreactor. The samples are digested in the reactor for two hours at 150°C. After the digestion, the vials are waited for about half an hour for cooling to 120°C or less. COD of the samples are determined by the help of a portable spectrophotometer at 620 nm. First, COD of the blank is set to zero; then, COD of the samples are measured directly in the units of mg COD/L.

Calculation of COD Corrected

First, the amount of thiosulfate that reacts with ozone in the sample is determined.

Reaction:

$$2Na_2S_2O_3 + O_3 + H_2O \rightarrow S_4O_6 + O_2 + 2OH^-$$

0.01 M of thiosulfate is used in the experiments and 10 mL of this solution is taken into the sample bottle.

n_i = 0.1 mmol

n = excess thiosulfate remaining = $n_i - n_s$

n_s = spent thiosulfate by ozone = $2 \text{ x } C_{O3} \times V_t$ (s) (mL) × (1 L / 1000 mL)

$$= 2.00 \times 10^{-3} \times C_{O3} \times V_t \text{ (s)}$$

n (mmol) = $0.1 - 2.00 \times 10^{-3} \times C_{O3} \times V_t$ (s)

$C_{thio\text{-}(excess)}$ (mM) = [n_t / V_t (T) (mL)] × (1000 mL / 1 L)

V_t (T) = V_t (s) + 10

COD corresponding to excess thiosulphate in the bottle is determined from COD (mg/L) vs. C_{thio} (mM) calibration graph in Figure B.3.

COD_{thio} (mg/L) = $11.695 \times C_{thio}$ (mM)

So, the corrected COD value is:

$$COD_{corr} = COD - C_{thio-(excess)}$$

$$COD_{corr} = COD - 11695 \times \frac{[0.1 - 2.00 \times 10^{-3} \times C_{O3} \times V_t\,(s)]}{V_t\,(T)}$$

A.4 Color Analysis

The samples withdrawn from the reactor at the beginning and at the end of the reaction are used in the color measurements.The platinum-cobalt method for measuring color is the standard method, the unit of color being that produced by 1 mg platinum/L in the form of the chloroplatinate ion.

Apparatus

A Hach DR-2010 Spectrophotometer and a sample cell are used.

Procedure

The samples to be measured are filled into the 25 mL glass vials. Then, their color values in the units of Pt-Co are measured using a spectrophotometer at 455 nm by dialing the program number to 120 [71], with respect to blank solution, which is pure distilled-deionized water, set as zero Pt-Co color unit.

APPENDIX B

CALIBRATION CURVES

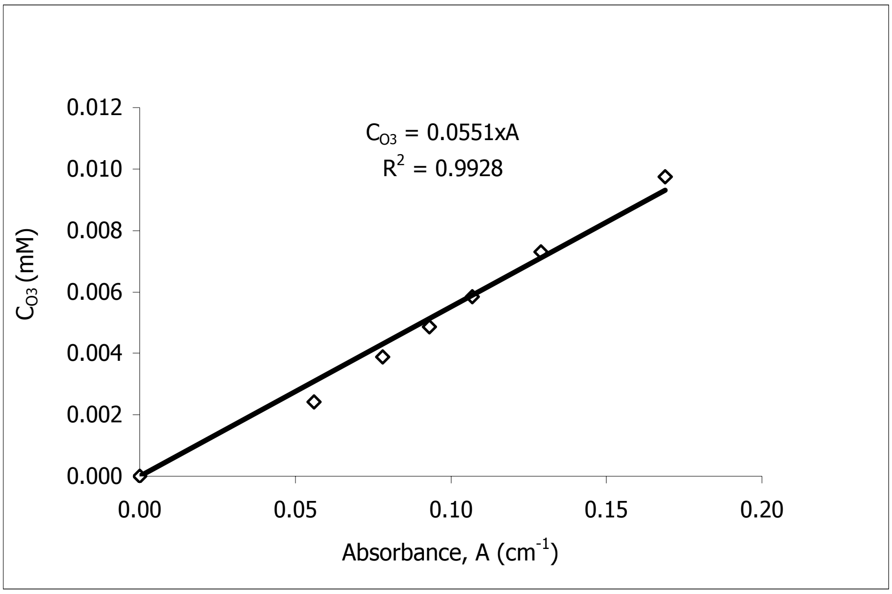


Figure B.1 Concentration vs. absorbance data at 600 nm, for Indigo calibration

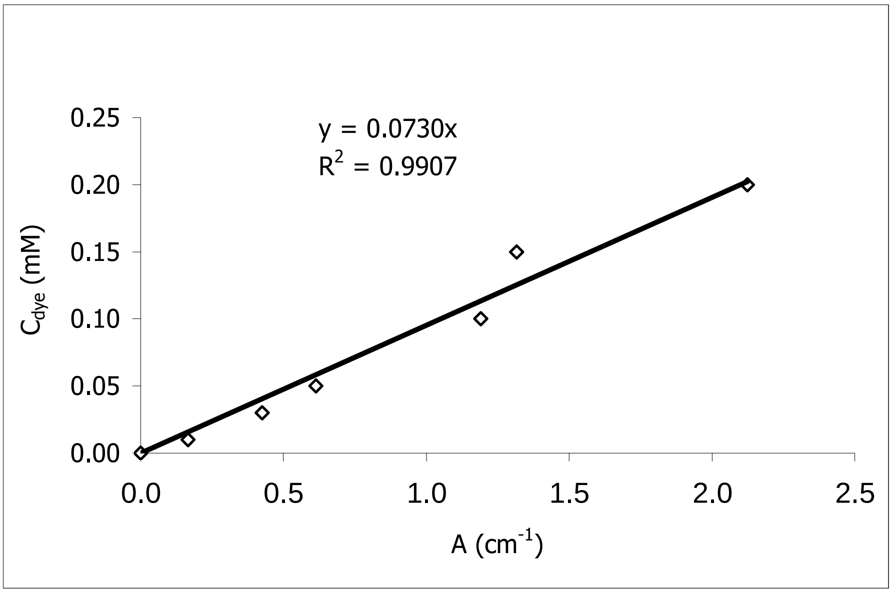


Figure B.2 Concentration vs. absorbance data at 512 nm, for Acid Red 151 calibration

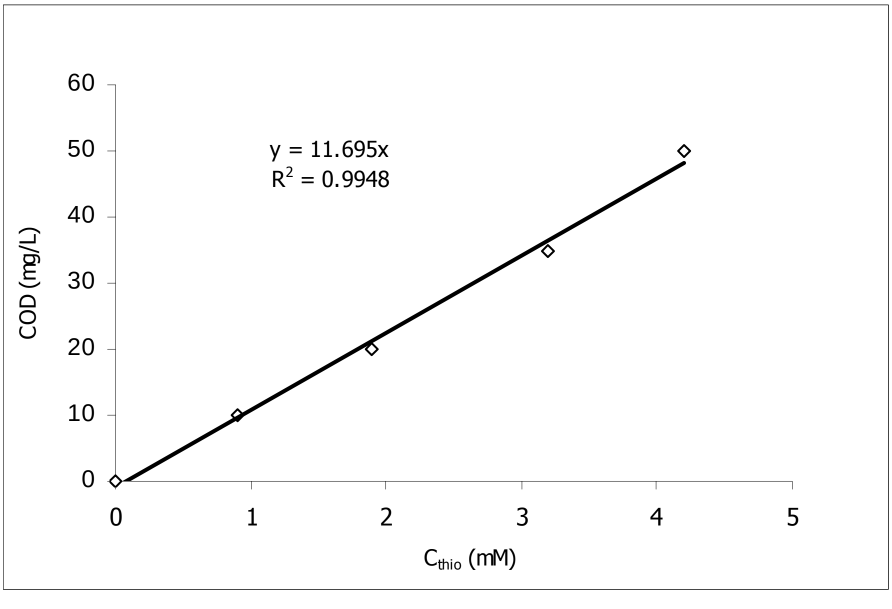


Figure B.3 Calibration curve for the correction of COD due to $Na_2S_2O_3$ in the sample.

APPENDIX C

EXPERIMENTAL DATA

Table C.1 Ozone absorption data at different pH values at T=25°C

pH	t (min)	V_{ind} (s) (ml)	A_{ind}	$C_{O3} * 10^3$ (mM)
2.5	0.0	-	-	0.0
	0.5	19.6	0.096	16.3
	1.0	21.5	0.058	24.6
	2.0	21.8	0.025	32.6
	2.5	20.0	0.029	34.4
	3.0	22.0	0.014	35.8
	5.0	19.8	0.024	35.9
	8.0	22.6	0.0065	36.0
	10.0	20.2	0.022	36.0
7	0.0	-	-	0.0
	0.5	22.5	0.110	10.8
	1.0	21.5	0.079	19.2
	2.0	22.6	0.034	29.3
	3.0	21.0	0.039	30.0
	5.0	21.5	0.037	30.0
	8.0	21.6	0.036	30.1
	10.0	21.5	0.037	30.1
10	0.0	-	-	0.0
	0.5	21.0	0.119	8.1
	1.0	19.8	0.116	9.5
	2.0	20.5	0.109	11.0
	3.0	20.8	0.102	12.7
	5.0	26.0	0.084	14.0
	8.0	26.0	0.083	14.1
	10.0	24.0	0.094	14.1

Table C.2 Ozone decomposition data at different pH values, T=25°C and in the absence of H_2O_2 (r=0)

pH	t (min)	V_{ind} (s) (ml)	A_{ind}	$C_{O3} * 10^3$ (mM)
2.5	0.4	22.0	0.015	35.0
	3.0	21.2	0.039	30.0
	5.0	20.0	0.050	29.0
	10.0	22.0	0.055	25.0
	15.0	20.0	0.067	24.0
	20.0	22.5	0.064	22.0
	25.0	21.8	0.075	21.0
	30.0	21.8	0.076	20.0
	40.0	21.8	0.076	20.0
7	0.1	21.2	0.040	29.0
	3.0	22.0	0.044	26.0
	5.0	20.8	0.056	24.0
	10.0	20.0	0.072	21.0
	15.0	22.8	0.072	18.0
	20.0	22.0	0.082	17.0
	25.0	23.5	0.083	15.0
	30.0	23.0	0.093	13.0
	40.0	24.6	0.094	12.0
10	0.2	22.8	0.111	13.0
	3.0	21.9	0.139	4.8
	5.0	21.5	0.140	4.6
	10.0	22.0	0.141	4.4
	15.0	22.5	0.141	4.3
	20.0	23.5	0.141	4.1
	25.0	22.0	0.142	4.0
	30.0	23.5	0.142	3.8
	40.0	20.8	0.144	3.7

Table C.3 Ozone decomposition data at different pH values, T=25°C at r=0.5

pH	t (min)	V_{ind} (s) (ml)	A_{ind}	$C_{O3} * 10^3$ (mM)
2.5	0	26.2	0.001	36.0
	3	20.5	0.034	32.0
	5	22.0	0.032	31.0
	10	18.6	0.057	29.0
	15	22.0	0.049	26.0
	20	20.5	0.056	23.0
	25	21.8	0.073	20.0
	30	23.0	0.074	17.0
	40	22.0	0.082	16.0
7	0	21.5	0.031	30.0
	3	22.0	0.076	20.0
	5	22.0	0.090	17.0
	10	23.0	0.100	14.0
	15	23.0	0.105	12.0
	20	24.0	0.110	11.0
	25	24.0	0.120	8.0
	30	22.6	0.125	7.1
	40	23.9	0.125	7.0
10	0	23.0	0.100	14.0
	3	22.9	0.140	4.5
	5	23.0	0.140	4.3
	10	20.2	0.144	3.8
	15	22.6	0.143	3.6
	20	20.5	0.146	3.3
	25	21.9	0.146	3.1
	30	22.8	0.146	2.9
	40	22.5	0.146	2.8

Table C.4 C_{O3} data: Experimental conditions: pH=2.5, $C_{dye,i}$=0.0220 mM, $C_{O3,i}$=0.035 mM, A_b =0.166, r=0.5, T=25°C

t (min)	V_{ind} (s) (ml)	A_{ind}	C_{O3} $*10^3$ (mM)
0.90	26.2	0.001	35.0
1.58	27.0	0.144	4.49
2.50	20.0	0.154	3.31
5.00	17.5	0.156	3.15
10.00	21.0	0.154	3.10
15.00	21.0	0.154	3.07
20.00	21.8	0.154	3.03
30.00	22.5	0.157	2.94
40.00	18.0	0.157	2.69
50.00	19.5	0.156	2.55

Table C.5 C_{dye} data: Experimental conditions: pH=2.5, $C_{dye,i}$=0.0220 mM, $C_{O3,i}$=0.035 mM, r=0.5, T=25°C

t (min)	V_t (T) (ml)	A_{dye}	$C_{dye}$$*10^3$ (mM)
0.00	-	-	22.0
1.32	33.2	0.052	5.4
2.00	31.5	0.049	5.2
2.92	33.0	0.047	4.9
5.42	34.0	0.045	4.7
10.42	30.5	0.04	4.3
15.42	32.5	0.027	2.8
20.42	32.0	0.021	2.2
30.42	30.5	0.014	1.5
40.42	32.2	0.012	1.3
50.42	30.5	0.008	0.9

Table C.6 C_{O3} data: Experimental conditions: pH=2.5, $C_{dye,i}$=0.0275 mM, $C_{O3,i}$=0.036 mM, A_b=0.167, r=0.5, T=25°C

t (min)	V_{ind} (s) (ml)	A_{ind}	C_{O3} $*10^3$ (mM)
0.00	26.2	0.001	36.0
0.90	19.8	0.149	4.90
1.58	19.8	0.155	3.23
2.50	20.0	0.156	3.09
5.00	21.8	0.155	3.02
10.00	19.2	0.157	3.00
15.00	21.5	0.156	2.90
20.00	19.8	0.157	2.82
30.00	17.2	0.159	2.65
40.00	19.8	0.158	2.55
50.00	20.8	0.158	2.50

Table C.7 C_{dye} data: Experimental conditions: pH=2.5, $C_{dye,i}$=0.0275mM, $C_{O3,i}$=0.036 mM, r=0.5, T=25°C

t (min)	V_t (s) (ml)	A_{dye}	$C_{dye}$$*10^3$ (mM)
0.00	-	-	27.5
1.32	32.5	0.070	7.4
2.00	33.9	0.068	7.0
2.92	32.5	0.052	5.5
5.42	31.8	0.049	5.2
10.42	33.5	0.043	4.5
15.42	33.8	0.033	3.4
20.42	31.2	0.023	2.5
30.42	32.5	0.014	1.5
40.42	34.2	0.012	1.2
50.42	34.5	0.011	1.1

Table C.8 C_{O3} data: Experimental conditions: pH=2.5, $C_{dye,i}$=0.033 mM, $C_{O3,i}$=0.036 mM, A_b=0.161, r=0.5, T=25°C

t (min)	V_{ind} (s) (ml)	A_{ind}	C_{O3} *10^3 (mM)
0.00	26.2	0.001	36.0
0.90	22.0	0.149	3.0
1.58	21.0	0.150	2.9
2.50	19.8	0.151	2.8
5.00	19.2	0.152	2.7
10.00	20.8	0.152	2.4
15.00	18.8	0.153	2.3
20.00	22.2	0.153	2.0
30.00	20.5	0.154	1.9
40.00	20.5	0.154	1.8
50.00	20.2	0.155	1.7

Table C.9 C_{dye} data: Experimental conditions: pH=2.5, $C_{dye,i}$ = 0.033 mM, $C_{O3,i}$=0.036 mM, r=0.5, T=25°C

t (min)	V_t (s) (ml)	A_{dye}	C_{dye}*10^3 (mM)
0.00	-	-	33.0
1.32	33	0.196	20.5
2.00	31.5	0.178	19.0
2.92	33.5	0.17	17.7
5.42	33.2	0.132	13.8
10.42	34.5	0.081	8.3
15.42	33.8	0.039	4.0
20.42	29.5	0.035	3.9
30.42	32.5	0.020	2.1
40.42	29	0.015	1.7
50.42	31.8	0.013	1.4

Table C.10 C_{O3} data: Experimental conditions: pH=2.5, $C_{dye,i}$=0.044 mM, $C_{O3,i}$=0.035 mM, A_b =0.161, r=0.5, T=25°C

t (min)	V_{ind} (s) (ml)	A_{ind}	C_{O3} *10^3 (mM)
0.1 0	26.2	0.001	36.00
0.90	22.2	0.151	3.20
1.58	19.5	0.154	2.70
2.50	21.5	0.154	2.61
5.00	22.0	0.155	2.21
10.00	22.0	0.156	2.10
15.00	21.5	0.156	2.00
20.00	22.2	0.157	1.80
30.00	20.5	0.158	1.70
40.00	20.2	0.158	1.51
50.00	19.2	0.159	1.50

Table C.11 C_{dye} data: Experimental conditions: pH=2.5, $C_{dye,i}$=0.044 mM, $C_{O3,i}$=0.035 mM, r=0.5, T=25°C

t (min)	V_t (s) (ml)	A_{dye}	C_{dye}*10^3 (mM)
0.00	-	-	44.0
1.32	32.5	0.171	18.0
2.00	31.9	0.16	17.0
2.92	32.8	0.152	16.0
5.42	32.2	0.142	15.0
10.42	32.9	0.092	9.6
15.42	32.5	0.061	6.4
20.42	34.2	0.048	5.0
30.42	33.8	0.029	3.0
40.42	32	0.024	2.5
50.42	31	0.020	2.2

Table C.12 C_{O3} data: Experimental conditions: pH=7.0, $C_{dye,i}$=0.0220 mM, $C_{O3,i}$=0.030 mM, A_b=0.166, r=0.5, T=25°C

t (min)	V_{ind} (s) (ml)	A_{ind}	C_{O3} *10^3 (mM)
0.00	21.5	0.031	30.0
0.33	18.5	0.155	2.7
1.45	21.8	0.154	2.5
2.50	21	0.155	2.4
5.00	21.2	0.155	2.3
10.00	19.0	0.157	2.1
15.00	21.8	0.156	2.0
20.00	20.8	0.157	1.8
30.00	20.5	0.158	1.6
40.00	20.8	0.158	1.5
50.00	22.9	0.158	1.4

Table C.13 C_{dye} data: Experimental conditions: pH=7.0, $C_{dye,i}$=0.0220 mM, $C_{O3,i}$=0.030 mM, r=0.5, T=25°C

t (min)	V_t (T) (ml)	A_{dye}	C_{dye}*10^3 (mM)
0.00	-	-	22.0
0.75	31.5	0.122	13.0
1.87	32	0.104	11.0
2.92	29.2	0.080	8.9
5.42	33.5	0.069	7.2
10.42	32.2	0.043	4.5
15.42	33.5	0.025	2.6
20.41	32.5	0.018	1.9
30.42	33.2	0.013	1.4
40.42	30.5	0.012	1.3
50.42	35.5	0.009	0.9

Table C.14 C_{O3} data: Experimental conditions: pH=7.0, $C_{dye,i}$=0.0275 mM, $C_{O3,i}$=0.030 mM, A_b=0.166, r=0.5, T=25°C

t (min)	V_t (T) (ml)	A_{dye}	C_{dye}*10^3 (mM)
0.00	-	-	22.0
0.75	31.5	0.122	13.0
1.87	32	0.104	11.0
2.92	29.2	0.080	8.9
5.42	33.5	0.069	7.2
10.42	32.2	0.043	4.5
15.42	33.5	0.025	2.6
20.41	32.5	0.018	1.9
30.42	33.2	0.013	1.4
40.42	30.5	0.012	1.3
50.42	35.5	0.009	0.9

Table C.15 C_{dye} data: Experimental conditions: pH=7.0, $C_{dye,i}$=0.0275 mM, $C_{O3,i}$=0.030 mM, r=0.5, T=25°C

t (min)	V_t (T) (ml)	A_{dye}	C_{dye}*10^3 (mM)
0.00	-	-	27.5
0.75	32.5	0.165	18.0
1.87	33.9	0.147	16.0
2.92	32.5	0.139	14.7
5.42	31.8	0.115	12.2
10.42	33.5	0.087	9.0
15.42	33.8	0.065	5.6
20.41	31.2	0.047	5.0
30.42	32.5	0.043	4.6
40.42	34.2	0.034	4.2
50.42	34.5	0.029	4.0

Table C.16 C_{O3} data: Experimental conditions: pH=7.0, $C_{dye,i}$=0.033 mM, $C_{O3,i}$=0.0295 mM, A_b=0.161, r=0.5, T=25°C

t (min)	V_{ind} (s) (ml)	A_{ind}	C_{O3} $*10^3$ (mM)
0.00	21.5	0.031	29.5
0.33	18.5	0.154	2.1
1.45	20.8	0.154	1.8
2.50	21.0	0.155	1.5
5.00	20.5	0.156	1.3
10.00	21.0	0.157	1.1
15.00	21.2	0.157	1.0
20.00	21.2	0.157	1.0
30.00	19.2	0.158	0.8
40.00	20.0	0.158	0.7
50.00	21.5	0.159	0.6

Table C.17 C_{dye} data: Experimental conditions: pH=7.0, $C_{dye,i}$=0.033 mM, $C_{O3,i}$=0.0295 mM, r=0.5, T=25°C

t (min)	V_t (T) (ml)	A_{dye}	$C_{dye}$$*10^3$ (mM)
0.00	-	-	33.0
0.75	32.0	0.168	17.8
1.87	34.0	0.155	16.0
2.92	33.0	0.150	15.7
5.42	31.8	0.113	12.0
10.42	31.8	0.072	7.7
15.42	33.9	0.054	6.5
20.41	31.6	0.041	6.3
30.42	31.5	0.032	6.2
40.42	32.8	0.031	6.2
50.42	33.0	0.032	6.1

Table C.18 C_{O3} data: Experimental conditions: pH=7.0, $C_{dye,i}$=0.044 mM, $C_{O3,i}$=0.030 mM, A_b=0.163, r=0.5, T=25°C

t (min)	V_{ind} (s) (ml)	A_{ind}	C_{O3} *10^3 (mM)
0.00	21.5	0.031	30.0
0.33	21.9	0.155	1.9
1.45	21.8	0.156	1.7
2.50	21.5	0.157	1.6
5.00	21.0	0.157	1.5
10.00	24.0	0.157	1.4
15.00	22.5	0.157	1.4
20.00	19.0	0.158	1.3
30.00	22.5	0.159	0.9
40.00	22.0	0.160	0.7
50.00	22.0	0.161	0.6

Table C.19 C_{dye} data: Experimental conditions: pH=7.0, $C_{dye,i}$=0.044 mM, $C_{O3,i}$ = 0.030 mM, r=0.5, T=25°C

t (min)	V_t (T) (ml)	A_{dye}	C_{dye}*10^3 (mM)
0.00	-	-	44.0
0.75	33	0.293	30.7
1.87	33	0.277	29.0
2.92	32	0.248	26.5
5.42	33	0.234	24.5
10.42	34	0.17	17.6
15.42	32	0.138	14.7
20.41	32	0.126	13.4
30.42	33	0.116	12.1
40.42	32	0.113	12.0
50.42	32	0.112	12.0

Table C.20 C_{O3} data: Experimental conditions: pH=10.0, $C_{dye,i}$=0.022 mM $C_{O3,i}$=0.0135 mM, pH=10.0, A_b=0.162, r=0.5, T=25°C

t (min)	V_{ind} (s) (ml)	A_{ind}	C_{O3} $*10^3$ (mmol/l)
0.00	23.0	0.100	14.00
0.83	22.5	0.149	3.31
2.50	21.0	0.150	3.25
3.00	21.0	0.151	2.89
5.00	21.5	0.151	2.82
10.00	21.2	0.152	2.60
15.00	21.0	0.152	2.57
20.00	21.0	0.152	2.55
25.00	22.0	0.152	2.53
30.00	22.0	0.152	2.51
40.00	22.0	0.152	2.50
50.00	22.5	0.149	2.45

Table C.21 C_{dye} data: Experimental conditions: pH=10.0, $C_{dye,i}$=0.022 mM, $C_{O3,i}$=0.0135 mM, r=0.5, T=25°C

t (min)	V_t (T) (ml)	A_{dye}	$C_{dye}$$*10^3$ (mM)
0.00	-	-	22.0
1.25	35.2	0.147	15.0
2.42	35.2	0.138	14.1
3.42	33	0.127	13.3
5.42	32	0.120	12.7
10.42	33.5	0.111	11.5
15.42	33.5	0.104	10.8
20.42	34	0.094	9.7
25.42	33.4	0.092	9.6
30.42	33.5	0.090	9.4
40.42	33.2	0.089	9.3
50.42	33	0.088	9.2

Table C.22 C_{O3} data: Experimental conditions: pH=10.0, $C_{dye,i}$=0.0275 mM, $C_{O3,i}$=0.014 mM, A_b=0.162, r=0.5, T=25°C

t (min)	V_{ind} (s) (ml)	A_{ind}	C_{O3} $*10^3$ (mM)
0.00	23.0	0.100	14
0.83	19.0	0.150	3.19
2.50	19.5	0.150	3.11
3.00	19.5	0.151	2.83
5.00	22.2	0.151	2.48
10.00	23.0	0.152	2.28
15.00	22.0	0.152	2.15
20.00	21.0	0.153	2.07
25.00	21.8	0.153	2.02
30.00	21.5	0.153	1.95
40.00	22.8	0.153	1.84
50.00	21.0	0.154	1.73

Table C.23 C_{dye} data: Experimental conditions: pH=10.0, $C_{dye,i}$=0.0275 mM, $C_{O3,i}$=0.014 mM, r=0.5, T=25°C

t (min)	V_t (T) (ml)	A_{dye}	$C_{dye}*10^3$ (mM)
0.00	-	-	27.5
1.25	33.00	0.189	19.8
2.42	34.50	0.180	18.5
3.42	32.80	0.168	17.6
5.42	33.00	0.157	16.4
10.42	34.00	0.150	15.5
16.42	32.00	0.139	14.8
20.42	36.00	0.140	14.1
25.42	34.90	0.132	13.5
30.42	35.00	0.125	12.8
40.42	32.00	0.114	12.1
50.42	33.80	0.115	11.9

Table C.24 C_{O3} data: Experimental conditions: pH=10.0, $C_{dye,i}$=0.0330 mM, $C_{O3,i}$=0.014 mM, A_b=0.161, r=0.5, T=25°C

t (min)	V_{ind} (s) (ml)	A_{ind}	C_{O3} *10^3 (mM)
0.00	23.0	0.100	14.00
0.83	22.5	0.151	2.42
2.50	21.0	0.153	2.16
3.00	21.0	0.153	2.01
5.00	21.5	0.154	1.92
10.00	21.2	0.154	1.85
15.00	21.8	0.154	1.72
20.00	20.2	0.155	1.63
25.00	22.8	0.155	1.56
30.00	20.5	0.155	1.48
40.00	21.8	0.156	1.37
50.00	22.0	0.156	1.25

Table C.25 C_{dye} data: Experimental conditions: pH=10.0, $C_{dye,i}$=0.033 mM, $C_{O3,i}$ = 0.014 mM, r=0.5, T=25°C

t (min)	V_t (T) (ml)	A_{dye}	C_{dye}*10^3 (mM)
0.00	-	-	33.00
1.25	32.60	0.258	27.30
2.42	32.50	0.243	25.60
3.42	33.00	0.231	24.20
5.42	33.00	0.220	23.10
10.42	33.00	0.212	22.20
16.42	32.00	0.202	21.40
20.42	32.00	0.192	20.40
25.42	33.00	0.189	19.70
30.42	31.40	0.179	19.20
40.42	33.00	0.176	18.40
50.42	33.00	0.172	18.00

Table C.26 C_{O3} data: Experimental conditions: pH=10.0, $C_{dye,i}$=0.0440 mM, $C_{O3,i}$ = 0.014 mM, pH = 10.0, A_b=0.161, r=0.5, T=25°C

t (min)	V_{ind} (s) (ml)	A_{ind}	C_{O3} *10^3 (mM)
0.00	23.0	0.100	14.00
0.83	22.5	0.153	1.96
2.50	21.2	0.154	1.82
3.00	24.0	0.153	1.74
5.00	21.9	0.155	1.51
10.00	22.0	0.156	1.35
15.00	19.5	0.156	1.30
20.00	25.5	0.156	1.12
25.00	22.5	0.157	1.05
30.00	21.0	0.157	1.00
40.00	21.9	0.157	0.96
50.00	21.0	0.157	0.94

Table C.27 C_{dye} data: Experimental conditions: pH=10.0, $C_{dye,i}$=0.0440 mM, $C_{O3,i}$=0.014 mM, r=0.5, T=25°C

t (min)	V_t (T) (ml)	A_{dye}	C_{dye}*10^3 (mM)
0.00	-	-	44.0
1.25	31.6	0.033	34.8
2.82	32.0	0.030	32.1
3.42	34.5	0.030	31.2
5.42	32.8	0.029	30.1
10.42	33.0	0.028	29.0
15.42	34.0	0.028	28.4
20.42	33.5	0.026	27.5
25.42	34.5	0.026	26.9
30.42	34.5	0.025	26.0
40.42	33.5	0.024	25.3
50.42	33.0	0.024	24.7

Table C.28 Percent differences in C_{O3} (mM) at each specific time at pH=7.0, T=25°C, $C_{O3,i}$=0.030±0.0005 mM, r=0.5

t (min)	$C_{dye,i}$=0.022 mM	$C_{dye,i}$=0.0275 mM	$C_{dye,i}$=0.033 mM	$C_{dye,i}$=0.044 mM
	% difference	% difference	% difference	% difference
0.00	-	-	-	-
0.33	4.25	4.35	5.00	4.40
1.45	3.31	-4.76	4.65	1.80
2.50	0.84	1.19	0.67	1.91
5.00	4.55	3.23	1.56	1.35
10.00	2.44	1.45	-1.79	2.90
15.00	2.56	2.36	5.00	3.68
20.00	2.86	2.56	2.04	3.17
30.00	3.90	4.76	2.56	2.27
40.00	1.35	2.04	1.45	-2.78
50.00	3.70	2.27	3.45	2.04

Table C.29 Percent differences in C_{dye} (mM) at each specific time at pH=7.0, T=25°C, $C_{O3,i}$=0.030±0.0005 mM, r=0.5

t (min)	$C_{dye,i}$=0.022 mM	$C_{dye,i}$=0.0275 mM	$C_{dye,i}$=0.033 mM	$C_{dye,i}$=0.044 mM
	% difference	% difference	% difference	% difference
0.00	-	-	-	-
0.75	4.00	3.45	2.89	2.33
1.87	-1.79	3.23	0.63	2.74
2.92	1.14	1.38	0.64	1.92
5.42	1.41	1.67	-0.83	1.66
10.42	1.12	2.97	-2.53	2.33
15.42	4.00	1.82	1.52	1.38
20.42	2.70	2.04	0.78	3.08
30.42	1.45	1.10	1.61	0.83
40.42	4.00	1.20	0.81	4.35
50.42	2.27	2.56	0.83	2.56

Table C.30 C_{dye} data: Experimental conditions: pH=2.5, $C_{dye,i}$=0.0330 mM, $C_{O3,i}$=0.0360 mM, T=25°C

t (min)	$C_{dye,i}$ (mM)			
	r=0.30	r=0.50	r=0.75	r=1.00
0.00	0.033	0.033	0.033	0.033
1.32	0.022	0.0205	0.0145	0.0144
2.00	0.0216	0.019	0.0138	0.0137
2.92	0.0196	0.0177	0.0131	0.0135
5.42	0.0133	0.0138	0.0107	0.0117
10.42	0.0110	0.0083	0.0102	0.0107
15.42	0.0097	0.004	0.0098	0.0104
20.41	0.0077	0.0039	0.0086	0.0075
30.42	0.0076	0.0021	0.0078	0.0068
40.42	0.0049	0.0017	0.0058	0.0063
50.42	0.0040	0.0014	0.0052	0.0042

Table C.31 C_{dye} data: Experimental conditions: pH=7.0, $C_{dye,i}$=0.0330 mM, $C_{O3,i}$ = 0.0300 mM, T=25°C

t (min)	$C_{dye,i}$ (mM)			
	r=0.30	r=0.50	r=0.75	r=1.00
0.00	0.0330	0.0330	0.0330	0.0330
1.00	0.0285	0.0178	0.0209	0.0241
1.92	0.0270	0.0160	0.0192	0.0230
2.92	0.0257	0.0157	0.0161	0.0203
5.42	0.0255	0.0120	0.0132	0.0162
10.42	0.0237	0.0077	0.0106	0.0114
15.42	0.0235	0.0056	0.0088	0.0097
20.41	0.0225	0.0044	0.0079	0.0085
30.42	0.0215	0.0034	0.0078	0.0079
40.42	0.0214	0.0033	0.0073	0.0078
50.42	0.0210	0.0032	0.0072	0.0077

Table C.32 C_{dye} data: Experimental conditions: pH=10.0, $C_{dye,i}$=0.0330 mM, $C_{O3,i}$ = 0.0140 mM, T=25°C

t (min)	$C_{dye,i}$ (mM)			
	r=0.30	r=0.50	r=0.75	r=1.00
0.00	0.0330	0.0330	0.0330	0.0330
1.25	0.0295	0.0272	0.0285	0.0290
2.42	0.0280	0.0240	0.0273	0.0280
3.42	0.0275	0.0236	0.0261	0.0268
5.42	0.0263	0.0230	0.0250	0.0255
10.42	0.0255	0.0222	0.0238	0.0242
15.42	0.0247	0.0220	0.0230	0.0232
20.42	0.0241	0.0212	0.0224	0.0223
25.42	0.0235	0.0203	0.0215	0.0218
30.42	0.0228	0.0193	0.0206	0.0211
40.42	0.0224	0.0191	0.0195	0.0205

Table C.33 C_{O3} data: Experimental conditions: pH=2.5, $C_{dye,i}$=0.0330 mM, $C_{O3,i}$=0.0360 mM, T=25°C

t (min)	$C_{O3}*10^3$ (mM)			
	r=0.30	r=0.50	r=0.75	r=1.00
0.00	36.0	36.00	36.00	36.00
0.90	3.90	3.20	4.80	6.80
1.58	3.60	2.90	4.30	6.50
2.50	3.10	2.80	4.20	6.10
5.00	2.70	2.70	3.60	6.00
10.00	2.40	2.40	3.30	5.50
15.00	2.30	2.30	2.80	5.40
20.00	2.20	2.00	2.70	5.30
30.00	2.10	1.95	2.30	5.30
40.00	1.80	1.82	2.20	5.10
50.00	1.80	1.71	1.90	4.90

Table C.34 C_{O3} data: Experimental conditions: pH =7.0, $C_{dye,i}$=0.0330 mM, $C_{O3,i}$=0.0300 mM, T=25°C

t (min)	$C_{O3}*10^3$ (mM)			
	r=0.30	r=0.50	r=0.75	r=1.00
0.00	30.00	30.00	30.00	30.00
1.00	2.69	2.10	2.50	2.55
1.67	2.56	1.80	2.35	2.43
2.50	2.20	1.50	2.26	2.30
5.00	2.15	1.30	2.10	2.21
10.00	2.11	1.10	1.85	1.94
15.00	2.05	1.05	1.74	1.83
20.00	1.95	1.00	1.62	1.66
30.00	1.92	0.80	1.50	1.60
40.00	1.87	0.70	1.45	1.57
50.00	1.85	0.60	1.43	1.50

Table C.35 C_{O3} data: Experimental conditions: pH=10.0, $C_{dye,i}$=0.0330 mM, $C_{O3,i}$=0.0140 mM, T=25°C

t (min)	$C_{O3}*10^3$ (mM)			
	r=0.30	r=0.50	r=0.75	r=1.00
0.00	14.00	14.00	14.00	14.00
2.50	2.81	2.16	2.54	2.61
3.00	2.61	2.01	2.41	2.51
5.00	2.52	1.92	2.34	2.47
10.00	2.41	1.85	2.22	2.36
15.00	2.38	1.72	2.03	2.18
20.00	2.21	1.63	1.92	2.03
25.00	2.12	1.56	1.82	1.92
30.00	2.07	1.48	1.75	1.84
40.00	2.01	1.37	1.67	1.74
50.00	1.98	1.25	1.60	1.72

Table C.36 Percent differences in C_{dye} with "r" ratio at each specific time at pH=7.0, T=25°C, $C_{O3,i}$=0.030±0.0005 mM, $C_{dye,i}$=0.033 mM

t (min)	r=0.30	r=0.50	r=0.75	r=1.00
	% difference	% difference	% difference	% difference
0.00	-	-	-	-
1.00	2.52	3.49	2.96	1.69
1.92	1.89	1.91	-3.03	2.22
2.92	0.78	1.95	-4.17	2.53
5.42	2.00	1.69	-4.35	3.85
10.42	-2.07	2.67	-3.64	0.71
15.42	1.29	1.21	2.33	0.52
20.41	2.74	0.78	1.28	-0.58
30.42	1.42	0.48	0.65	0.89
40.42	2.88	1.31	0.97	0.78
50.42	2.44	0.83	0.56	0.65

Table C.37 C_{dye} data at different initial O_3 concentrations: Experimental conditions: pH=2.5, $C_{dye,i}$=0.0330 mM, T=25°C, r=0.5

t (min)	C_{dye} (mM)		
	$C_{O3,i}$=0.017 (mM)	$C_{O3,i}$=0.026 (mM)	$C_{O3,i}$=0.036 (mM)
0.00	0.0330	0.0330	0.0330
0.59	0.0293	0.0270	0.0241
1.92	0.0266	0.0245	0.0205
2.00	0.0260	0.0234	0.0190
2.92	0.0243	0.0224	0.0177
5.42	0.0222	0.0189	0.0138
10.42	0.0214	0.0149	0.0083
20.42	0.0206	0.0128	0.0039
30.42	0.0202	0.0110	0.0021
40.42	0.0194	0.0106	0.0017

Table C.38 C_{dye} data at different initial O_3 concentrations: Experimental conditions: pH=7, $C_{dye,i}$=0.0330 mM, T=25°C, r=0.5

t (min)	C_{dye} (mM)		
	$C_{O3,i}$=0.007 (mM)	$C_{O3,i}$=0.012 (mM)	$C_{O3,i}$=0.030 (mM)
0.00	0.0330	0.0330	0.0330
0.59	0.0319	0.0289	0.0178
1.92	0.0296	0.0275	0.0160
2.92	0.0285	0.0266	0.0157
5.42	0.0269	0.0249	0.0120
10.42	0.0260	0.0230	0.0077
20.41	0.0257	0.0220	0.0065
30.42	0.0250	0.0218	0.0063
40.42	0.0248	0.0216	0.0062

Table C.39 C_{dye} data at different initial O_3 concentrations: Experimental conditions: pH=10, $C_{dye,i}$=0.0330 mM, T=25°C, r=0.5

t (min)	C_{dye} (mM)		
	$C_{O3,i}$=0.0036 (mM)	$C_{O3,i}$=0.0042 (mM)	$C_{O3,i}$=0.0140 (mM)
0.00	0.0330	0.0330	0.0330
0.59	0.0272	0.0314	0.0306
1.92	0.0240	0.0288	0.0273
3.42	0.0236	0.0272	0.0271
5.42	0.0230	0.0269	0.0270
10.42	0.0222	0.0262	0.0269
20.42	0.0212	0.0260	0.0260
30.42	0.0180	0.0255	0.0258
40.42	0.0175	0.0250	0.0255

Table C.40 Decolorization data at different pH values and initial dye concentrations: Experimental conditions: r=0.5, T=25°C

$C_{dye,i}$ (mmol/l)	Decolorization, %		
	pH=2.5 ($C_{O3,i}$=0.036 mM)	pH=7.0 ($C_{O3,i}$=0.030 mM)	pH=10.0 ($C_{O3,i}$=0.014 mM)
0.0220	95.9	95.9	58.2
0.0275	95.8	85.5	56.7
0.0330	95.8	81.5	45.5
0.0440	95.0	72.7	43.9

Table C.41 Decolorization data at different pH and "r" values: Experimental conditions: $C_{dye,i}$=0.0330 mM, T=25°C

r	Decolorization, %		
	pH=2.5 ($C_{O3,i}$=0.036 mM)	pH=7.0 ($C_{O3,i}$=0.030 mM)	pH=10.0 ($C_{O3,i}$=0.014 mM)
0.30	87.9	36.4	33.3
0.50	95.8	81.5	45.5
0.75	84.2	78.2	41.2
1.00	87.3	76.7	39.4

Table C.42 COD Removal data at different pH and “r” values: Experimental conditions: $C_{dye,i}$=0.0330 mM, T=25°C

r	COD Reduction, %		
	pH=2.5 ($C_{O3,i}$=0.036 mM)	pH=7.0 ($C_{O3,i}$=0.030 mM)	pH=10.0 ($C_{O3,i}$=0.014 mM)
0.30	28.3	14.0	10.0
0.50	36.8	36.4	24.6
0.75	23.9	29.7	23.0
1.00	23.9	17.9	16.0

APPENDIX D

KINETIC DATA

Table D.1 Representative data of the corresponding rates for excess initial dye experiments calculated by differential method at pH=2.5, r=0.5

pH = 2.5						
$C_{dye,i}$ (mM)						
	0.551		0.881		1.321	
t (min)	C_{O3}*10^3 (mM)	-dC_{O3}/dt (mM/min)	C_{O3}*10^3 (mM)	-dC_{O3}/dt (mM/min)	C_{O3}*10^3 (mM)	-dC_{O3}/dt (mM/min)
0.00	36.0	-	36.00	-	36.00	-
0.70	1.5200	0.1650	1.2500	0.1470	1.1100	0.1241
1.17	1.3200	0.1560	1.1000	0.1390	0.7080	0.1086
2.50	0.8200	0.1320	0.8900	0.1270	0.1290	0.0860
5.00	0.5100	0.1130	0.2900	0.1020	0.1100	0.0656
7.50	0.3100	0.0890	0.2200	0.0790	0.0680	0.0475
10.00	0.2200	0.0690	0.1400	0.0590	0.0520	-
15.00	0.1200	-	0.0800	0.0240	0.0020	-
22.00	0.0600	-	0.0300	-	0.0018	-
25.00	0.0250	-	0.0200	-	0.0016	-
30.00	0.0070	-	0.0195		0.0013	
40.00	0.0050	-	0.0194		0.0010	

Table D.2 Representative data of the corresponding rates for excess initial dye experiments calculated by differential method at pH=7.0, r=0.5

pH = 7.0						
$C_{dye,i}$ (mM)						
	0.551		0.881		1.321	
t (min)	$C_{O3}*10^3$ (mM)	$-dC_{O3}/dt$ (mM/min)	$C_{O3}*10^3$ (mM)	$-dC_{O3}/dt$ (mM/min)	$C_{O3}*10^3$ (mM)	$-dC_{O3}/dt$ (mM/min)
0.25	30.1	-	30.1	-	30.1	-
1.00	1.0200	0.0645	1.0200	0.0836	0.8930	0.0944
3.17	0.8200	0.0623	0.7800	0.0811	0.6430	0.0974
5.00	0.7200	0.0561	0.6900	0.0736	0.5220	0.1073
7.50	0.6000	0.0453	0.5800	0.0603	0.3718	0.1295
10.00	0.5700	0.0356	0.5000	0.0481	0.2941	0.1478
15.00	0.5000	0.0270	0.3600	0.0370	0.1800	0.1701
20.00	0.4200	-	0.1600	-	0.1205	-
25.00	0.3500	-	0.1400	-	0.0800	-
30.00	0.3200	-	0.1010	-	0.0600	-
40.00	0.2900	-	0.0970	-	0.0540	-
50.00	0.2500	-	0.0930	-	0.0520	-

Table D.3 Representative data of the corresponding rates for excess initial dye experiments calculated by differential method at pH=10.0, r=0.5

pH = 10.0						
$C_{dye,i}$ (mM)						
	0.551		0.881		1.321	
t (min)	$C_{O3}*10^{3}$ (mM)	$-dC_{O3}/dt$ (mM/min)	$C_{O3}*10^{3}$ (mM)	$-dC_{O3}/dt$ (mM/min)	$C_{O3}*10^{3}$ (mM)	$-dC_{O3}/dt$ (mM/min)
0.00	14.00	-	14.00	-	14.00	-
1.08	2.8000	0.3486	2.6420	0.3980	2.4300	0.3661
2.50	2.6500	0.3110	2.6020	0.3720	2.3800	0.3466
5.00	1.6500	0.2500	2.5210	0.3310	2.1500	0.3052
7.50	1.4500	0.1968	1.0180	0.2529	0.9500	0.2329
10.00	0.5960	0.1510	0.5600	0.1827	0.4500	0.1682
15.00	0.3200	0.0820	0.2870	0.1199	0.2200	0.1109
20.00	0.1900	-	0.2150	0.0169	0.1990	-
25.00	0.1050	-	0.1400	-	0.1320	-
30.00	0.0820	-	0.0930	-	0.0860	-
40.00	0.0810	-	0.0750		0.0650	

Table D.4 Representative data of initial rates at different conditions at pH=2.5, r=0.5

pH = 2.5			
$C_{O3,i}$ = 0.0360 mM		$C_{dye,i}$ = 0.0330 mM	
$C_{dye,i}$ (mM)	$r_{dye,i}$ (mM/min)	$C_{O3,i}$ (mM)	$r_{O3,i}$ (mM/min)
0.0220	-0.0281	0.0170	0.0399
0.0330	-0.0380	0.0260	0.0604
0.0440	-0.0650	0.0360	0.0903

Table D.5 Representative data of initial rates at different conditions at pH=7.0, r=0.5

pH = 7.0			
$C_{O3,i}$ = 0.0300 mM		$C_{dye,i}$ = 0.0330 mM	
$C_{dye,i}$ (mM)	$r_{dye,i}$ (mM/min)	$C_{O3,i}$ (mM)	$r_{O3,I}$ (mM/min)
0.0220	-0.0120	0.0070	-0.0116
0.0330	-0.0203	0.0120	-0.0152
0.0440	-0.0300	0.0300	-0.0845

Table D.6 Representative data of initial rates at different conditions at pH=10.0, r=0.5

pH = 10.0			
$C_{O3,i}$ = 0.0140 mM		$C_{dye,i}$ = 0.0330 mM	
$C_{dye,i}$ (mM)	$r_{dye,i}$ (mM/min)	$C_{O3,i}$ (mM)	$r_{O3,i}$ (mM/min)
0.0220	-0.00280	0.0036	-0.0164
0.0330	-0.00460	0.0042	-0.0180
0.0440	-0.00820	0.0140	-0.0430

APPENDIX E

STATISTICAL ANALYSIS OF COD-REMOVAL DATA

In order to see the effects of initial dye concentration and pH (or accordingly, the maximum attainable dissolved ozone concentration at each pH) on the COD removal (%), thus in turn on the oxidation efficiency, blocking design (see reference [72]) is used; the significance levels for null hypothesis of 1 and 2 are determined, by taking initial dye concentration values as treatments and pH values as blocks.

Table E.1 summarizes the results from randomized block design [72] on COD removal (%).

Hypothesis 1: No $C_{dye,i}$-to-$C_{dye,i}$ variation is observed among the data of COD removal (%)

Hypothesis 2: No pH-to-pH variation is observed among the data of COD removal (%)

Table E.1 Results from randomized block design [72] on COD removal (%)

Blocks (pH)	Treatments ($C_{dye,i}$, mM)				
	0.022	0.0275	0.033	0.044	$y_{b,ave}$
2.5 ($C_{O3,i}$=0.036 mM)	40.5	36.5	36.8	31.2	36.25
7 ($C_{O3,i}$=0.030 mM)	33.8	34.6	36.4	37.4	35.55
10 ($C_{O3,i}$=0.014 mM)	23.1	22.0	24.6	24.9	23.65
$y_{t,ave}$	32.47	31.03	32.6	31.17	y_{ave}=31.82

$y_{b,ave}$: block average

$y_{t,ave}$: treatment average

y_{ave} : grand average

k: number of treatments=4

n: number of blocks=3

S_B: Sum of squares between blocks

$$S_B = k \sum_{i=1}^{n=3} ((y_{b,ave})_i - y_{ave})^2$$

$$S_B = 4\,[(36.25-31.82)^2+(35.55-31.82)^2+(23.65-31.82)^2]=401.15$$

S_T: Sum of squares between treatments

$$S_T = n \sum_{t=1}^{k=4} ((y_{t,ave})_t - y_{ave})^2$$

$$S_T = 3\,[(32.47-31.82)^2+(31.03-31.82)^2+(32.60-31.82)^2+(31.17-31.82)^2]$$
$$= 6.23$$

S_R: Sum of squares of residuals

$$S_R = \sum_{t}^{k}\sum_{i}^{n} [y_{ti} - (y_{b,ave})_i - (y_{t,ave})_t + y_{ave}]^2$$

$$S_R=(40.50-36.25-32.47+31.82)^2+(36.50-36.25-31.03+31.82)^2+(36.80-36.25-32.60+31.82)^2+(31.20-36.25-31.17+31.82)^2+(33.80-35.55-32.47+31.82)^2+(34.60-35.55-31.03+31.82)^2+(36.40-35.55-32.60+31.82)^2+(37.4-35.55-31.2+31.82)^2+(23.1-23.7-32.5+31.82)^2+(22-23.65-31.03+31.82)^2+(24.60-23.65-32.60+31.82)^2+(24.90-23.65-31.17+31.82)^2=12.96+1.08+0.0529+19.36+5.76+0.0256+0.0049+6.25+1.44+0.7396+0.0289+3.61=51.31$$

Table E.2 shows the Analysis of Variance (ANOVA) table for the determination of significance level.

Table E.2 Analysis of Variance (ANOVA) Table

Source of variation	Sum of squares	Degrees of freedom	Mean square	Ratio of mean squares
Between blocks (pH)	S_B=401.47	n-1=2	s_B^2=401.47/2 =200.74	s_B^2/s_R^2=23.48
Between treatments ($C_{dye,i}$)	S_T=6.23	k-1=3	s_T^2=2.08	s_T^2/s_R^2=0.24
Residuals	S_R=51.31	(n-1)(k-1)=6	s_R^2=8.55	s_R^2/s_T^2=4.12

For s_R^2/s_T^2= 4.12 (ν_1=6 and ν_2=3)
From $F_{6,3}$ Table [72] → $Pr(s_R^2/s_T^2 \geq 4.12)$~16%

Since significance level is higher than 5%, we can conclude that the null hypothesis of no significant $C_{dye,i}$-to-$C_{dye,i}$ variation among the COD removals at the same pH and initial ozone concentration is accepted.

s_B^2/s_R^2=23.48 (ν_1=2 and ν_2=6)
From $F_{2,3}$ Table [72] → $Pr(s_B^2/s_R^2 \geq 23.48)$~ 0.1%

Since significance level is less than 5%, it can be said that the null hypothesis of no pH-to-pH variation is discredited. This shows that there is a significant effect of pH (and thus accordingly of $C_{O3,i}$) on the COD removal percentage.